The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

The chemistry of
organophosphorus compounds

Volume 1

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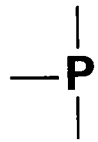

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organophosphorus compounds

Volume 1

Primary, secondary and tertiary phosphines, polyphosphines and heterocyclic organophosphorus(III) compounds

Edited by

FRANK R. HARTLEY

Cranfield Institute of Technology
Cranfield, UK

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Foreword

The Chemistry of Organophosphorus Compounds will be a multi-volume work within the well established series of books covering *The Chemistry of Functional Groups*. It is proposed to cover the extensive subject matter in four volumes.

Volume 1 covers primary, secondary and tertiary phosphines (PR_nH_{3-n}, $n = 1$–3), polyphosphines [both $P—C_n—P$ and $R(P)_nR'$, $n > 1$] and heterocyclic compounds containing phosphorus.
Volume 2 will cover phosphines oxides, sulphides and selenides.
Volume 3 will cover phosphonium salts, phosphonium ylides and phosphoranes.
Volume 4 will cover phosphinous, phosphonous, phosphinic and phosphonic acid compounds and their halogen derivatives, R_2PY, RPY_2, $R_2P(X)Y$ and $RP(X)Y_2$, where Y = halogen and X = O, S or Se.

For many years the nomenclature used in organophosphorus chemistry was extremely frustrating with different compounds being given the same name by different authors. The nomenclature has, however, now been rationalized and is summarized in Chapter 1, Section IV.

In common with other volumes in *The Chemistry of the Functional Groups* series, the emphasis is laid on the functional group treated and on the effects that it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. The coverage is restricted in that material included in easily and generally available secondary or tertiary sources, such as *Chemical Reviews* and various 'Advances' and 'Progress' series, as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes), is not as a rule repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore, each of the authors was asked not to give an encyclopaedic coverage of his or her subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself or herself to a reader who is assumed to be at a fairly advanced postgraduate level. With these restrictions, it is realised that no plan can be devised for a volume that would give a complete coverage of the subject with no overlap between the chapters, while at the same time preserving the readability of the text.

The publication of the Functional Group Series would never have started without the support of many people. This volume would never have reached fruition without the

help of Mrs Baylis, Mrs Vitale, Mr Mitchell with typing and the efficient and patient cooperation of several staff members of the Publisher. Many of my colleagues in England, Israel and elsewhere gave help in solving many problems, especially Professor Saul Patai, without whose continual support and encouragement this work would never have been attempted. Finally, that the project ever reached completion is due to the essential support and partnership of my wife and family, amongst whom my eldest daughter provided both moral support and chemical understanding in the more difficult areas of the subject.

Cranfield, England FRANK HARTLEY

Contents

List of abbreviations used

Ac	acetyl (CH_3CO)
acac	acetylacetone
Ad	adamantyl
aibn	azobisisobutyronitrile
All	allyl
Ar	aryl
BSA	bovine serum albumin
Bu	butyl (also *t*-Bu or Bu^t)
Bz	benzyl
cd	circular dichroism
cod	cycloocta-1,5-diene
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
CPMAS	cross-polarization magic angle spinning
Cy	cyclohexyl
dbn	1,5-diazabicyclo[5.4.0]non-5-ene
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
diop	2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dme	1,2-dimethoxyethane
dmg	dimethylglyoximate
dmpe	1,2-bis(dimethylphosphino)ethane
dmso	dimethyl sulphoxide
DNA	deoxyribonucleic acid
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
ee	enantiomeric excess
EPR	electron paramagnetic resonance
ESR	electron spin resonance
FAD	flavine adenine dinucleotide
FT	Fourier transform

Hex	hexyl
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
LC_{50}	concentration causing lethality to 50% of the population
LD_{50}	dose causing lethality to 50% of the population
lda	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M	metal
Me	methyl
Mes	mesityl
MNDO	modified neglect of diatomic overlap
NADP	nicotinamide adenine dinucleotide phosphate
Np	naphthyl
ORD	optical rotatory dispersion
Pe	pentenyl
Pen	pentyl (C_5H_{11})
PES	photoelectron spectroscopy
Ph	phenyl
ppm	parts per million
Pr	propyl (also *i*-Pr or Pr^i)
R	any radical
RNA	ribonucleic acid
SCF	self-consistent field
tbp	trigonal bipyramid
thf	tetrahydrofuran
tms	trimethylsilyl
Tol	tolyl ($CH_3C_6H_4$)
Tos	tosyl
Tript	9-triptyl
VSEPR	valence shell electron pair repulsion
X	halide

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FRANK R. HARTLEY

CHAPTER 1

Introduction

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I. HISTORICAL INTRODUCTION

The first preparation of a relatively pure sample of phosphorus was accomplished by Hennig Brand in 1669. In the process of trying to convert silver into gold he had to distil large volumes of urine, from which he obtained as one of the later products of the distillation a white liquid which emitted a strange light. This was, of course, white phosphorus, which fairly quickly oxidized in air and ceased to phosphoresce.

The first synthetic chemical study of organophosphorus compounds began in the early nineteenth century. Lassaigne in 1820 reported work on the esterification of dehydrated

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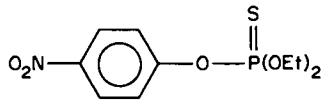
phosphoric acid[1]. In 1845 Thénard prepared a series of phosphine derivatives[2] and from then on progress was fairly rapid. Michaelis and then A. E. Arbuzov and later his son B. A. Arbuzov dominated the field for many years, although there were many others in the UK and Germany over many years.

II. COMMERCIAL USES OF PHOSPHORUS COMPOUNDS

The inorganic compounds of phosphorus dominate the commercial application of phosphorus compounds, with the fertilizer industry accounting for about 70% of all the phosphorus used, primarily in the form of phosphates such as $CaHPO_4$. Detergents, which are essentially a mixture of a polyphosphate and a surfactant such as sodium alkylbenzene sulphonate, account for 15% of phosphorus used, animal feedstuffs for 8% and the use of phosphoric acid for corrosion control about 5%. The pharmaceutical, insecticidal and plastics industries, all of which use organophosphorus compounds, together account for about 2% of the total phosphorus used, although these are high added value chemicals so that they account for a very much greater proportion of the commercial value of the phosphorus industry.

The oldest major use of organophosphorus compounds is as antioxidants and stabilizers in rubbers and plastics (phosphites). Triphenyl phosphate and later tricresyl phosphate were widely used as plasticizers in early plastics such as celluloid. Such phosphates are also used to flameproof fabrics, particularly for children's clothing. Phosphates have been used as petroleum additives to control preignition or 'knocking' and are used extensively used in hydraulic fluids, particularly for aircraft applications because of their ability to impart fire resistance. The *O,O*-dialkyl phosphorodithioates, $(RO)_2P(S)SH$, are used in high-pressure lubricating oils where their ability to 'bond' to metal surfaces prevents their being squeezed out from between surfaces that are forced into contact by very high imposed loads. In such situations, which apply in certain gearboxes and drive systems, hydrocarbon oils are squeezed out of the gap between the gear components and cease to provide effective lubrication.

A major driving force in the development of organophosphorus compounds was the recognition of their biochemical properties. This culminated with the discovery of their insecticidal activity and as a spin-off from this the discovery in Germany of the nerve agents developed but never used as chemical warfare agents in the Second World War. The first patents for the agricultural use of organophorus compounds were taken out in 1942[3] and in 1944 the first commercial product of this new range of insectides, parathion (**1**), was



(**1**)

introduced. Since then, hundreds of organophosphorus insecticides have been developed. Their particular attraction is their high toxicity coupled with their relatively limited stability in the biosphere, which results in their not being persistent in the way that DDT is. Typical organophosphorus insectide half-lives in plants are between 2 and 10 days.

III. CHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS

Most organophosphorus compounds are manufactured from elemental phosphorus, obtained by the electrothermal reduction of calcium phosphate with coke in the presence

of silica (equation 1)[4]:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO \quad (1)$$

This phosphorus is then converted to phosphorus trichloride by direct reaction with excess of chlorine or phosphoryl chloride, $POCl_3$, formed by exposure of the trichloride to air. PCl_3 and $POCl_3$ are then used as the starting points for the preparation of most organophosphorus compounds.

The chemistry of organophosphorus compounds falls into two areas: reactions involving the phosphorus atom itself, which form the majority of the chemistry, and reactions in which the presence of the phosphorus atom contributes to the reactions of the organic moieties present in the molecule. Phosphorus lies in Group V of the Periodic Table and forms two series of compounds. In the first series phosphorus is in the +3 oxidation state and the phosphorus itself carries a lone pair of electrons, which contribute markedly to the chemistry and stereochemistry of these compounds. This lone pair of electrons enable phosphorus(III) compounds to undergo nucleophilic attack on a wide range of compounds. Phosphorus itself is a relatively electropositive element and so can also act as an electrophile; such reactions are particularly important for compounds of phosphorus in its higher oxidation state of +5.

Phosphorus forms stable bonds to a wide range of elements. It forms particularly stable bonds to oxygen, so that whenever the opportunity arises phosphorus tends to form such bonds, often accompanied by oxidation. However, strong bonds to hydrogen, carbon, nitrogen, fluorine and chlorine give rise to a rich chemistry. Although the valence electrons of phosphorus are two 3s and three 3p electrons, there are relatively low-lying empty 3d orbitals which contribute significantly to many aspects of phosphorus chemistry, particularly the stability and high bond energies involved in the phosphonium ylide system $\geqslant\overset{+}{P}-\overset{-}{C}<$, the strength of the $\geqslant P=O$ double bond in the phosphine oxides and the stability of radicals such as $R_4P^{\bullet}$ in which phosphorus is surrounded by more than eight valence electrons[5].

IV. NOMENCLATURE

The complexity of organophosphorus compounds is considerable, so that there is ample room for confusion even to specialists in the field. Accordingly, in 1952 the Chemical Society in London and the American Chemical Society established a series of Rules of Nomenclature[6,7]. These rules were very precise and therefore greatly simplified the reader's understanding of what an author was trying to convey. However, they did give rise to some very lengthy names. Perhaps because of this the IUPAC Nomenclature Commission issued a revised system of nomenclature which was more flexible than the previous system and gave some element of choice, allowing a particular compound to be named in the simplest and most easily interpretable manner.

In naming organophosphorus compounds it is often helpful to have in minds names for the parent structures[6,7]. These are as follows:

Hydrides:

Phosphine	H_3P
Phosphine oxide	$H_3P{=}O$
Phosphine sulphide	$H_3P{=}S$
Phosphine selenide	$H_3P{=}Se$
Phosphine imide	$H_3P{=}NH$
Phosphorane	H_5P

Phosphorus (III) acids:

Phosphorous acid	$(HO)_3P$
Phosphonous acid*	$HP(OH)_2$
Phosphinous acid	H_2POH
Phosphenous acid	$HOP{=}O$

Phosphorus (V) acids:

Phosphoric acid	$(HO)_3P{=}O$
Phosphonic acid	$HP(=O)(OH)_2$
Phosphinic acid	$H_2P(=O)(OH)$
Phosphenic acid*	$HOP(=O)_2$
Phosphoranoic acid	H_4POH
Phosphoranedioic acid	$H_3P(OH)_2$
Phosphoranetrioic acid	$H_2P(OH)_3$
Phosphoranetetroic acid	$HP(OH)_4$
Phosphoranepentoic acid	$(HO)_5P$

Those names marked with asterisks are used for naming organophosphorus compounds only; the corresponding inorganic acids are known as hypophosphorous acid, $HP(OH)_2$, and metaphosphoric acid, $HOP(=O)_2$, respectively.

The IUPAC rules[8] of nomenclature are summarized below.

A. Compounds of Phosphorus (III)

1. Phosphines, their analogues and their metal derivatives (coordination number 3)

Organic derivatives of the parent hydride, phosphine (PH_3), are named as substituted phosphines by use of appropriate prefixes in alphabetical order, e.g.

ethylphosphine, $EtPH_2$

triphenylphosphine, PPh_3

ethyl(phenyl)propylphosphine, $P(Et)(Ph)(Pr)$

butane-1,2,3-triyltris(phosphine), $H_2PCH_2CH(CH_2PH_2)CH_2PH_2$

When $-PH_2$ does not constitute the principal group, it is designated by the prefix phosphino, e.g.

phosphinoacetic acid, H_2PCH_2COOH

2-dimethylphosphinoethylamine, $Me_2PCH_2CH_2NH_2$

When —PH— does not constitute the principal group, it is designated phosphinediyl and $-P<$ is designated phosphinetriyl. When there are several $-P<$ atoms in a chain, then the prefix 'phospha' is used. When one or more H atoms of PH_3 derivatives have been replaced with a metal atom, then the compounds are known as phosphides, e.g.

sodium diphenylphosphide, $NaPPh_2$

calcium ethylphosphide, $CaPEt$

2. Phosphines with electronegative substituents (X, OH, SH, etc.)

These compounds may be named in one of three ways, with the examples given below:

(i) as substitution products of phosphine;

(ii) as derivatives of the parent acids, phosphinous acid, H_2POH, phosphonous acid, $HP(OH)_2$, or phosphorous acid, $P(OH)_3$; or
(iii) as coordination compounds of phosphorus.

$Ph_2P(OMe)$: (i) methoxydiphenylphosphine;
(ii) methyl diphenylphosphinite;
(iii) methoxydiphenylphosphorus (III).

Ph_2PCl: (i) chlorodiphenylphosphine;
(ii) diphenylphosphinous chloride;
(iii) chlorodiphenylphosphorus (III).

3. Phosphorus (III) onium salts

These compounds are named phosphonium salts with the appropriate prefixes to indicate the radicals, listed alphabetically, e.g.

benzyltriphenylphosphonium chloride, $[PhCH_2PPh_3]^+ Cl^-$

B. Compounds of Phosphorus (V)

1. Phosphine oxides and their analogues

R_3PX, where X = O, S, Se, NH, may be named in one of three ways, with the example given:

(i) as oxides, sulphides, etc.;
(ii) as substitution products of phosphorane, PH_5;
(iii) as coordination compounds of phosphorus

Ph_3PO: (i) triphenylphosphine oxide;
(ii) oxotriphenylphosphorane;
(iii) oxotriphenylphosphorus (V).

2. Oxo acids of phosphorus (V)

These compounds are named as substitution products of the parent acids, phosphinic acid, $H_2PO(OH)$, and phosphonic acid, $HPO(OH)_2$. When multiplying affixes are required, bis, tris and tetrakis are used, e.g.

diphenylphosphinic acid, $Ph_2PO(OH)$
1,4-butylbis(phosphoric acid), $(HO)_2OP(CH_2)_4PO(OH)_2$

When the acid group is not the principal group then the prefixes phosphono $[-PO(OH)_2]$, phosphinato $[-PO(O^-)_2]$, phosphinico $[>PO(OH)]$ and phosphinato $[>POO^-]$ are used, e.g.

phosphoroacetic acid, $(HO)_2OPCH_2COOH$

3. Analogues and derivatives of the oxo acids of phosphorus (V) in which =O or —OH have been replaced by other electronegative substituents

These compounds can be named in one of three ways, with the examples given:

(i) as substitution derivatives of the acids named using the appropriate prefixes such as thio, chloro or amido;
(ii) by use of infixes such as -thio-, -amid(o)- or -chlorid(o)-;
(iii) as 'hydrogen salts' naming the anion by coordination nomenclature.

$Et_2PS(SH)$: (i) diethyldithiophosphinic acid;

(ii) diethylphosphinodithioic acid;
(iii) hydrogen diethyldithiophosphate(V).

$PhPO(Cl)(OH)$: (i) phenylchlorophosphonic acid;
(ii) phenylphosphonochloridic acid;
(iii) hydrogen chlorodioxophenylphosphate(V).

$PhPO(Cl)(OMe)$: (i) methyl phenylchlorophosphonate;
(ii) methyl phenylphosphonochloridate;
(iii) chloro(methoxy)oxophenylphosphorus(V)
(note: the parentheses around 'methoxy' are optional);

$PhPOCl_2$: (i) and (ii) phenylphosphonic dichloride;
(iii) dichlorooxophenylphosphorus(V).

When another group is present that has priority for citation as the principal group, the oxo radicals are named:

phosphinoyl, $H_2P(O)$—
phosphonoyl, $HP(O)<$
phosphoryl, $P(O)\equiv$

4. Phosphoranes (PH_5) and their analogues

Derivatives of PH_5, generically called phosphoranes, may be named in one of two ways, with the examples given:

(i) as substitution derivatives of phosphorane;
(ii) as coordination compounds.

PPh_5: (i) pentaphenylphosphorane;
(ii) pentaphenylphosphorus(V).

Ph_3PCl_2: (i) dichlorotriphenylphosphorane;
(ii) dichlorotriphenylphosphorus(V).

When they do not constitute the principal groups, radicals derived from phosphorane may be named as phosphoranyl (H_4P—), phosphoranediyl ($H_3P<$) or phosphoranetriyl ($H_2P\equiv$).

5. Anions containing phosphorus(V)

These are named by listing the ligands alphabetically as prefixes to the word 'phosphate' followed by either (i) the oxidation state of the phosphorus (Stock system) or (ii) the charge on the anion (Ewens–Bassett system).

For example, $NaPPh_6$: (i) sodium hexaphenylphosphate(V);
(ii) sodium hexaphenylphosphate(1 −).

6. Ring compounds

The more commonly encountered monocyclic ring systems involving phosphorus are named as in Table 1.

V. THE LITERATURE OF ORGANOPHOSPHORUS CHEMISTRY

There is a vast literature covering organophosphorus chemistry which is well referenced in the chapters that follow. Major secondary sources of literature include the following:

Review series:

Organophosphorus Chemistry[9];
Topics in Phosphorus Chemistry[10];
Organic Phosphorus Compounds[11].

TABLE 1. Nomenclature of heterocyclic ring compounds containing phosphorus

Ring size	Saturated	Unsaturated
3	Phosphirane	Phosphirene
4	Phosphetane	Phosphete
5	Phospholane	Phosphole
6	Phosphorinane	Phosphorin
7	Phosphenane	Phosphepin
8	Phosphocane	Phosphocin
9	Phosphonane	Phosphonin
10	Phosphecane	Phosphecin

Major texts:

K. Sasse, *Organische Phosphor-Verbindungen*[12];
R. F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*[13];
A. J. Kirby and S. G. Warren, *The Organic Chemistry of Phosphorus*[14];
B. J. Walker, *Organophosphorus Chemistry*[15];
W. E. McEwan and K. D. Berlin, *Organophosphorus Stereochemistry*[16];
D. J. H. Smith and R. S. Edmundson, in *Comprehensive Organic Chemistry*[17];
J. I. G. Cadogan (Ed.), *Organophosphorus Reagents in Organic Synthesis*[18];
L. D. Quin, *The Heterocyclic Chemistry of Phosphorus*[19];
L. D. Quin and J. G. Verkade (Eds), *Phosphorus Chemistry*[20];
K. D. Dimroth, in *Comprehensive Heterocyclic Chemistry*[21];
R. S. Edmundson (Ed.), *Dictionary of Organophosphorus Compounds*[22].

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The Chemistry of Organophosphorus Compounds
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CHAPTER 2

Structure and bonding in organophosphorus(III) compounds

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I. INTRODUCTION

The electronic configuration of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$. It is a typical non-metal, located near the centre of the Periodic Table, with a relatively high first ionization potential (10.49 eV, 1011.8 kJ mol^{-1}) and a low electron affinity (estimated as 0.77 eV, 75 kJ mol^{-1})[1]. Thus, although mainly covalent bonding to phosphorus is to be expected, ionic bonding is also possible (for example, the phosphide ion exists[2]). However, the electronegativity of phosphorus(III) on the Pauling scale is 2.19 and on the Allred–Rochow scale is 2.06[1]. Therefore, bonds to carbon (2.5) are expected to be weakly ionic with charge displaced towards carbon and bonds to hydrogen (2.2) are expected to be hardly ionic at all. Note that the orbital electronegativities[3] of phosphorus are 1.84 for p^3 and 2.79 for sp^3.

It is natural and has been common practice to compare the bonding in phosphorus with that in nitrogen and the differences in bonding to nitrogen and phosphorus are often taken to be typical of those between the first and subsequent rows of the Periodic Table[4]. For these reasons, much of the following discussion is couched in such terms.

In order to predict those orbitals likely to be used in covalent bonding, an estimate of their relative energies is required. For this purpose, the valence orbital energies obtained from the corresponding valence orbital ionization energies[5] can be used and those for phosphorus and nitrogen are shown in Figure 1. Note the relatively lower s–p 'promotion energy' in the case of phosphorus (8.7 eV, 840 kJ mol^{-1}) compared with nitrogen (12.4 eV, 1197 kJ mol^{-1}). However, it should be noted that such data have only qualitative significance in this context since the notion of promotion energy is not well defined[4] and other estimates are 7.5 eV[6] and 5.8 eV[3] for phosphorus and 10.9 eV[6] and 9.9 eV[3] for nitrogen. It is clear, though, that the s and p orbitals are closer in energy in the second and subsequent rows of the Periodic Table than in the first[4]. Even greater difficulty attends the estimation of the promotional energy to unoccupied (virtual) orbitals, for example the phosphorus 3d orbitals, but a reasonable estimate[4,6] for promotion from 3s to 3d appears to be approximately 16–17 eV (1540–1640 kJ mol^{-1}) in the free atom. This is a large amount of energy to be recovered in bonding, but it is generally accepted[4,7,8] that phosphorus d orbitals are available for bonding in some cases.

With the above energies in mind and using a simple valence bond approach, some

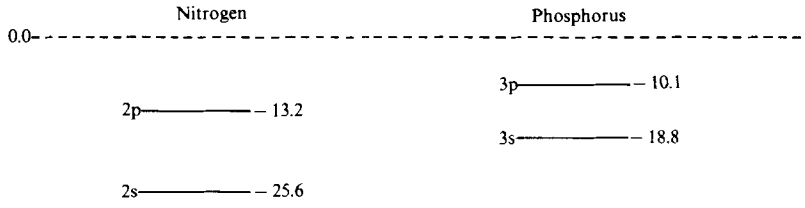

FIGURE 1. Valence orbital ionization energies (eV) for phosphorus and nitrogen.

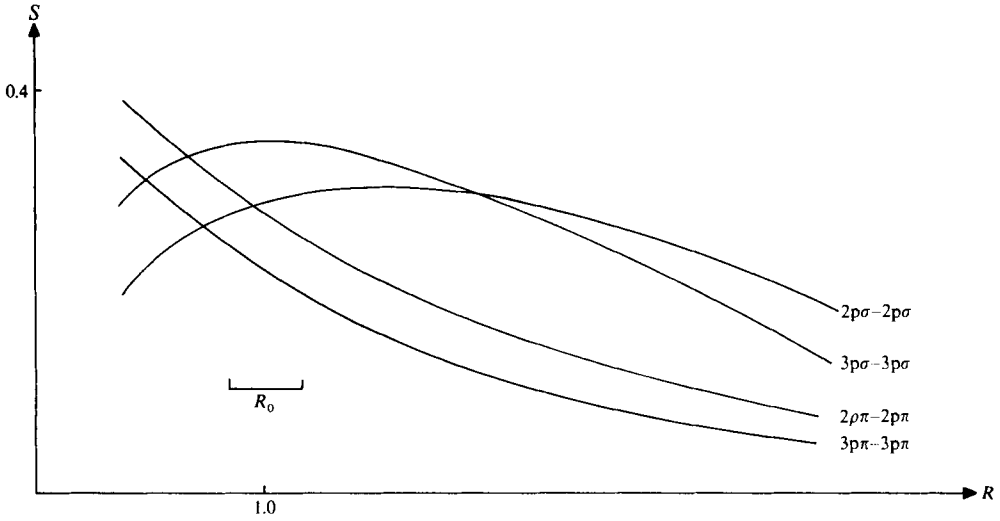

FIGURE 2. Variation of Slater overlap integrals (S) with reduced internuclear separation (R).

feeling for possible bonding situations involving phosphorus can be derived. Possible procedures are:

(i) using the three singly occupied p orbitals to form three bonds, leaving a lone pair in an s orbital;
(ii) assuming that promotion energies can be offset by increased strength of bonds formed and constructing various sets of hybrid orbitals, some possibilities being (a) three sp^2 hybrids for three bonds leaving a lone pair in a p orbital, or (b) again three sp^2 hybrids and a p orbital but using one of the hybrids for the lone pair, leaving a p orbital for π bonding, or (c) four sp^3 hybrids, three bonding and one for a lone pair;
(iii) allowing use of an unoccupied d orbital by promotion of an s electron, again assuming that the strengths of extra bonds formed offset the promotion energy, gives the possibility of up to five bonds in a number of hybridization schemes.

Assuming that orbital energies are matched, the other major factor controlling bond strength is efficiency of orbital overlap. In a number of the above schemes, both σ and π bonds can be formed utilizing s, p and d orbitals and it is instructive to consider some relative efficiencies of overlap. Figure 2 shows qualitatively how the overlap integrals of $np\sigma$ and $np\pi$ bonds vary with internuclear separation[6,9] (corrected so that comparisons can be made on a common axis). Note that these overlap integrals are based on Slater atomic orbitals, which may not be properly relevant to the second row elements since they

do not take account of the presence of the radial nodes in, for example, 3p orbitals. Most equilibrium bond lengths fall in the region marked R_0 and in this region it can be seen that for first-row elements $p\sigma$ and $p\pi$ overlap integrals are approximately equal but for second-row elements $p\sigma$ overlap is greater than $p\pi$ overlap. This is because in second-row atoms the longer bond lengths reduce the efficiency of π overlap. Note also that $3p\sigma$ overlap is greater than $2p\sigma$ overlap, but this may be an artifact of the use of Slater atomic orbitals. Second-row bond lengths may be longer than those of the first row because the maximum $3p\sigma$–$3p\sigma$ overlap occurs at a greater internuclear separation than the maximum $2p\sigma$–$2p\sigma$ overlap[9] or because of the repulsion of the 3p orbitals by the filled core orbitals of the other atom (which is greater for the second-row atom, there being a greater number of inner electrons)[10]. In any event, it is to be expected that σ bonding plays a greater role in second-row bonding than in first-row bonding. However, the $3p\pi$ overlap integral is not negligible so that π bonding in the second row is not ruled out.

The s orbital overlap integrals are also different in first- and second-row elements, being uniformly less (but still significant) in the second row, so that in the R_0 region 2s–2s overlap is about 0.45 and 3s–3s overlap is about 0.38[9].

The d orbitals in the free atom are too diffuse[7] to overlap effectively with likely partners so such bonds cannot be expected to be strong. However, when phosphorus is in a bonding situation it may be that these factors are not too significant. For example, if phosphorus were to carry a degree of positive charge by being bonded to an electronegative atom, the d orbitals might be contracted enough to overlap more effectively[7].

These ideas are borne out to some extent by the bond enthalpies[11,12] in phosphorus and nitrogen compounds, some of which are given in Table 1. Phosphorus thermochemistry is not well developed[13,14] and the values given are for specific trivalent compounds (see the relevant references) and may be very different for other compounds; for example, the mean dissociation energy[15] for phosphorus to aliphatic carbon is 276 kJ mol^{-1} whereas that to aromatic carbon is 293 kJ mol^{-1}. However, a number of observations are possible. First, it can be seen that these energies are easily of the same order of magnitude (when multiplied by three) as even the highest of the s–p promotion energies referred to above, both for phosphorus and for nitrogen. In addition, in the case of the P—F bond, three times the bond energy is of the order of magnitude of the s–d promotion energy, consonant with the idea of the involvement of d orbitals in the bonding. However, such comparisons are fraught with difficulty, and break down in the case of the phosphaethyne, where the lowest estimate[3] of promotion energy to the $di^2di\pi\pi$ configuration is 4.4 eV (425 kJ mol^{-1}) and the bond energy is only half of this value.

A qualitative comparison between first- and second-row bond energies can be made from Table 1. Thus it is indeed true that the homopolar single bond energy of phosphorus is greater than that of nitrogen, whereas the triple bond energy of dinitrogen is much larger than that of phosphaethyne, indicating that σ bonds are stronger in the second row whereas π bonds are stronger in the first. However, the situation is less clear for the heteropolar bonds. Thus, in bonds to the more electronegative atoms the phosphorus single bond is stronger than that of nitrogen but to the less electronegative carbon and

TABLE 1. Enthalpies of some bonds to phosphorus and nitrogen[a]

P—P	200	P—H	321	P—C	264	P≡P	486
N—N	159	N—H	391	N—C	292	N≡N	946
P—O	360	P—F	503	P—Cl	322		
N—O	222	N—F	278	N—Cl	193		

[a] Values in kJ mol^{-1}; from refs 11, 12, and 16.

hydrogen it is weaker. This may be because there is a greater ionic contribution to bonding where the electronegativity difference is greater or because there is a greater contribution of d orbitals to the bonding[16].

Given the above considerations, it is not surprising that phosphorus has a very large number of known bonding situations. All coordination numbers from 1 to 10 are known[2,17] and single, double and triple bonds are known for many of them. However, as intimated above, in many situations it is difficult to tell precisely whether one is dealing with, for example, a pure single bond because of the effects of differing electronegativity leading to some ionic character and the possibility of some π bonding utilizing either p or d orbitals, both effects often being small but relevant[8]. One consequence of the greater strength of second-row single bonds is that, in contrast to nitrogen, there is a substantial chemistry of polyphosphorus compounds.

The first comprehensive discussion of structure and bonding in phosphorus compounds was by Hudson[6] and it is still relevant in parts. Later work has taken the form of introductory chapters in general books on organophosphorus chemistry[2,13,14,18,19], that by Emsley and Hall[13] still being useful. However, the subject has not been reviewed in detail (although there is an overview in the book by Goldwhite[14]) since the advent of accurate quantum chemical calculations or the full application of symmetry and group theoretical techniques to chemical bonding. Thus the following discussion contains much new material.

The rest of this chapter is concerned with bonding in organophosphorus(III) compounds. By this is meant those bonding situations where phosphorus uses (1) three single bonds, (2) a double bond and a single bond and (3) a triple bond. These correspond to normal phosphines, phosphaalkenes and phosphaalkynes, respectively. It is also appropriate to discuss the bonding in transition metal complexes of phosphines and the possibility, if any, of hydrogen bonding to phosphines.

II. SINGLY BONDED PHOSPHORUS

The discussion starts with the structure and bonding in normal phosphines with a section on the most recent calculations. Then additional topics relevant to certain phosphines are discussed. During the discussions it is appropriate to compare and contrast phosphines with other phosphorus derivatives and non-phosphorus compounds not strictly relevant to this chapter, in particular PH_3, halophosphines and amines.

A. Structure of Phosphines

Structure in organophosphorus chemistry was last reviewed comprehensively by Corbridge[2], and his section on phosphines is still very useful because the number of subsequent studies has not been large. Many useful data are also included in some older more general compilations[20,21], while material published after 1974 may also be located in general publications[22-24]. A useful comparison of experimental and theoretical results across a wide range of phosphorus compounds may be found in a recent paper by Jug and Schulz[25].

Table 2 gives some structural data for selected organophosphorus(III) compounds. Since its purpose is to illustrate the subsequent discussions, no effort has been made in Table 2 to ensure comprehensive coverage, and readers requiring data on particular compounds should refer, in the first instance, to *Chemical Abstracts*. Readers should also refer to the original publications for details of the structure determinations, error limits and the other molecular dimensions of the compounds quoted. Some general trends may be gleaned from an examination of Table 2.

TABLE 2. Selected structural data[a] for some phosphines

Phosphine	Method[b]	r(P—H)	∠HPH	r(P—C)	∠HPC	∠CPC	Ref.
PH_3	M/I	142.0	93.5				26
	I	142	93.8				27
	M	141.5	93.3				28
	M	141.15	93.36				29
PH_2CH_3	M	141.4	93.4	186.3	97.5		30
	E	142.3		185.8	96.5[c]		31
$PHMe_2$	E	144.5		185.3	96.5[c]	99.2	31
	M	141.9		184.8	96.9	99.7	32
PMe_3	E			184.7		98.6	33
	M			184.1		99.1	34
$PEtMe_2$	E			184.8		99.6[d]	35
$PH_2C(SiMe_3)_3$	E	140.1	97[c]	180.8	100[c]		36
PH_2CF_3	M	143	97	190.0	92		37
PHF_2	M	141.2					38
$PhPH_2$	E	142.0	93.5	183.9	94.0		39
Ph_2PH	E	142.0		183.1	95.0	100.8	40
Ph_3P	X			183.0		103	41
$PhPMe_2$	E			184.4[e]		96.9[f]	42
$(4\text{-}MeC_6H_4)_3P$	X			183.2		101.7	43
$(4\text{-}MeOC_6H_4)_3P$	X			182.7[g]		101.3[h]	44
$PhPF_2$	E			180.9			45
CH_3PCl_2	E			183.1			39
$PhP(COC(CH_3)_3)_2$	X			191.0[i]		95[j]	46
Me_2PCOCH_3	X			186.3[k]			47
$C_5Me_5(CO)_2FeP(Bu^t)Cl$	X			187.1			48
$P(CF_3)_3$	E			190.4		97.2	49
$P(CN)_3$	X			178.0		93	50
$P(C{\equiv}CPh)_3$	X			176.5		101.0	51
Phosphirane	M	142.8		186.7	95.2	47.4	52

[a] r(P—X), bond length in pm; ∠XPY, bond angle in degrees.
[b] M, microwave spectroscopy; E, electron diffraction; X, X-ray crystallography; I, infrared spectroscopy.
[c] Assumed.
[d] $\angle C_{Me}PC_{Me} = 101.5$.
[e] $P—C_{Ph} = 184.5$.
[f] $\angle C_{Me}PC_{Ph} = 103.4$.
[g] ± 0.3.
[h] ± 1.6.
[i] $P—C_{Ph} = 183.8$.
[j] $\angle C_{Ph}PC_{Ph} = 100$.
[k] $P—C_{Me} = 186.3$.

1. *Bond lengths*

The P—H bond length is usually about 142 pm and no real trend is apparent in substituent effects on it. There may be a slight lengthening with sequential methyl substitution, perhaps reflecting the fact[53] that methyl substitution weakens the P—H bond by about 12 kJ mol^{-1}. Even in the phosphine tris(trimethylsilyl)methylphosphine, the P—H and P—C bond lengths are similar to the unencumbered methyl phosphine.

The P—C(alkyl) bond length is usually about 186 pm, reduced on further alkyl substitution (to 144 pm), while the P—C(aryl) bond length is nearly always 183 pm. Groups that are both electron-donating and-withdrawing by induction can lower the P—C bond length to 180 pm while conjugated C=O groups lengthen it so that, unlike the acyl

TABLE 3. Single bond lengths[a] to trivalent tricoordinate phosphorus and nitrogen[b]

P—H	142					N—H	101
P—B	196						
P—C	183 (aryl)					N—C	147
P—C	185 (alkyl)	P—Si	225				
P—N	177	P—P	222			N—N	146
P—O	164	P—S	209			N—O	136
P—F	157	P—Cl	204	P—Br	222	N—F	136

[a]In pm.
[b]From Table 2 and refs 2, 13 and 24.

amides, acyl phosphines can show P—C(O) bond lengths that are longer by up to about 6 pm. Also acylphosphines may be enolic[47]. Attachment of a metal (iron) also lengthens the P—C bond length (to 187 pm). In dimethylphenylphosphine the P—C(Me) and P—C(Ph) bond lengths are identical within experimental error and very similar to that in trimethylphosphine. In the case of aromatic amines there is appreciable shortening of the N—C bond in comparison with aliphatic amines, which is usually attributed to $p\pi$ conjugation. Hence such conjugation must be considerably weaker in phosphines than in amines[42]. Although the P—C bond length is fairly predictable, there are some remarkably anomalous values; for example, the value for $P(CF_3)_3$ is substantially longer than expected (see Section II.B.2) and those for $P(CN)_3$ and $P(C{\equiv}CPh)_3$ are considerably shorter.

As can be seen from Table 2, it is often particularly difficult to assign a characteristic single bond length to phosphorus because the observed ranges can be very large[2], but some attempt can be made and Table 3 sets out some typical values in comparison with those to nitrogen. It can be seen that, as expected, bonds to phosphorus are considerably longer than those to nitrogen. Further, in most cases, after correcting for electronegativity differences[16,54], the phosphorus single bond lengths are those expected on the basis of covalent radii estimates[16]. In other words, there can only be a small contribution of π bonding in bonds to trivalent tricoordinate phosphorus.

2. *Bond angles*

Obviously, from Table 2, phosphines are pyramidal. Thus the HPH angle is usually 93.5°, except where there are strong electron-withdrawing or -donating groups. The HPC angle is less than 100°, usually in the range 95–97°, except again in the case of electron-withdrawing or -donating groups. The CPC angle is usually in the range 99–101°, but in this case there are many more exceptions, especially where there are very bulky substituents, as can be seen from Table 2. The widest angle seen so far for a phosphine is probably the 109.7° in trimesitylphosphine[55].

The pyramidal nature of phosphines leads to appreciable dipole moments[13]. Also, there is the possibility of inversion isomers and indeed phosphines are more stable to inversion than the corresponding amines and asymmetric phosphines can be resolved. This is discussed further in Section II.B.6.

It is sometimes said (see Section II.B.2.b) that there should be a relation between bond length and bond angle such that as the bond angle increases (tending to planar geometry) the bond length should decrease. Examination of Table 2 provides no evidence for such a relation because (a) it is difficult to make comparisons which are free from other complicating factors and (b) there is some evidence to the contrary, for example, the bond length in tricyanophosphine is less than expected but the bond angle is also noticeably less than expected.

TABLE 4. Comparison of bond angles[a] in phosphines and amines[b]

PH_3	93.5	NH_3	107
PMe_3	98.3	NMe_3	106
PF_3	97.3[c]	NF_3	102
PCl_3	100		

[a]In degrees.
[b]From Table 2 and refs 2, 20 and 24.
[c]Reported values range from 96.3 to 98.2.

A comparison of trimethyl-, triphenyl-, dimethylphenyl- and difluorophenylphosphines indicates that increasingly electronegative substituents do not lead to smaller bond angles; indeed, if anything, the trend is in the other direction. Similarly, there is no meaningful relation between trends in the sums of the bond angles at phosphorus and those of the basicity of, for example, the methylphosphines (Section II.B.1.a).

Table 4 shows the angle at phosphorus in some symmetrical phosphines in comparison with the analogous amines. Note that bond angles in phosphorus derivatives are always narrower than in their nitrogen counterpart and the response of the bond angle to substitution is different in the two cases.

3. Saturated ring systems

Inclusion of phosphorus in a saturated ring causes no structural changes other than those directly related to the presence of the ring. Thus, for example, in phosphirane the CPC bond angle is dramatically reduced owing to the ring geometry but the P—C bond length and the HPC bond angle are hardly affected. Similar results are found for other saturated rings and even some unsaturated rings[56].

4. Cone angles

A useful structural characteristic of a ligand in a complex is its cone angle, which is the plane angle at the apex of a cone located at the centre of the central metal atom of the complex and where the surface of the cone encompasses the ligand, passing at a distance from the outer atoms of the ligand equal to the effective van der Waals radii of those atoms. The cone angle is a measure of the steric bulk of a ligand and was originally determined for phosphines in nickel complexes by examination of molecular models of those complexes[57]. It was then found that the cone angle correlated with many properties of the ligands, with ligand exchange thermodynamics, with kinetics and with many other data[58]. Table 5 shows some representative cone angles for phosphines.

In a recent useful study, Imyanitov[59] developed a set of equations for the calculation of the cone angles of ligands of the type AB_n, A being coordinated to a metal M. Thus, on the basis of the internuclear distance M—A, the covalent radii of A and B, the van der Waals radius of B and the angle MAB, one may calculate the cone angle of new ligands without recourse to molecular models.

Imyanitov[60] also has presented calculated cone angles for a series of potential ligands (both phosphorus and non-phosphorus) and analysed trends within the series. Thus, in the case of variable B, downward movement in the Periodic Table is, not surprisingly, accompanied by a significant increase in cone angle (e.g. an increase of 30–40° from fluorine to iodine), whereas in the case of variable A it is accompanied by some decrease in cone angle (most marked in the change from first- to second-row A). The cone angles in

TABLE 5. Representative cone angles[a] for phosphines

	Measured[b]	Calculated[c]
PH_3	87	90.2
$P(CH_3)_3$	118	123
PPh_3	145	150
PF_3	104	107.3
PCl_3	125	127.7
PBr_3	131	133.8

[a]In degrees.
[b]Ref. 57.
[c]Refs 59 and 60.

hydrides are only slightly dependent on A and range from 90° to 93°. In addition, if the values for ligands with identical substituents are known, the values for ligands with combinations of substituents can be calculated. Finally, the effect of changing the metal atom has been examined and found to be not very significant except in certain predictable cases.

5. *Conformation*

The methyl groups in the methylphosphines are in a staggered conformation analogous to that in ethane in the case of methylphosphine, propane in the case of dimethylphosphine and 2-methylpropane in the case of trimethylphosphine[61]. The barrier to rotation in each case is small, of the order of 8 kJ mol^{-1} for methylphosphine and 11 kJ mol^{-1} for trimethylphosphine[15]. These barriers are smaller than those in the analogous amines as a result of the larger P—C bond distance[15].

Recently, there has been a series of studies[35,62,63] of the conformations of $EtPX_2$, where X = Me, H, F and other substituents. These show that depending on the circumstances, either the *gauche* or the *trans* (lone pair *trans* to methyl group) may be the more stable conformer. For example, for ethyldimethylphosphine[35] in the gas phase the conformers have almost equal energy (electron-diffraction study) whereas in the liquid phase the *gauche* conformer is more stable (vibration spectrum) by ca 1.6 kJ mol^{-1}. On the other hand, for ethylphosphine[62] and ethyldifluorophosphine[63] the *trans* conformer is usually the more stable (there may be differences between the liquid and gas phases).

B. Bonding in Phosphines

Naturally, discussions of the bonding in phosphines must account for the structure and reactivity of the compounds. Also, it is to be hoped that differences between phosphines and any compounds with which they might reasonably be compared would also be explained by a discussion of the bonding. Examples of such comparisons are other phosphorus compounds, nitrogen compounds and compounds of lower members of Main Group 5. Subjects which have been of particular concern in bonding theory applied to phosphines are (i) the much smaller bond angle in phosphines than in amines, (ii) the differing variation of the bond angle with substituent in phosphines and amines, as revealed by Table 4, (iii) the much larger barrier to inversion in phosphines than in amines, (iv) the lower basicity and greater nucleophilicity of phosphines than amines, (v) the possibility, if any, of involvement of d orbitals in the bonding and (vi) how the previous topics relate to each other. All of these matters are characteristic of differences between the first and subsequent rows of the Periodic Table.

1. Qualitative studies

Previous reviews of the bonding in phosphorus compounds have been of a qualitative nature only. It is necessary to restate this work in order to detail some of the deficiencies in it and to show how the newer results remedy them. There are three qualitative approaches which have been used extensively: the directed valence, valence shell electron pair repulsion (VSEPR) theory and the molecular orbital (Walsh diagram) approaches. The first two have been the usual basis of previous discussions[2,6,13,14,18,19] whereas the Walsh diagram approach to bonding specifically in phosphines has not been reviewed before.

a. The directed valence approach. This is the simplest, most accessible and so most common analysis of the bonding in phosphines[2,6,13,14,18,19]. On the basis that ground-state phosphorus has three singly occupied p orbitals in its valence shell, these are available for σ bonding to three one-electron donors (e.g. an H atom or a CR_3 fragment). Since the three p orbitals are at right-angles to each other, it is to be expected that the three bonds so formed will have bond angles of approximately 90°. This is in accord with observation in the case of phosphine itself. For nitrogen in ammonia, the angle of 107° which is found is claimed then to suggest sp^3 hybridization of nitrogen.

The increase in bond angle in halogenophosphines to approximately 100° is then explained using the electronegativity difference which makes the phosphorus atom more positive, decreasing the s–p promotion energy and allowing a certain amount of hybridization of the p orbitals with s orbitals. Unfortunately, this argument cannot be applied to the amines, since the bond angle *decreases* on fluorine substitution of ammonia. Also, the increase in bond angle in methyl-substituted phosphines cannot be explained and recourse has to be made to steric arguments.

The analysis assigns the phosphine lone pair of electrons to the phosphorus valence s orbital, which requires a spherical distribution of this electric charge. The lower basicity of phosphine than ammonia is often taken as evidence for this non-directionality of the phosphorus lone pair because it is less available for bonding to an incoming hydrogen than is the nitrogen lone pair. An alternative casting of this basicity argument is that protonation to give phosphonium ion involves rehybridization from p^3 to sp^3 in the case of phosphorus but not in the case of nitrogen. This requires energy, and therefore phosphines are weaker bases. The greater basicity of the methylphosphines fits the pattern[13] since as the bond angle increases there is more s character in the bonding and so less rehybridization is required, and as the methyl phosphines have wider bond angles they are stronger bases. However, there is not a strong relation between bond angle and basicity in the methylphosphines (Section II.A.2). Also, there is evidence (dipole moments, nucleophilicity) that the phosphorus lone pair does have directional properties.

The directed valence approach is unsatisfactory for a number of reasons: (i) it is really a description of how the bonding must be, based on observation, and no real predictions are made (for example, the fact that ammonia has an angle of 107° is explained by saying that must mean that it has sp^3 hybridization); (ii) more seriously, the p^3 vs sp^3 argument is actually counter to the promotional energies involved because, using promotional energies, sp^3 hybridization is predicted to be more likely in phosphorus than in nitrogen (for example, the N—H bond strength is 391 kJ mol^{-1} and that of P—H is 321 kJ mol^{-1}, and the 2s–2p promotional energy is 956–1197 kJ mol^{-1} for nitrogen and 560–840 kJ mol^{-1} for phosphorus); hence the use of promotional energies to explain details of the bond angles is unreasonable; (iii) no allowance is made for the possibility of a planar configuration for which the VSEPR argument is usually used.

b. The VSEPR approach. The application of VSEPR to phosphines is straightforward[13]. Phosphorus has five electrons in the valence shell and three one-electron ligands lead to a classification of an eight-electron AX_3 system. The four electron pairs are

expected to adopt a tetrahedral arrangement. Since one of the electron pairs is non-bonding, a pyramidal arrangement around A is expected with the bond angle less than the regular tetrahedral 109.5°. The difference between the angles at phosphorus and those at nitrogen remains to be explained. A further axiom of VSEPR is that as the size of the atom core increases, the nucleus retains more control over its non-bonding pair. This increases the repulsion between non-bonded and bonded electron pairs. Hence the larger phosphorus is expected to have narrower angles to ligands than nitrogen.

However, the subtler variations of angle with ligand are not easy to explain using VSEPR and the explanation of the greater angle at phosphorus is in direct conflict with the idea that the phosphorus lone pair is less directional than the nitrogen lone pair. More seriously, the VSEPR theory itself has a shaky theoretical basis. Not only are there a number of well known exceptions[5], but also studies[64,65] have shown that the lone pair–lone pair repulsions are not stronger than bond pair repulsions.

c. The Walsh correlation diagram analysis. Recently, a more satisfactory approach based on qualitative molecular orbital theory has been developed[5,66–71]. This is well documented in the excellent book by Albright *et al.* (ref. 66, pp. 93–97 and 140–148), and the discussion here follows theirs closely.

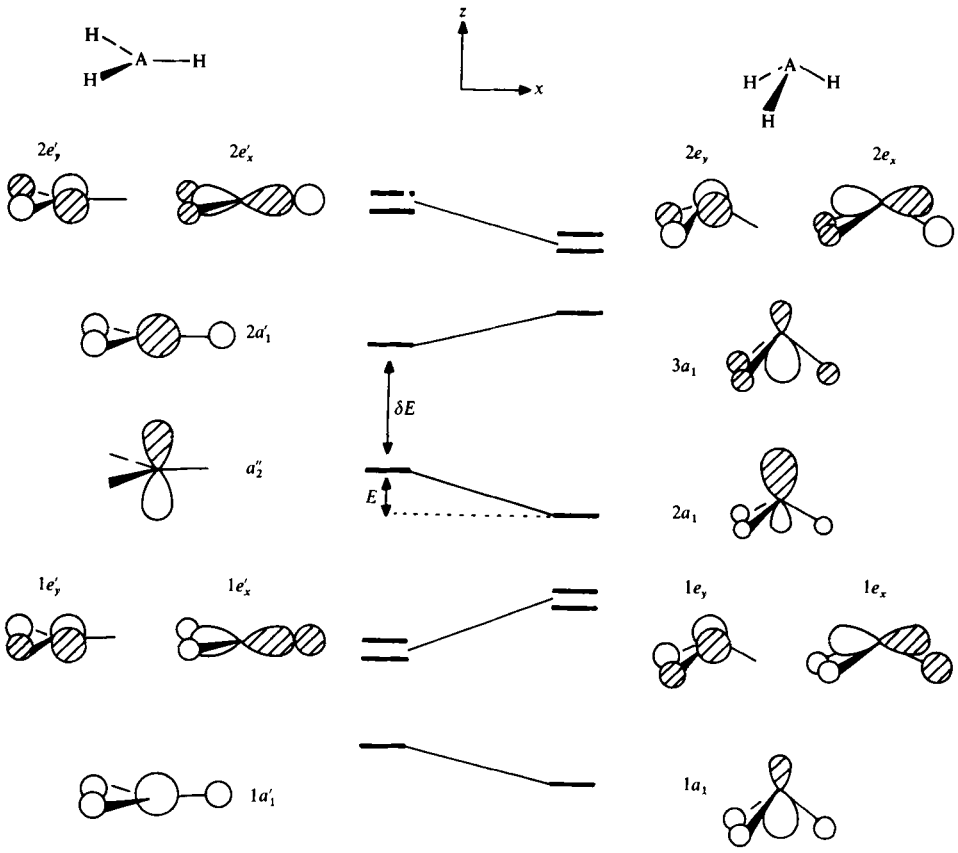

FIGURE 3. Correlation between the molecular orbitals of planar and pyramidal AH_3.

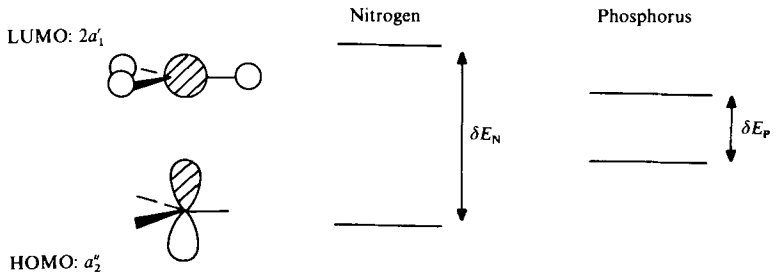

FIGURE 4. Effect on HOMO–LUMO energy separation in planar AH_3 of a change from nitrogen to phosphorus.

Walsh's rule[72] for predicting molecular shape may be stated simply as follows[66]: 'a molecule adopts the structure that best stabilizes the HOMO. If the HOMO is unperturbed by the structural change under consideration, the occupied molecular orbital lying closest to it governs the geometrical preference'. The valence molecular orbitals of planar trigonal and pyramidal AH_3 are shown in Figure 3, as is the correlation between them as a function of the change in geometry—the Walsh diagram. A detailed discussion of how the two sets are constructed (from one s orbital and three p orbitals on A and three s orbitals on the hydrogens) and correlated was given by Albright *et al.*[66], as well as ample theoretical justification. In particular, they showed how the molecular orbitals are related to the non-symmetry adapted bond orbitals derived from overlapping of four sp^3 hybrids on A with the three s orbitals of three hydrogens[66,70]. Note that these orbitals are derived by simple qualitative symmetry considerations and thus any calculation that may be done on the system must yield results of these symmetries although, of course, the energy ordering may be different[70]. In particular, the $3a_1$ and $2a_1$ orbitals may be in the opposite order, but this does not affect any of the qualitative conclusions below since their symmetries are the same.

From Figure 3 it can be seen immediately that for eight-electron systems such as amines and phosphines the pyramidal geometry will be preferred. However, the degree of pyramidalization is not predicted. The directed valence approach above suggests that for phosphines the non-bonding pair of electrons resides in an unhybridized s orbital on phosphorus. Examination of either a_2'' of the planar configuration or $2a_1$ of the pyramidal configuration shows that this is far from reality.

The difference in bond angle between amines and phosphines and the higher barrier to inversion of phosphines can be easily explained as a second-order Jahn–Teller effect as follows. It is easy to show by perturbation theory that the amount of stabilization E of the HOMO on pyramidalization depends inversely on the energy gap δE between HOMO and LUMO in the planar form[66]. The energy gap δE in turn is influenced by the nature of the central atom A (its size, electronegativity, etc.) and by the nature of the ligands. Figure 4 shows the effect of δE of changing from nitrogen to phosphorus. The smaller δE for phosphorus leads to a greater stabilization energy E in the pyramidal case, so we expect phosphines to be more pyramidal than amines i.e. to have smaller bond angles. Also, the energy barrier to the inversion process is higher since the transition state for that process is assumed to be the planar configuration (but see Section II.B.6).

We may enquire further into the factors that influence the energy gap δE. Two types of effect are expected: those which change the energy of the HOMO and those which affect the LUMO. We expect some factors to affect both HOMO and LUMO and some to have a disproportionate effect on one or the other. First, increasing the effective nuclear charge of atom A will draw all electrons closer to the nucleus and lower their orbital

energies. This would have the effect of decreasing the gap δE. However, some orbitals will be affected more than others, these being the inner orbitals, orbitals mainly localized on A and those with more s character (since they penetrate to the nucleus more effectively). Now, a_2'' of the planar geometry is affected more than $2a_1'$ because it is completely located on A (although it could be argued that this might be offset by the fact that it is p-type and the LUMO is s-type). This has the effect of increasing the gap δE with increased effective nuclear charge (i.e. increased electronegativity, e.g. a change from P to N). Second, bond length is relevant because in the LUMO increasing the bond length (e.g. a change from N to P) would decrease the antibonding character and so lead to a lowering of the energy of the LUMO. Again, the effect is to increase the gap δE on change from P to N. Since the most electronegative elements are in the first row, a change to longer bond length inevitably means moving to a less electronegative element.

Changing the ligands from hydrogen to fluorine or methyl will have even more complex effects. The hydrogen s orbitals are replaced by sp^3 orbitals in the case of methyl and p orbitals of fluorine. For the methyl case, the analysis[66] is similar to the above but requires a quantitative study of the variation of overlap integrals with bond length and angle to determine the magnitude of the HOMO–LUMO energy gap. For the fluorine case, the filled p orbitals on fluorine cannot be ignored and the analysis requires a correlation diagram between 16 valence orbitals. Although this is complex, it has been done[68,73].

The effect of the electronegativity of substituents can be explained by the same analysis. A very electronegative substituent causes all orbitals to decrease in energy, especially those which have coefficients on the substituent. Consider Figure 3 again; on replacement of hydrogen with fluorine, for example, all of the occupied MO levels will move down but that of the a_2'' orbital will be less affected since it is completely located on A. Thus the energy gap δE will be smaller for AF_3 than AH_3 and it is expected to have a smaller valence angle and larger inversion barrier. Hence the smaller valence angle in NF_3 than in NH_3 and its larger inversion barrier are explained. Unfortunately for this rather neat theory, the valence angle of PF_3 is larger than that of PH_3. The truth is probably that it is the valence angle that controls HOMO–LUMO splitting and not the other way around (see Section II.B.6).

An analysis of the effect of π-bonding capability of the ligands is also possible and is detailed in the book by Albright *et al.*[66]. In particular, they showed how π-acceptor properties of ligands (e.g. p orbital of a BH_2 group or π^* of a CO group) should lead to planarity at A and decreased inversion barrier and *vice versa* for π-donor ligands such as a halogen atom or NH_2 group.

Note that the fact that the HOMO is stabilized on pyramidalization and more so for phosphorus *suggests* that the angle at phosphorus will be narrower, *if there is a difference*. A quantum chemical calculation is required to determine whether there is such a difference. However, the usefulness of the Walsh diagram approach is not that everything is explained, but that the analysis shows naturally where all the complications arise. Thus we are not tempted to graft on *ad hoc* explanations to explain observations, but we may see where possible difficulties might arise and should be warned when to do a calculation.

d. Dangers in qualitative studies. Simple qualitative approaches can be misleading because, of their nature, they introduce simplifying assumptions that may not be valid. Consideration of the factors that may be operational in differences between first- and second-row compounds enables a check to be made of those which are ignored or poorly treated. Possible factors are the following:

(i) the difference in effective nuclear charge felt by the valence electrons;
(ii) the s–p energy separations are 10–12 eV for nitrogen and 6–9 eV for phosphorus;
(iii) the radial maxima for phosphorus 3s and 3p orbitals occur at larger distance from the nucleus than in nitrogen;

(iv) the sizes of s and p orbitals are comparable for the first row, whereas for lower rows the s orbitals are significantly smaller than the p orbitals[4]. Thus the nitrogen 2s and 2p orbitals both have their radial maxima at about 50 pm from the nucleus whereas for the phosphorus 3s it is at about 80 pm and for phosphorus 3p at about 100 pm. The difference arises because the 2p orbitals are not subject to an orthogonality constraint from core orbitals, whereas 2s and all other p orbitals are subject to such constraint[74]. The similarity in size for the first-row orbitals will lead to a greater importance of 2s–2p correlation effects;

(v) difference in overlap capability to the same atom for N and P—this is probably less important. For example, the overlap integral (calculated using the tables given by Mulliken *et al.*[75]) between N—H at the typical bond length of 101 pm is 0.55 whereas the same calculation for P—H gives 0.5, both values based on overlap of s orbitals. A similar calculation for N—C and P—C based on the overlap of s and p orbitals gives 0.55 and 0.29, respectively, and for N—F and P—F the values are 0.2 and 0.16, respectively;

(vi) possibly the most important, the 'size' of the atoms is different and so there is far more room around the phosphorus atom. Thus a simple trigonometric calculation shows that at the N—H bond distance of 101 pm, the distance between the hydrogens at a bond angle of 106.7° is 160 pm, whereas the corresponding distance in phosphine at its bond angle of 93.3° is 206 pm. The difficulty is to compare these two numbers meaningfully, since they are both well within twice the van der Waals radius for hydrogen (240 pm). Hence there is a contribution to bonding from H—H overlaps and it is difficult to give a radius value for the onset of internuclear or Pauli repulsions in the absence of an analysis of this bonding. If, for example, this were the dihydrogen molecule (which most emphatically it is not), then the H—H internuclear distance in ammonia would correspond to a position about one third of the way down the binding energy curve and a binding energy of about 0.06 hartree (the binding energy of H_2 being 0.17 hartree). In phosphine, the internuclear distance would correspond to a binding energy in H_2 of about 0.02 hartree. Also, the overlap of the hydrogens leads to a non-orthogonality of the p orbitals utilized in bonding and so there will be a Pauli repulsion between the bond pairs around a small atom[4].

It can be seen that all of the above qualitative approaches ignore at least one of these considerations. Indeed, some of the qualitative studies overlook some very important and well established considerations in bonding theory. As argued by Pauling[16], p orbitals can overlap the orbital of another atom more effectively than can the s orbital of the same shell so that, all else being equal, bonds made using p orbitals are stronger than those using s orbitals. Further, as he also showed[16], if there is an unshared pair there will be a tendency to keep it in the s orbital, which is more stable than the p orbitals, again all else being equal. Thus maximum non-bonding occupation of the s orbital and maximum utilization of p orbitals in bonding are expected to be dominant factors.

2. *Survey of* ab initio *calculations on phosphines*

Apart from some notable exceptions[76–79], it is only in the last decade that 'useful'[80] calculations on these systems have become available because of the advent of faster, more powerful computers and the availability of better basis sets and geometry optimization techniques. While the earlier studies could reproduce, after great effort, energies and experimental parameters (for example, inversion barriers[76]), computational limitations restricted detailed studies of geometry and orbital occupancy.

Indeed, even now, the introduction of more than a few heavy atoms restricts the amount of reliable information that can be obtained. An example of this can be seen in the work on

the concept of 'altruistic bonding'. This has been advanced to explain the longer P—C bond in tris(trifluoromethyl)phosphine than in phosphine (see Section II.A.1). The hypothesis was that the d orbitals on phosphorus weaken the P—C bonding while enhancing the P—F bonding[49]. Doubt was cast on this idea by calculations with and without d orbitals in the basis set, both of which gave the longer P—C bond[81], and further calculations[82] with a larger basis set failed to explain the phenomenon.

a. Basis set problems. Considerations of basis set and geometry optimization are very important in calculations on systems including second-row elements. Some of the problems are illustrated by the following examples.

Bernardi *et al.*[83] tried to test the Walsh diagram approach described above by calculating (using the STO-3G basis set) the total energy of the molecule and then recalculating in the absence of the HOMO–LUMO interaction. They found that the energy of the interaction was of a similar magnitude to the stabilization energy on pyramidalization, supporting the hypothesis that the HOMO–LUMO interaction is the controlling one. However, at the 4-31G level, the energy of the HOMO–LUMO interaction was dramatically reduced to one third of its previous value.

Marynick and Dixon[84] studied the basis set dependence of the inversion barrier in PH_3 and found that it depended strongly on basis. The most reliable value was that obtained with double zeta Gaussians plus polarization terms and including configuration interaction correcting for the effects of quadrupole excitations. The effect of correlation was found to be moderate at about 5% but they found that care needs to be taken in its use because they also showed that a minimum basis set gave a value high by 16% and configuration interaction at the same level almost doubled the error to 28% high.

In a study of substituent effects in second-row molecules, Magnusson[85] found that there were large discrepancies in substituent interaction energies at different basis set levels, particularly in electron-rich molecules, and the 6–31G basis set supplemented by d functions was required for reasonable results. However, molecular geometry and population analysis were found to be less sensitive, the 3–21G set being adequate, a result also found by Glidewell and Thomson[86]. Magnusson[85] also showed that care should be taken in the use of d functions. This is not surprising, since it is now well known that deficiencies in the starting basis can be compensated for by the addition of d functions leading to an artificial overestimate of their importance[87]. Notwithstanding this, Magnusson[85] did find a valence role for d functions. He also found that care needs to be taken in the use of split valence sets where the valence shell electron density is concentrated in the diffuse component of the valence shell functions[85].

In a study of the NMR chemical shift in PH_3, Chesnut and Foley[88] found that a triple valence split with two sets of d functions was necessary for the correct prediction of chemical shift. They also found that the interpretation of the change of chemical shift with change in geometry (from planar to pyramidal) was complicated by the choice of basis set and whether the bond length had been optimized at the two geometries (which required diffuse s and p functions). In other words, if one achieves a result at the experimental geometry and then tries to see what factors lead to that result by changing the geometry, there is no guarantee that the basis set remains adequate.

In a study of magnetic susceptibility and the NMR chemical shift tensor, Kutzelnigg and coworkers[89] confirmed the results of Chesnut and Foley[88], finding that the smallest reliable basis consisted of 11s,7p,2d for phosphorus and 5s,1p for hydrogen, contracted to (7s,6p,2d/3s,1p)—practically triple zeta. However, they cautioned that for multiply bonded systems even larger bases may be necessary[89].

It is then clear that the split valence and even double-zeta basis sets which are acceptable for carbon and other first-row elements are unsuitable generally for the *detailed* investigation of compounds of higher row elements. At least double-zeta quality basis sets

TABLE 6. Results of selected *ab initio* calculations on phosphines

Molecule	Calculation[a]	Energy[b]	r(P—H)[c]	∠XPX[d]	r(P—X)[c]	∠HPX[d]	Ref.
PH_3	STO-3G	−338.6364	137.8	95.0			93
	3-21G	−340.7045	142.3	96.1			93
	3-21G#	−340.7542	140.2	95.0			85
	3-21G*	−340.8140	140.2	95.2			94
	4-31G	−342.0256	143.3	95.0			93
	4-31G#	−342.0763	140.8	94.0			85
	4-31G*	−342.0903	140.9	92.8			95
	6-31G#//4-31G#[e]	−342.4529					95
	DZ + P		141.9	95.3			96
	> DZ + P	−342.3764	141.4	94.0			79
	> DZ + P[f]	−342.4560	142.1	93.8			76
	EST HF LIMIT	−342.5060					76
	DZ[g] + P + CI		141.6	95.4			97
	> DZ + P + CI	−342.4772	141.4				90
	> DZ[h] + P + CI	−342.5055					77
	DZ + P + CI	−342.5551	141.6	92.5			98
	> DZ + P + C	−342.6064	140.7	95.2			99
	DZ + P + CI[i]	−342.6437	141.3	93.7			84
	EXPT[j]	−343.9150	141.2	93.4			76
PH_2CH_3	STO-3G	−377.2239	138.1	93.7	184.1	98.9	93
	3-21G	−379.5337	142.5	95.6	190.8	93.0	93
	3-21G	−379.5337			191.0	98.1	86
	3-21G#	−379.5810	140.3	94.5	186.4	101.5	85
	3-21G*	−379.6411	140.4	94.6	185.5	102.3	94
	4-31G	−381.0128	143.5	94.6	191.6	101.0	93
	4-31G#	−381.0611	140.9	93.7	186.4	100.5	85
	6-31G#//4-31G#[e]	−381.4933					85
	6-31G* + C		141.6	94.7	185.7	101.7	91
	DZ + P + DF	−381.4918	140.4	94.7	185.6	97.8	100
	DZ[h,k]	−381.1505					78
	DZ[h,l] + P + DF + CI	−381.5865	140.4	94.7	185.6	97.8	101
	EXPT[j]		141.4	93.4	186.3	97.5	
$PH(CH_3)_2$	3-21G	−418.3632	142.8	98.9	190.7	97.6	86
	EXPT[j]		141.9	99.7	184.8	96.9	
$P(CH_3)_3$	STO-3G#	−454.4613		97.6	184.8		85
	3-21G	−457.1955		98.6	190.3		86
	3-21G#	−457.2378		101.5	187.7		85
	4-31G#	−459.0200		101.1	188.3		85
	EXPT[j]			99.1	184.1		
PH_2F	STO-3G#	−436.2089	139.9	91.4	155.3	94.8	85
	3-21G#	−439.1062	140.1	93.0	159.4	99.7	85
	4-31G#	−440.8356	140.8	93.0	162.5	97.2	85
	6-31G#//4-31G#[e]	−441.3218					85
	DZ + P		140.8	94.1	160.2	98.1	102
	> DZ + P[m]	−441.1100	141.3	92.9	162.5	98.7	79
PHF_2	DZ + P		140.9	98.5	158.1	96.3	102
	> DZ + P[m]	−539.8668	141.6	96.7	160.0	98.0	79
	EXPT		141.2	99.0	158.2	96.3	22
PF_3	STO-3G#	−631.3073		98.2	154.1		85
	3-21G#	−635.8855		97.1	155.0		85
	4-31G#	−638.4124		97.0	157.4		85
	DZ	−638.4605					89
	DZ[i,k] + P[m]	−639.2213					103
	> DZ + P[n]	−639.2697					89
	> DZ + P + C	−639.8578		97.1	156.3		99
	EXPT			97.1	156.1		23

[a]All self-consistent field, contracted Gaussian-type basis sets and geometry optimized by the gradient method unless noted otherwise, symbols STO-3G, DZ, 3-21G, 4-31G, and 6-31G have their usual meaning[92];* = a set of six d-type polarization functions added to basis set; # = set of five d-type functions added; P = other combinations of

(*continued opposite*)

with polarization terms and full geometry optimization along with some form of electron correlation[84,90,91] in general seem to be necessary.

b. Survey of calculations. Table 6 gives the results (geometry and total energy) of some selected calculations on phosphines. The results are mainly from the period after about 1982. Earlier calculations are listed in the papers by Kutzelnigg and coworkers[89] and Marynick and Dixon[84], the latter also giving a detailed comparison of their results with previous work. The literature has been surveyed as far as late 1988. Other useful calculations not included in Table 6 are those on silylphosphines by Glidewell[86], fluoromethylphosphines by Dixon and Smart[100] and aminophosphines and hydroxyphosphines by Magnusson[85,104].

As can be seen from Table 6, it does indeed require very large basis sets with polarization and correlation corrections to obtain acceptable results. A common observation is that the bond distance is too short by about 2 pm and the bond angle is too large by 2°. These features are coupled, since a shorter bond distance increases the repulsion between the hydrogens, leading to an increased bond angle. These discrepancies are usually remedied by the correlation correction. Note, however, that the number of calculations which include such corrections is small.

3. *Detailed* ab initio *studies of the bonding in phosphines*

Mindful of the basis set problems above, only the more recent studies of phosphine and simple derivatives are discussed[4,101,104-108].

a. Magnusson. One of the more detailed studies of the bonding in phosphines is contained within the series of papers by Magnusson[104-107]. The range of molecules studied included AH_4, AH_3, AH_2 and AH in addition to derivatives substituted by CH_3, NH_2, OH and F. The analysis was based on the results of calculations at the single configuration restricted Hartree–Fock level using the 3–21G basis set supplemented by polarization functions in the case of the second-row elements (3–21G# basis set). The calculations were carried out at optimum geometries but the results of bond angle variation studies were obtained at fixed A—H bond length (this may compromise any conclusions about the effects of geometry variation because it is well known[76,84,96] that the equilibrium bond length decreases on going from the D_{3h} to the C_{3v} conformation).

The actual analysis of the bonding was done by examination of the contribution each atomic orbital makes to Mulliken overlap populations *in conjunction* with its contribution to gross atomic populations (for a discussion of the various population analyses, see ref. 92). Populations were analysed *both within each MO and over the whole molecule.* The

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polarization functions added; DF = diffuse functions added; CI = with electron correlation by configuration interaction; C = with correlation by Møller–Plesset perturbation theory.
[b]Total electronic energy in hartrees; 1 hartree = 27.2 eV = 2625 kJ mol^{-1}.
[c]Bond length in pm.
[d]Bond angle in degrees.
[e]6–31G# basis set with geometry optimized for 4–31G# basis set.
[f]Geometry optimized but not by the gradient method.
[g]Pseudopotential method.
[h]Using experimental geometry.
[i]Slater-type basis set.
[j]From Table 2.
[k]951/52/3 uncontracted basis set.
[l]Generalized Valence Bond calculation.
[m]On phosphorus only.
[n]Four sets of d-type functions.

advantages, difficulties and justifications of this approach have been extensively discussed[85,104–107]. In particular, it is well known that Mulliken populations are sensitive to the basis set used[92], and this danger was averted by standardizing the basis sets and checking that they were adequate[85,104–107]. However, the reader can judge from Table 6 that the 3–21G and 3–21G# basis sets are at the lower end of a scale of adequacy. In response, Magnusson showed that some of his qualitative conclusions are not affected by changing to a larger basis[105].

The idea is that the contribution of a particular orbital to gross population will run counter to its contribution to overlap densities. An atomic orbital involved heavily in bonding must share charge with the orbitals of its partner atom; its contribution to the overlap density may be high but the gross population term will be very much reduced from the value expected for orbitals that are substantially non-bonding (about 2.0).

The key finding is that there is not a simple relationship between molecular geometry and the ratio of central-atom s-orbital involvement in molecular bonding to that of central-atom p-orbital involvement, as reflected in electron-density distributions. It was found that there is not a smooth increase in the s-orbital contribution to bonding as the bond angle rises. This is not surprising in the light of the discussion in Section II.B.1; rather, the tendency to maximize non-bonding s density results in no s-orbital contribution to bonding over much of the lower part of the bond-angle range. In fact, it was found that in the Main Group V hydrides the contribution of s electrons to overlap density is *antibonding* at a bond angle of 90°. As the bond angle increases, this contribution crosses to bonding (the crossover point is different for the hydrides of other groups), but only approaches significance near to 120°. This comes about because the coefficients of the atomic orbitals in each MO vary with bond angle (again, not linearly). Specifically, the proportion of s density contributing to the lowest energy valence MO rises.

One difficulty in reading Magnusson's papers[85,104–107] is that he refers to this ratio of s to p orbital involvement in bonding as a hybridization ratio. While this is perfectly valid, it is different from the usual idea of hybridization, familiar to organic chemists for example, which refers to a localized description of the bonding. This is discussed again in Section II.B.3.b.

i. Comparison of phosphine and ammonia. Magnusson's comparison between the bonding in ammonia and phosphine is shown in Tables 7 and 8. As expected, the calculation yields four valence MOs with the symmetries as in Figure 3, although the exact

TABLE 7. Bond angle variation of the composition[a] of the valence MOs in NH_3 and PH_3

MO	angle[b]	N2s	N2p	H1s	P3s	P3p	H1s
$2a_1$	90	−0.62	0.78	0.17	−0.61	0.75	0.23
	109.5	−0.40	0.91	0.11	−0.51	0.86	0.21
	120	0.00	1.00	0.00	0.00	1.00	0.00
$1e$	90	0.00	0.61	0.36	0.00	0.52	0.38
	109.5	0.00	0.59	0.35	0.00	0.49	0.37
	120	0.00	0.58	0.34	0.00	0.48	0.38
$1a_1$	90	0.72	0.19	0.15	0.71	0.09	0.21
	109.5	0.74	0.13	0.16	0.72	0.08	0.21
	120	0.74	0.00	0.17	0.72	0.03	0.22

[a]AO coefficients from STO-3G basis set calculations from ref 105 and 107; the p coefficient is that of the p orbital appropriate to the symmetry of the MO and the 1s coefficients are the r.m.s. values of the coefficient for the three 1s AOs; axes conventions as in Figure 3.
[b]In degrees.

TABLE 8. Variation with bond angle of s and p orbital atomic (q) and overlap (p) populations in NH_3 and PH_3

	NH_3[b]		PH_3[c]					
Angle[a]	p(s)	p(p)	q(s)	p(s)	q(p)	p(p)	q(d)	p(d)
90	0.00	0.62	1.80	−0.02	3.29	0.64	0.13	0.06
100	0.05	0.59	1.74	0.01	3.34	0.62	0.12	0.05
109.5	0.12	0.55	1.65	0.06	3.46	0.58	0.11	0.05
120	0.19	0.50	1.45	0.22	3.84	0.49	0.10	0.05

[a]In degrees.
[b]3–21G basis set results from ref. 105.
[c]3–21G# basis set.

form of the orbitals is different. The compositions of the orbitals and their variation with bond angle are given in Table 7. Table 8 gives the overlap density contributions to the A—H bond and their variation with bond angle. Unfortunately, some of the values quoted in Tables 7 and 8 are at different basis set levels, so some care should be taken in making comparisons between tables. The contributions of the valence orbitals to gross atomic and overlap (in parentheses) populations in NH_3 and PH_3 at their respective minimum-energy-optimized geometries are as follows (these optimized geometries are not the exact experimental ones but, as Magnusson showed[105], this does not affect the qualitative conclusions):

NH_3: 2s, 1.67(0.10); $2p_{xy}$, 2.32(0.49); $2p_z$, 1.90(0.05)
PH_3: 3s, 1.77(0.00); $3p_{xy}$, 1.76(0.45); $3p_z$, 1.55(0.19); 3d, 0.127(0.054)

In NH_3, at its optimized geometry, the 2s orbital provides a proportion of the N—H overlap density. In PH_3, at its optimized geometry, the 3s provides none. This arises because its contribution to bonding in the lowest valence MO ($1a_1$ in Figure 3) is exactly cancelled by an antibonding contribution in the HOMO ($2a_1$ in Figure 3). In ammonia, on the other hand, the bonding contribution is much larger than the antibonding contribution. Since the 3s orbital in phosphine provides no contribution to the P—H bonding, we must regard it as the main component of non-bonding electron density. However, the main contribution to the s density comes from the lower $1a_1$ MO and the HOMO is mainly the $3p_z$ orbital.

There is a relation between bond angle and orbital occupancy—s orbital occupations fall as the bond angle is raised, but the relation is not linear. The fall is more rapid near the end of the range (120° for AH_3). Thus, even in NH_3, where the bond angle is constrained to be 106.7°, the s electrons only account for about 15% of the nitrogen contribution to bonding.

Hence the s electrons remain non-bonding and the bond angle can be mainly understood as the balance between the p_z and the p_xp_y orbitals, the latter orbitals providing most of the bonding. It remains to be explained why the angle is large in ammonia if the more stable case is where s electrons are non-bonding. According to Magnusson, this is due to steric factors because bond angle cannot be reduced any further since the hydrogens, which are already very close (see Section II.B.1.d), will be forced too close together. This explanation was also advanced by Petke and Whitten[77] in their early *ab initio* comparative study of phosphine and ammonia and Goddard and Harding[74] advanced a similar argument but stated that it is repulsion between the bond pairs that is important. Hall[65] argued similarly and tried to quantify such an interaction.

Petke and Whitten[77] were also able to rule out the effects of d-orbital hybridization and examination of the d-orbital populations in Table 8 confirms that they are low. These d-orbital populations are typical (see also Lehn and Munch[76] and Trinquier *et al.*[97]), and most workers now agree that there is only a small valence role for d orbitals which, however, increases with more electronegative substituents. In particular, Magnusson[107] found that in PH_2CH_3 the d population occurs in the uppermost *e* orbital where it appears to improve the directional properties of phosphorus 3p orbitals overlapping with carbon 2p orbitals, 3s orbitals being unavailable in MOs of *e* symmetry.

In summary, the advantage gained by isolating s electrons in a non-bonding role often appears to offset any potential value of sp mixing in bonding. Where there is relatively low symmetry, s orbitals can contribute in an antibonding manner to the HOMO, thus cancelling out any bonding in the lowest energy valence MO. Reducing the bond angle in AH_3 reduces the symmetry and hence increases the non-bonding s density, thus lowering the energy, until the process is halted by steric constraints. Therefore, s-orbital contributions to bonding are most in evidence in the first row because it is here that steric constraints are largest, the atoms being smaller.

Hybridization in lower symmetry molecules is thus expected to be negligible in many cases and the ground-state configurations of many molecules, especially second-row hybrides, will have central atom s populations close to s^2, with bonding provided mainly by p orbitals. It is only in higher symmetry molecules (e.g. D_{3h} in the cases considered here) that s orbital bonding can be expected to be significant where s density is debarred from contributing to the HOMO by symmetry considerations. Also, s orbitals may be bonding where the s–p promotion energy is not high, i.e. to the left of the Periodic Table.

ii. Bonding in substituted phosphines. Magnusson[107] also studied substituted Main Group hydrides. He found the same patterns of s and p orbital contributions to bonding as for the hydrides described above. The s orbitals are chiefly employed in the lower and p orbitals in the upper MO but, as in PH_3, the HOMO is exceptional, containing substantial antibonding s character.

The variations with bond angle of atomic and overlap populations in trimethylphosphine and trifluorophosphine are given in Table 9. In the trimethyl case, once again, as symmetry is lowered (bond angle decrease) the s orbital overlap density drops to negative values and the s orbital populations rises to nearer the s^2 non-bonding values. Once again the variation with bond angle is not linear and the s orbital only begins to make a significant contribution to bonding at the top of the range of bond angle[107]. The trifluoro case is different (see below).

Table 10 gives the s and p orbital contributions to atomic and overlap populations in various substituted phosphines at their optimized minimum energy geometries, together with their respective HOMO energies. The monosubstituted phosphines inevitably are less symmetrical and it can be seen that segregation of the s and p electron density to non-

TABLE 9. Variation with bond angle of s and p orbital atomic and overlap[a] populations[b] in some trisubstituted phosphines

Molecule	At 90°	At 120°
PH_3	3s: 1.78 (−0.01); 3p: 3.30 (0.65)	3s: 1.45 (0.22); 3p: 3.83 (0.49)
$P(CH_3)_3$	3s: 1.61 (−0.64); 3p: 2.66 (0.57)	3s: 1.29 (0.18); 3p: 3.32 (0.32)
PF_3	3s: 1.61 (−0.08); 3p: 1.94 (0.40)	3s: 2.04 (−0.46); 3p: 1.44 (0.37)

[a]In parentheses.
[b]3-21G# basis set results from ref. 107.

TABLE 10. HOMO energies and contributions of the atomic valence orbitals to gross atomic and overlap[a] populations[b] in some phosphines[c]

				ε_{HOMO}(eV)
PH_3	3s: 1.77 (0.00)	3p: 3.31 (0.64)	3d: 0.13 (0.05)	−10.39
$P(CH_3)_3$	3s: 1.53 (−0.13)	3p: 2.70 (0.55)	3d: 0.13 (0.16)	−8.59
PF_3	3s: 1.61 (−0.11)	3p: 1.97 (0.40)	3d: [0.75(0.31)][d]	−12.30
PH_3	3s: 1.77 (0.00)	3p: 3.31 (0.64)	3d: 0.13 (0.05)	−10.39
PH_2CH_3	3s: 1.71 (−0.10)	3p: 3.11 (0.53)	3d: 0.13 (0.07)	−9.71
PH_2NH_2	3s: 1.63 (−0.09)	3p: 2.97 (0.57)	3d: 0.18 (0.12)	−9.68
PH_2OH	3s: 1.65 (−0.10)	3p: 2.83 (0.50)	3d: 0.20 (0.15)	−10.07
PH_2F	3s: 1.67 (−0.08)	3p: 2.74 (0.39)	3d: 0.20 (0.15)	−10.56
PH_3	3s: 1.77 (0.00)	3p: 3.31 (0.64)	3d: 0.13 (0.05)	−10.39
PH_2F	3s: 1.67 (−0.08)	3p: 2.74 (0.39)	3d: 0.20 (0.15)	−10.56
PF_3	3s: 1.61 (−0.11)	3p: 1.97 (0.40)	3d: [0.75(0.31)][d]	−12.30
PH_3	3s: 1.77 (0.00)	3p: 3.31 (0.64)	3d: 0.13 (0.05)	−10.39
PH_2CH_3	3s: 1.71 (−0.10)	3p: 3.11 (0.53)	3d: 0.13 (0.07)	−9.71
$PH(CH_3)_2$	3s: 1.64 (−0.12)	3p: 2.89 (0.55)		
$P(CH_3)_3$	3s: 1.53 (−0.13)	3p: 2.70 (0.55)	3d: 0.13 (0.06)	−8.59
$N(CH_3)_3$	2s: 1.69 (0.05)	2p: 4.00 (0.49)		

[a] In parentheses.
[b] 3-216# basis set results from ref. 107.
[c] At their minimum energy optimized geometries.
[d] At STO-3G* level.

bonding and bonding orbitals, respectively, is achieved to a high degree in them even though the bond angles are near 100° in most cases. Even in the higher symmetry trisubstituted cases there may be additional valence shell MOs to which the s density may contribute in an antibonding manner and a certain amount of segregation is still possible, in contrast to phosphine itself, which has only four valence shell MOs. A striking example of this effect is seen in the planar geometry of PF_3 in Table 9, where there is indeed an extra high lying a_1' orbital[68,73] and maximum non-bonding s density is achieved.

There is a small d-orbital contribution to bonding. Once again it occurs mainly in the uppermost *e* orbital, where it appears to improve the directional properties of phosphorus 3p orbitals overlapping with carbon or other 2p orbitals[107]. The d-orbital populations are higher in derivatives with electronegative substituents, as expected (see Section 2.II.A).

Increasing effective charge of the X atom has a predictable effect on polarity of the A—X bond and along the sequence $X = CH_3$, NH_2, OH, F there is a uniform fall in p-orbital populations. However, when the charge transfer is taken into account, the effectiveness of the p orbitals in bonding shows a smaller fall along the sequence[107]. This fall can be rationalized by the increasing imbalance between the energies of the central atom p orbital and the X orbitals. The variation in s-orbital utilization is less uniform.

In trimethylphosphine, the HOMO is highly localized on phosphorus and has an $sp^{2.0}$ ratio and thus marked directional character. Because the P3s orbital is better matched with the C2s than with H1s orbital, addition of the CH_3 group increases the utilization of the phosphorus 3s orbital in the bonding orbitals of the molecule. Therefore, there is a steady drop in the availability of the 3s for the HOMO and therefore a rise in the HOMO energy. This is in qualitative agreement with the results of photoelectron spectroscopy[109] (see Section II.B.4).

The difference in s orbital bonding in trimethylamine may be attributed to the larger

CNC bond angle (optimized at 112.6, compared with 101.5 for PMe_3) and the differences in gross atomic population to the larger effective charge of nitrogen.

Working with AH_3X series (X = CH_3, NH_2, OH, F), Magnusson showed that the s-orbital contribution to the A—X overlap density is much reduced from its value in the parent hybride irrespective of the electronegativity of the substituent[106]. The effect did not extend to the A—H bonds, which retain the characteristics they possess in the unsubstituted hydrides. This effect is also present in the PH_2X series but to a much lesser degree, because the s-orbital contribution is already very low in PH_3. This is relevant to the Walsh–Bent hypothesis, i.e. that atomic p character tends to concentrate in orbitals directed towards electronegative substituents[110]. The idea is that the energy is minimized by placing charge in those parts of the molecule where the potential is lowest, tightly bound s character near the central atom in its bond to the less electronegative atom(s) and less tightly bound p character near the electronegative substituent in its bond to the central atom. There are then consequences for bond angle in the s:p ratios that result. Magnusson has shown[106], again for AH_3X molecules, that, although there is a sharp drop in s-orbital participation in the A—X bond, this response is unrelated to the electronegativity of the substituent and all of it is due to the mechanism of segregation which can occur when the symmetry is lowered by substitution.

Finally, by analysis the energy of interaction between a substituent and the PH_2 group, Magnusson[104] found PH_2 to be a weak σ-acceptor and a weak π-donor group.

b. Kutzelnigg. A different perspective is provided by Kutzelnigg[4] with results also based on SCF calculations but with much larger basis sets (triple zeta plus polarization). However, the results are difficult to compare with those of Magnusson[85,104–107] considered above, because the delocalized canonical MOs (presumably similar to those of Magnusson) were subjected to a transformation to convert them to localized molecular orbitals (LMOs). This is a common procedure in calculations[92] and leads to a set of MOs that would appeal to a chemist, the charge probability density of each bonding MO being localized in the region of one of the bonds and the overall wavefunction being unaffected[92]. In this case the transformation used was that of Foster and Boys[111]. This type of calculation is more appropriate for making statements on the nature of hybridization in a molecule because separate population analyses of each LMO indicate which hybrid AO is involved in a given bond.

Kutzelnigg[4] found that the s:p ratio for the hybrids forming the N—H bonds in NH_3 was 1:2.90 whereas that for the P—H bonds in PH_3 was 1:3.83. The s:p ratios for the lone pairs was 1:2.37 for ammonia and 1:0.95 for phosphine. It can be seen that the values for the first and second rows are not as dramatically different as would be expected from their different valence angles. In particular, in phosphine, there can be no suggestion of pure p bonds, nor can the lone pairs be regarded as pure 3s AOs. The reason why there is confusion about the s:p ratios calculated on the basis of the valence angle is that such a calculation assumes that the hybrids are orthogonal, which they are not[4].

Kutzelnigg[4] also explained why there is a higher s:p ratio (less hybridization) in phosphine than ammonia and the origin of the difference in their valence angles. His explanation lies in why there is hybridization in the first place, for which he gave three reasons: (i) hybrid AOs overlap more efficiently, (ii) hybridization reduces the repulsion between the X—H bond and the lone pairs and (iii) hybridization favours larger bond angles. For the second-row compounds all three of these reasons are less important[4], because the 3s AOs are smaller and less diffuse than the 3p AOs, which reduces the Pauli repulsions both between the P—H bonds and between the bonds and the lone pair and makes for less strengthening of the bonding on hybridization.

c. Other studies. Lehn and Munch[76] found that the HOMO is 88% localized on phosphorus with 15% P3s and 73% P3p character according to gross population analysis. This is in qualitative agreement with the results of Magnusson[107].

Røeggen and Wisløf Nilssen[108] studied the difference between phosphine and ammonia using the extended geminal model[108] by partitioning the system into fragments corresponding to the core and valence parts of the molecule. They then examined how the intra- and inter-fragment energies varied with bond angle. They found that the difference in bond angle between phosphine and ammonia was due to a difference in the interaction of the valence and core fragments—this rises in energy with decreasing bond angle to a much greater extent in ammonia than in phosphine. The difficult part was analysing which part(s) of the valence fragment was responsible for the difference and the authors did not commit themselves as to whether the bond pairs, lone pairs, hydrogens or a combination were responsible.

Dixon *et al.*[101] reported, in the course of studies on simple ylides, the only detailed valence bond calculation on phosphines. They gave contour plots for the generalized valence bond orbitals, which are composed of two one-electron orbitals, in phosphine and methylphosphine and for comparison those of ammonia and methylamine. Mainly the results are similar except that the orbitals are more diffuse on phosphorus, as expected from electronegativity. The difference is in the lone pair on phosphorus. In methylphosphine the outer, more diffuse, of the one electron orbitals of the lone pair shows a striking difference to its nitrogen counterpart. It is significantly broadened and no longer has its maximum density along the same vector as the maximum of the inner orbital of the lone pair. Rather, the maximum lies almost directly behind the P—C bond with some density over the P—C bond. Dixon *et al.*[101] stated that this is evidence for d-orbital character in the lone pair. A similar difference was noted between the lone pairs of phosphine and ammonia. The presence of the CH_3 group is a significant perturbation on the lone pair on phosphorus in methylphosphine and it moves away from the CH_3 group.

4. Empirical calculations and studies of ionization potentials

Given that there are serious computational difficulties in doing *ab initio* calculations on compounds of second-row elements, it is surprising that there have been relatively few empirical calculations. This is particularly noticeable in the case of the MNDO method because, despite the fact that parameters have been available for a long time[112,113], it has been applied only sporadically to phosphines[114-118].

The results (molecular geometry and ionization potentials) of some empirical calculations are given in Tables 11 and 12, with comparisons with *ab initio* results and with experiment. Unfortunately, the comparison with *ab initio* ionization potentials in Table 12 is not as useful as it could be because none of the later larger *ab initio* calculations give listings of orbital energies. There is also some disagreement in assignment, in particular between the results of Xiao *et al.*[121] and those of Sodhi and Brion[123], and in the absence of some of the experimental orbital energies these cannot be resolved. Additional data and references for ionization potentials may be found in ref. 107.

a. SCM–Xα–DV calculations. In a careful study using this method, Xiao *et al.*[121] investigated the nature of the frontier orbitals in phosphine, trimethylphosphine and trifluorophosphine. The method used the experimental gas-phase geometries and reproduced accurately the experimental ionization potentials[111,121], as can be seen from Table 12. The only real discrepancy is the reversal of the $6e$ and $1a_2$ ionization potentials in PF_3. Detailed atomic compositions for the three compounds were given, which are reproduced in an abbreviated form together with the orbital energies in Table 13.

TABLE 11. Comparison of experimental results and *ab initio* and empirical calculations on some phosphines—molecular geometry

Molecule	Calculation[a]	r(P—H)[b]	∠ XPX[c]	r(P—C)[b]	∠ HPC[c]
PH_3	EXPT	142.0	93.5		
	SCF	141.3	93.7		
	SINDO1	142.4	95.4		
	MNDO[d]	134.0	96.1		
PH_2CH_3	EXPT	141.4	93.4	186.3	97.5
	SCF	140.4	94.7	185.6	97.8
	SINDO1	143.0	94.3	181.8	98.9
	MNDO[e]	134.3	96.1	174.9	100.9
$PH(CH_3)_2$	EXPT	144.5	99.2	185.3	96.5
	SCF	142.8	98.9	190.7	97.6
	SINDO1	143.4	106.4	183.9	97.3
	MNDO[e]	134.6	106.9	175.7	100.6
$P(CH_3)_3$	EXPT		98.3	184.1	
	SCF		101.1	188.3	
	SINDO1		103.2	185.9	
	MNDO[e]		106.8	176.1	
PF_3	EXPT		97.3	157.0[f]	
	SCF		97.1	156.3[f]	
	SINDO1		97.7	157.8[f]	
	MNDO[d]		98.9	155.6[f]	

[a]Experimental data from Tables 2–4, best SCF calculation from Table 6, SINDO1 results from ref. 25.
[b]Bond length in pm.
[c]Bond angle in degrees.
[d]Ref. 114.
[e]Ref. 118.
[f]r(P—F).

Examination of Table 13 shows that all orbital energies are lowered by methyl substitution and all are raised by fluorine substitution. It should be noted that the same result was found experimentally for the core levels by Sodhi and Cavell[124]. The orderings of frontier orbital energies in the three compounds are depicted schematically in Figure 5 and it can be seen that the LUMO is of *e* symmetry in PH_3 and PF_3 but is of a_1 symmetry in $P(CH_3)_3$. As expected, the HOMO is of a_1 symmetry.

As can also be seen from Table 13, the HOMO of PX_3 consists primarily of a lone pair s–p hybrid on phosphorus. The ionization energy and orbital energy ordering $P(CH_3)_3 < PH_3 < PF_3$ parallels the phosphorus s character of the HOMO: $P(CH_3)_3$ 11% s and 60% p; PH_3 14% s and 67% p; PF_3 29% s and 32% p. All of these trends follow the expected electron-withdrawing ability of the substituents, $CH_3 < H < F$, and apparently conform to Bent's rule, but the analysis is partly flawed because no overlap populations are given.

From an analysis of contour maps[121] of the HOMO in each case, the back lobe of the s–p hybrid interacts with the substituent attached to phosphorus in a σ-bonding fashion. However, it is the LUMO contour maps which are the most interesting. In PH_3 the 3*e* orbital possesses π symmetry with respect to the principle axis of symmetry and a similar type of orbital is found in PF_3 and $P(CH_3)_3$, although in the latter it is not the LUMO. Although the symmetry is the same in these acceptor orbitals, there are some significant differences between them. In particular, the energy of 7*e* in PF_3 is lower than that in PH_3 or $P(CH_3)_3$, which might be expected to enhance the acceptor properties of PF_3. Also, the composition of the *e* orbital is different in the three phosphines because

TABLE 12. Comparison of experimental results and *ab initio* and empirical calculations on some phosphines—ionization potentials[a]

Molecule	Orbital	Expt[b]	Xα[c]	MNDO[d]	SCF
PH_3	$5a_1$	10.59	10.39	11.43	10.52[e]
	$2e$	13.60	13.09	13.56	14.18[e]
	$4a_1$	21.20	20.43		
PH_2CH_3	$5a'$	9.70		10.49	9.78[f]
	$4a'$	12.40		11.96	
	$2a''$	12.70		13.37	
	$3a'$	14.45		14.68	
$PH(CH_3)_2$	$6a'$	9.10		10.43	9.26[f]
	$4a''$	12.95		12.31	
	$5a'$	13.65		12.74	
	$3a''$	14.15		14.19	
	$2a''$	15.00		14.37	
$P(CH_3)_3$	$8a_1$	8.58	8.41	10.30	8.95[f]
	$6e$	11.31	10.67	12.21	
	$1a_2$		12.01	13.96	
	$5e$	12.70	12.11	14.20	
	$7a_1$		13.13	15.18	
	$4e$	15.80	13.07	14.87	
	$6a_1$		15.75		
	$3e$	19.60	19.53		
PHF_2	$11a'$	11.00		12.27	
	$10a'$	15.10		14.49	
	$6a''$			15.54	
	$5a''$	15.80		15.81	
	$9a'$			16.36	
	$4a''$			17.73	
	$8a'$	17.6		17.85	
	$7a'$	18.3		21.94	
PF_3	$8a_1$	12.28	12.19		
	$6e$	15.89	15.00		
	$1a_2$	16.29	14.68		
	$5e$	17.35	16.00		
	$7a_1$	18.51	17.17		
	$5e$	19.31	17.83		

[a] In eV.
[b] HeI PES band maxima (vertical ionization potentials) from refs 109, 116, 119, 120.
[c] Refs 109 and 121.
[d] Ref. 116.
[e] Ref. 76.
[f] Ref. 122.

in PH_3 $3e$ is a hybrid of 36% 3p and 23% 3d on phosphorus, while the respective percentages are 14% and 10% for $P(CH_3)_3$ ($7e$) and 44% and 23% for PF_3 ($7e$). This point will be returned to in Section II.E on the bonding in transition metal complexes, but it can be noted that this is different from the usual description of the acceptor orbitals in phosphines acting as ligands in such complexes. Note that there is disagreement on whether the LUMO in PH_3 is of a_1 or e symmetry[121] (cf. Figures 3 and 5).

b. MNDO calculations. In a combined MNDO and PES study, Cowley *et al.*[116] tried to explain the enhanced basicity of less symmetrical phosphines—for example, PHF_2 is much more basic than a consideration of the basicities of PH_3 and PF_3 would lead one to

TABLE 13. SCM–Xα–DV[a] ground-state valence orbital energies and Mulliken gross populations in some phosphines

Molecule	Orbital[b]	Energy[c]	P3s	P3p	P3d	C(F)2s	C(F)2p	H1s
PH_3	$6a_1$	1.61	0.08	0.12	0.01			0.19
	$3e$	0.88		0.36	0.23			0.30
	$5a_1$*	−6.08	0.14	0.67				0.33
	$2e$	−8.63		0.47	0.01			0.52
	$4a_1$	−15.47	0.64	0.01				0.33
$P(CH_3)_3$	$7e$	0.85		0.14	0.10	0.06	0.05	0.10
	$9a_1$	0.43		0.01			0.05	0.19
	$8a_1$*	−4.90	0.11	0.60		0.01	0.12	0.11
	$6e$	−7.52		0.26	0.01	0.07	0.50	0.12
	$5e$	−8.96		0.02			0.44	0.50
	$1a_2$	−9.00					0.40	0.52
	$4e$	−10.03		0.05			0.43	0.49
PF_3	$9a_1$	1.94		0.24		0.08	0.21	
	$7e$	−1.05		0.44	0.23	0.04	0.26	
	$8a_1$*	−7.90	0.29	0.32	0.01		0.36	
	$1a_2$	−10.14					0.99	
	$6e$	−10.55			0.01		0.99	
	$5e$	−11.61			0.02		0.97	
	$7a_1$	−12.92	0.06	0.14	0.02	0.01	0.77	

[a] From ref. 121.
[b] Asterisk denotes the HOMO.
[c] In eV.

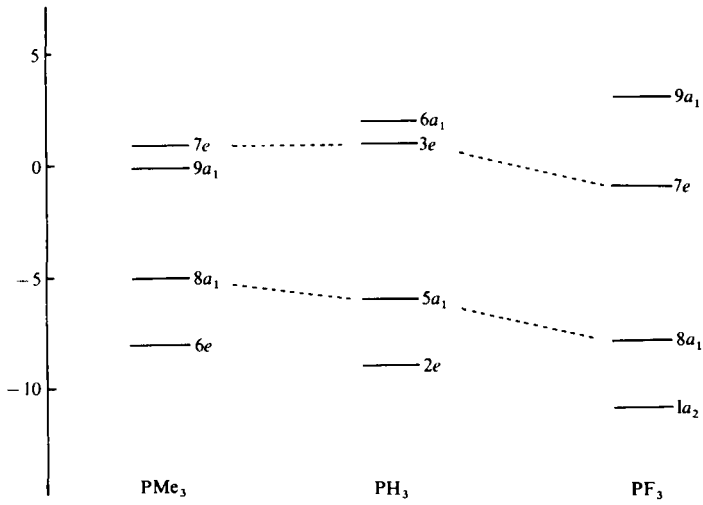

FIGURE 5. Valence orbital energies (eV) of some phosphines.

expect. They found that this was reflected in the trends of the ionization energies (see Table 12), in that PHF_2 has a significantly lower first ionization energy than expected by extrapolation of those of PH_3 and PF_3. This can be ascribed, in the now familiar way (see Section II.B.3.a), to the lower symmetry, which allows lower energy orbitals to interact with the HOMO because they now have the same symmetry.

c. Ionization potentials. The first ionization energy in the photoelectron spectrum of a phosphine is normally in the range 6–11 eV and is taken to correspond to the removal of an electron from the phosphorus 'lone pair'. Although the HOMO usually contains a strong contribution from the 3s and 3p orbitals of phosphorus, the extent to which these atomic orbitals are mixed with bonding orbitals of the rest of the molecule is very variable, ranging from 10 to 70%, so that it is dangerous to assume that it is a property of phosphorus that is being measured. Hence it is important in the interpretation of observed trends to restrict explanations to series of molecules that show similar responses to substitution.

It is often presumed that a relation exists between the ionization energy and the substituent electronegativity and that the lack of an actual correlation is due to steric effects. Although the correlation between proton affinity and ionization potential is very useful in closely related groups of compounds[125], ionization energy is unsatisfactory as a general indication of phosphorus donor power[107]. However, by analysing population and energy data for PX_3 and PX_3^+, Magnusson[107] showed that the composition of the HOMO is sufficiently similar to the hole density that is left behind on ionization to justify the use of the HOMO properties as an explanation of substitution-induced trends. He found that charge displacement in the HOMO, to which ionization energy should be very sensitive, is the best explanation for the experimental results, not alteration of s:p ratios. Response to substitution can be complex, as can be seen in Table 14, which shows the results of methyl and trifluoromethyl substitution on HOMO energy, proton affinity, charge on phosphorus and HOMO localization. Both substituents withdraw electrons from phosphorus but the respective ionization energies move in opposite directions. Population analysis does not support the idea that this behaviour is the simple consequence of adding an electron donor (CH_3) as opposed to an electron acceptor (CF_3). The calculated charge distributions show phosphorus being depleted of electron density by both substituents. This loss of charge occurs in the HOMO and in the molecule as

TABLE 14. Response of some orbital and molecular properties to substitution in selected phosphines[a]

Molecule	ε_{HOMO}[b]	PA[c]	q_P[d]	HOMO s/p utilization and localization[e]	Gross atomic and overlap populations[f]
PH_3	−8.19	970	14.79	0.38/0.56 90%	3s: 1.68 (0.00); 3p: 3.01 (0.57)
$P(CH_3)_3$	−6.86	1222	14.64	0.58/1.14 74%	3s: 1.54 (0.00); 3p: 2.84 (0.55)
$P(CF_3)_3$	−8.69	920	14.70	0.30/0.14 67%	3s: 1.71 (−0.02); 3p: 2.87 (0.48)
PF_3	−8.63	882	14.48	0.74/0.70 71%	3s: 1.61 (−0.05); 3p: 2.24 (0.35)

[a] Results of calculations using the STO3-G* basis set at experimental geometries from ref. 107.
[b] In eV.
[c] Proton affinity in kJ mol^{-1}.
[d] Total electronic charge on phosphorus in negative atomic units.
[e] Orbital utilization is the sum of the squares of the s/p orbital coefficients in the HOMO, localization is the sum of the squares of the phosphorus orbital coefficients as a percentage of the total sum of squares of coefficients of all contributing orbitals in the HOMO.
[f] Contribution to overlap population of P—X bond in parentheses.

whole, but it is the manner in which the charge is transferred that affects the orbital energies.

Comparison of methylphosphines with fluorophosphines shows some similar responses to the orbital energies of the attached atoms, but although the more electronegative substituent produces the expected effect on the ionization energy (a rise of 1.7 eV), the manner of its action is not merely the obverse of the action of the less electronegative methyl group[107]. In the PH_nF_{3-n} series the HOMO energies fall because of the increase in F2p character, whereas in the $PH_n(CH_3)_{3-n}$ series it is the increased utilization of the P3s atomic orbital in the lower MOs that depletes the HOMOs of 3s character and raises the energy. The p character remains constant but the s:p ratios fall from $sp^{1.4}$ in PH_3 to $sp^{1.9}$ in $P(CH_3)_3$.

In contrast to substituent effects, which are felt throughout all occupied MOs, the effect of bond angle is concentrated in the HOMO[107]. The changes in ionization energy are much larger than the effect of bond angle on donor properties would suggest. From CPC angles of 94° to 106° the HOMO s:p ratio changes from $sp^{1.8}$ to $sp^{2.5}$ compared with a change of only $sp^{1.7}$ to $sp^{1.8}$ overall. Likewise, the HOMO component of the calculated charge on phosphorus changes by four times that of the overall q_P value. Widening the CPC bond forces a reduction in the 3s contribution to the HOMO because of its increased contribution in other molecular orbitals even though the overall change is small[107].

5. Summary of the bonding in phosphines

The simple approaches to the bonding in phosphines have been shown to be not very useful. The VSEPR method is gravely deficient for the description of phosphines; it can only explain the bond angle after grafting on yet another axiom and then it fails totally to explain changes on substitution. Even the axioms that it uses have been shown to be incorrect, for example a calculation[64] of repulsion effects in H_2O and H_2S shows that lone pair–bond pair repulsion is less than bond pair–bond pair repulsion.

The directed valence method is useful for teaching in freshman courses—it gives a feeling for the orbitals being used, the $3 \times p$ in phosphine and $4 \times sp^3$ in ammonia. However, the inherent predictions of a non-directional lone pair and the derivation of simple bond angle/sp ratio equations are shown by calculation to be incorrect. Crucially, the relative magnitude of promotion energies in the first and second rows, on which the whole idea is based, is not in the right direction! Also, since it is merely a restatement of the obvious, it can make no prediction about the effects of substitution.

The Walsh diagram approach is by far the most satisfactory of the qualitative approaches, but that satisfaction is bought at the expense of more complexity. However, for any serious qualitative analysis, it must be used.

Deeper understanding can only be achieved within the framework of quantum chemistry calculations which resolve some of the paradoxes generated by the qualitative methods. For example, by the directed valence approach, phosphine has its lone pair in a pure s orbital and not only is it predicted to be non-directional but also the non-bonding electrons have to be of lower energy than the bonding electrons! Also, in ammonia, by the directed valence approach, the s electrons take part in bonding, which is reasonable because simple arithmetic shows that the nitrogen 'promotion energy' just balances the energy recovered from $3 \times N—H$ bonds. However, the same calculation for phosphine suggests more strongly that the s orbital should be involved in bonding, apparently in contradiction to the observed bond angle.

On solving the Schrödinger equation for pyramidal AH_3, one must obtain a series of MOs, the important seven of one such series being shown on the right in Figure 3. By symmetry these will have to have approximately the shapes shown, but there may be disagreement about the relative size of lobes, etc., depending on the level of sophistication

of the calculation. Although it is difficult (and in some cases confusing), the practising chemist needs to connect this description to the atomic orbitals of the atoms making up the molecule.

On examination of the results of the calculations for phosphine and referring again to Figure 3, it can be seen that:

(i) the $1a_1$ and $1e$ orbitals provide the bonding by virtue of their overlap population being positive;
(ii) $2a_1$ is non-bonding because the bonding of the p orbital contribution to it is exactly balanced by the antibonding of the s-orbital contribution;
(iii) the contribution of the s electrons to chemical bonding is zero overall, this being achieved by their bonding in $1a_1$ being balanced by antibonding in $2a_1$;
(iv) all the bonding is done by p orbitals when it is all added up, including the bonding by p_z in $2a_1$ and $1a_1$;
(v) the lone non-bonding pair is located in $2a_1$ (which is the HOMO) and therefore has the observed directional properties;
(vi) the LUMO may be $3a_1$ or $2e$ and this is not yet settled by the calculations—(see Section II.B.4.a) and also it will depend on the phosphine substituents[121].

In this way, the s electrons do not contribute to bonding and yet the non-bonding electrons are not in the s orbital! This is a paradox only if one forgets that there is no phosphorus s orbital in PH_3, only the utilization of the phosphorus s orbital in various MOs of PH_3.

Ammonia can be compared with phosphine using the same procedure, again referring to Figure 3:

(i) again the bonding is provided by the $1a_1$ and $1e$ orbitals;
(ii) the $2a_1$ orbital is still non-bonding but its character is different from the same orbital in phosphine in that there is a lower contribution to it by s electron density, because the separation of s and p orbital energies is larger in nitrogen than in phosphorus;
(iii) the important difference is that the s electrons are bonding to a certain extent, this being caused by their lower contribution to antibonding in $2a_1$ and their higher contribution to bonding in $1a_1$, and this change is due to the higher symmetry (larger bond angle) ammonia;
(iv) the bonding is done by a combination of s and p orbitals but not the 25%–75% split as suggested by the directed valence approach (the s contribution being less than expected);
(v) the HOMO is again $2a_1$ (the lone pair of electrons);
(vi) the LUMO is presumed to be $3a_1$ or $2e$.

The differences between phosphine and ammonia become relatively easy to understand if one takes the view that it is bond angle which controls the utilization of central atom s and p orbitals in bonding and not the other way around. In turn, the bond angle is dictated by steric factors—it cannot go below 107° in ammonia because there is not enough room around the nitrogen. Indeed, a picture emerges[4] that the first row of the Periodic Table is the anomalous one, whether this be because the atoms are smaller or because the 2s and 2p orbitals have similar radial extents.

6. Other studies of structure and bonding in phosphines

a. Inversion barriers in phosphines. Inversion barriers in Main Group 5 compounds were critically reviewed last by Lehn[126] and Rauk *et al.*[127]. Their careful discussions are still relevant, especially the treatment of classical versus tunnelling mechanisms and the

resultant non-correlation of barrier heights and rates of inversion, the distinction between repulsive and attractive dominant barriers and the difficulties in the experimental determination of barriers (especially when another conformational change may be occurring, e.g. bond rotation).

The factors affecting the size of barriers were also discussed in earlier reviews[14,126,127], some being better understood than others. Five major factors were identified, as follows, the first three presenting fewer problems in understanding:

i. Steric effects. As the steric requirement of a substituent increases, the pyramidal ground state is destabilized relative to the less crowded transition state (assumed to have planar trigonal geometry), with a resultant decrease in the barrier to inversion[126,127].

ii. Angular constraint. Inclusion of the inversion centre in a small ring can lead to substantial increases in the barrier to inversion, presumably because the smaller angles imposed by the ring have to be opened to 120° in the transition state[126,127].

iii. Conjugative effects. Adjacent unsaturated systems lead to significantly lower barriers to inversion at nitrogen and phosphorus. This can be rationalized as a stabilization of the transition state by increased conjugative interaction of the unsaturated system with the lone pair of electrons which are contained in a p orbital in the transition state (again assumed to be planar trigonal) leading to the delocalization of the lone pair of electrons[126,127]. Electronegative groups alpha to the inversion centre can also assist in delocalization by hyperconjugation.

iv. Substituent electronegativity. Increasingly electronegative substituents lead to an increase in the inversion barrier. This was less well understood at the time of the earlier reviews[126,127], the explanation advanced being that electronegative substituents increase the s character of the ground state lone pair.

v. Nature of inversion centre. As mentioned in Section II.A.2, the inversion barrier in phosphines is much larger than that in amines so that, apparently, the less electronegative the atom that is inverting the higher the barrier to inversion. This effect was very poorly understood at the time of the earlier reviews and no attempts were made to explain the phenomenon[126,127].

Since then there have been a number of studies (both qualitative and quantitative) which have gradually led to an understanding of the trends in inversion barrier[76,79,84,103,107,128–131]. In particular, the much larger barrier to inversion in phosphines than in amines has been explained. The arguments based on the Walsh diagram approach (used in Section II.B.1.c) for the difference in bond angle between amines and phosphines may also be utilized for the difference in their inversion barriers. Referring to Figure 3 again, when the energy gap δE between the HOMO and the LUMO of the planar geometry is made smaller, the difference in energy between a_2'' of the planar geometry and $2a_1$ of the pyramidal geometry is increased thus increasing the inversion barrier[66]. Again, it may be incorrect to ascribe these changes solely to the electronegativity change since such change inevitably accompanies the change to lower group on the Periodic Table. In support of these arguments Levin[128] and Epiotis and Cherry[129] have shown that there is relationship between barrier increase and HOMO–LUMO splitting in the D_{3h} transition state and Dougherty *et al.*[130] have shown that introduction of π-acceptor groups lowers the barrier.

However, in the last few years some important new work[96,99,102,103] has shown that there is another mechanism, other than the commonly accepted pyramidal–planar trigonal process, namely inversion via a T-shaped transition state[102]. It turns out that

AX_3 molecules fall into two groups—one inverting via the classical D_{3h} transition state and the other by the C_{2v} T-shaped transition state. The former group includes, for example, NH_3, PH_3, AsH_3, NF_3 and NCl_3, while the latter group contains, for example, PF_3, PCl_3, PBr_3 and AsF_3. The form of the MOs of such a T-shaped structure can be derived by qualitative molecular orbital methods (similar to those described in Section II.B.1.c) and are well documented in the book by Albright *et al.*[66].

A consequence of these new findings is that many previous calculations of inversion barrier which were done on the assumption of a D_{3h} transition state may need to be re-examined. For example, the difference in energy between the two transition states[99] in the case of PF_3 is approximately 132 kJ mol^{-1}. Also, some of the previous calculations did not optimize the geometry of the planar transition state and it is now well known[76,84,96] that the bond length is shorter in that transition state.

b. Hyperconjugation. In studies on monomethyl- and monotrifluoromethyl-substituted silicon, phosphorus and sulphur compounds, Magnusson[133] showed that in molecules containing second-row elements effects due to hyperconjugation (bond length disparities, conformer energies) will occur in an experimentally observable range (see Table 15). The structural and energy effects in methyl compounds are calculated to be smaller than in the corresponding first-row molecules. However, trifluoromethyl compounds are expected to show structural effects comparable to those of the first-row species even though the energy effects are not as large. Magnusson suggested that the disposition of charge density around second-row atoms and lone pair orientation both contribute to the weakness of second-row hyperconjugation.

For calculations on model phosphorus compounds, the data display the same features that hyperconjugation is called on to explain for first-row compounds, but the interactions are not as strong. Magnusson tried to explain the weakness of the effects by a number of factors, including the small size of the first-row core. This makes it impossible for bond angles to fall as low, or p character to rise as high, as in compounds of the second-row elements. A high level of p character in the bonds around phosphorus suggests a corresponding increase in the hybrid character of the lone pairs, which would therefore be more strongly directed away from the CH_3 or CF_3 group and interact more weakly than lone pairs of NH_2.

TABLE 15. Calculated[a] bond lengths[b] and bond orders[c] for methyl- and trifluoromethyl-substituted phosphorus and nitrogen compounds

Molecule	$r(H—C_1)$ $r(H—C_{2,3})$	$p(H—C_1)$ $p(H—C_{2,3})$	$r(N—C)$ $r(P—C)$	$r(C—F_1)$ $r(C—F_{2,3})$	$p(C—F_1)$ $p(C—F_{2,3})$
CH_4	108.1	0.766			
CH_3PH_2	108.0	0.760	186.4		
	108.3	0.749			
CH_3NH_2	108.9	0.782	145.0		
	108.1	0.792			
CF_3H	106.6			135.2	0.360
CF_3PH_2			187.2	136.1	0.317
				136.3	0.306
CF_3NH_2			136.4	137.3	0.446
				135.8	0.424

[a]All SCF geometry optimized—staggered conformation, 4–31G# basis set for phosphorus compounds, 4–31G basis set for nitrogen compounds, from ref. 133.
[b]$r(C—X)$ = bond length in pm.
[c]$p(C—X)$ = bond order.

As can also be seen from Table 15, the C—P bond length in trifluoromethylphosphine is shorter than that in methylphosphine. This suggests that hyperconjugative effects are responsible for the anomalous bond length in tristrifluoromethylphosphine (see Sections II.A.1 and II.B.2). However, since it takes very high levels of calculation[133] to reproduce the correct experimental bonds lengths in $P(CF_3)_3$, caution needs to used in extending the argument to that molecule.

c. Conformation of phosphines. Conformational preferences in phosphines were also studied by Magnusson[134,135] using calculation methods similar to those used in his other studies[104–107]. He found that there was no qualitative difference between the kind of energy surface produced by rotation about single bonds to phosphorus and that produced by rotation about bonds to first-row elements[134]. However, there was a quantitative difference because the energy differences between alternative conformations were much less[134]. The only exception to this generalization was that trifluoromethyl-substituted hydrides had energy differences between conformations which were of comparable magnitude to those of their first-row counterparts[135].

C. Conjugated Phosphines

The evident weakness of π bonding at trivalent phosphorus (Section I) suggests that overlap with adjacent unsaturated centres should not be important. However, some extra considerations of structure and bonding are introduced when there is unsaturation α to the phosphorus in phosphines.

1. Phosphines with aromatic substituents

The structures of aromatic phosphines do not suggest that there is much interaction of the lone pair on phosphorus with an adjacent aromatic ring, because the bond lengths and angles are little changed relative to those in comparable phosphines with non-aromatic substituents (see Sections II.A.1 and II.A.2). However, the physical properties of aromatic phosphines do suggest a modest extension of delocalization from phosphorus to the aromatic nucleus. For example, the ultraviolet spectra show a bathochromic shift and a hyperchromic effect[6] and the basicities are slightly lower than expected[18], both supporting a weak involvement of the lone pair of phosphorus in delocalization. There has therefore been continuing interest in the study of possible delocalization in aromatic phosphines but, since these molecules contain many atoms, there have been few theoretical studies[107].

Most of the recent work has used ultraviolet absorption spectroscopy[136–141], electron transmission spectroscopy[142] and photoelectron spectroscopy[143–147], with some attention to dipole moments[148], gas-phase basicity[149] and vibrational spectroscopy[150]. From these studies, a concensus has emerged that there is an appreciable interaction between the orbitals of the benzene ring and the lone pair on phosphorus. However, it is much reduced from that in aromatic amines (one estimate[146] put the reduction at 50%).

The electronic spectra of aryl phosphines were overviewed by Fife *et al.*[138], who carefully assigned the various transitions. Note that earlier work was complicated by unrecognized interference from phosphine oxide contamination[138]. Schiemenz and Nielsen[139,140] investigated ring-substituted aryl phosphines and showed that, although there may be an interaction of the aromatic nucleus and the lone pair on phosphorus, this does not lead to through-conjugation via phosphorus. In other words, phosphorus is a barrier to conjugation between aryl rings even though it exerts a strong +M effect[139,140]. Frey *et al.*[141] investigated the spectral characteristics and association constants of charge-transfer complexes of Main Group 5 aryl derivatives with tetracyanoethylene. They were able to

assign all bands but unfortunately the phosphine derivative used reacted to form a different adduct, rendering comparisons difficult[141]

Giordan *et al.*[142] employed electron transmission spectroscopy to determine the energies of low-lying negative ion states of methyl and aryl phosphines. They found that benzene-substituent lone pair $p\pi$–$p\pi$ interactions decrease sharply from first- to second-row substituents, primarily as a result of decreased the $p\pi$–$p\pi$ overlap. They also found that Main Group 5 elements exert a stabilizing inductive effect on the benzene π^* orbitals[142].

There was some confusion in the assignment of the ultraviolet photoelectron spectra of phosphines, which was cleared up by Cabelli *et al.*[143], who showed that the assignments in phenylphosphine and aniline are similar. In fact, through the observed changes in orbital energies[143–146], photoelectron spectroscopy provides the best evidence for the interaction of the lone pair of phosphorus with the aromatic system.

2. *Vinyl phosphines*

Although susceptible to relatively easy analysis by calculation, vinylphosphine and its derivatives have only recently been synthesized[151].

Schade and Schleyer[152], in relatively high-level calculations (using the 6–31G* basis set with electron correlation and zero-point energy correction), found that the preferred geometry of vinylphosphine was that in which the lone pair on phosphorus was 'non-conjugating' (i.e. not oriented perpendicular to the π system). They concluded that there is only a very weak P–C π interaction in vinylphosphine. They found also that this was not because of inherently weak first row–second row overlap. Rather, it was because planarization at phosphorus is very costly compared with the gain in π-resonance energy. These results were confirmed by a study of the photoelectron spectrum of vinylphosphine and a derivative[153].

3. *Acyl phosphines*

Xie *et al.*[154] investigated the geometries of formylphosphine and acetyldimethylphosphine by *ab initio* methods. They found that there was a single total-energy minimum corresponding to the amide-type conformation. They also found that, as expected, the rotation barriers to internal rotation of the acyl group were lower in phosphines than in the analogous amines. They concluded that, although there is a certain contribution of $p\pi$ conjugation, the magnitude of the effect is small. They also found that the P—C bond to the C=O carbon was noticeably longer than that to the carbon of a methyl group[154]. This is in agreement with the results reported in Section II.A.1.

4. *Phospholes*

In phospholes, the phosphorus lone pair can interact with the four π-electrons of the diene unit to constitute an aromatic system analogous to that in pyrrole. During the 1970s, the development of an understanding of the electronic structure of phospholes was accompanied by a great deal of controversy. References to this, to its resolution and to the currently accepted description of the bonding in phospholes may be found in the book by Quin[56]. It is now clear that there is a certain amount of delocalization, but much less than that in pyrrole, and phospholes can be described as only weakly aromatic. Once again it is found that there is a balance between the energy gained on delocalization and that lost on planarization, and it turns out that phospholes have a distinctly pyramidal phosphorus atom. One accepted manifestation of aromaticity in phospholes is their dramatically reduced barrier to inversion because the planar transition state is stabilized by its aromaticity[56].

D. Polyphosphines

The introduction of more than one phosphorus atom into a phosphine has very little effect on the structure[155], the only exception being the case where two phosphorus atoms are directly bonded together. The P—P bond length[2] in P_2H_4 is 221.8 pm, which appears to be little changed by substitution because it is the same in PH_2PF_2, 222.8 pm in the nearly strain-free black phosphorus[156] and 219.2 pm in P_2Me_4, the P—H and P—C bond lengths being unchanged[2] from their usual values given in Table 2. Bond angles are also unchanged from those expected. For example[2], the CPC and CPP angles in P_2Me_4 are 99.6° and 101.1°, respectively, reduced to approximately 97° in PH_2PF_2.

There have been very few theoretical studies of polyphosphines. In an MNDO study. Bews and Glidewell[157] reported the mass spectral fragmentation of tetramethyldiphosphine. Schleyer *et al.*[158] examined the question of the anomeric effect involving second-row substituents using an *ab initio* method that included a calculation on $PH_2CH_2PH_2$. They found that the anomeric effect is much weaker for second-row substituents and suggested that this was because of the poorer π-donating ability and lower electronegativity of the second-row groups[158].

There has been some interest in the conformation of polyphosphines. In the liquid and gaseous states, Raman and IR data favour a *gauche* C_2 for both P_2H_4, P_2D_4 and P_2Me_4 but a *trans* C_{2h} configuration in the solid[2]. Thus it appears that the *gauche* and *trans* rotamers are of comparable energy, and this was confirmd by a photoelectron spectroscopic study[159]. However, electron diffraction data indicate that P_2Me_4 has a *trans* configuration[2], as has PH_2PF_2. The matter has been addressed theoretically using relatively high-level calculations without success[160]. Note that the form of the MOs of AH_2AH_2 systems may be derived easily by qualitative molecular orbital methods[66].

Structural data on polyphosphines with a high proportion of phosphorus atoms may be found in the review by von Schnering[156] and some recent theoretical work on such systems may be found in ref. 161.

E. Phosphine Metal Complexes

Phosphines are very useful ligands in organometallic chemistry and the known number of complexes is very large[2,162]. Many structural data are reported in the book by Corbridge[2], where the metal—phosphorus bond distance is reported to vary from approximately 215 to 255 pm.

In many transition metal organometallic compounds, and especially those in which the metal is in a low oxidation state, the bonding is thought to involve back-donation of electron density from a metal d orbital to an unoccupied ligand orbital of appropriate symmetry[162]. For example, in metal–carbonyl and metal–alkene complexes the ligand orbital is a π^* orbital[162]. There has been a great deal of discussion about whether such back-bonding occurs in metal–phosphine complexes and many methods have been used to investigate it[13,14,162–164]. However, it now seems clear that, although there is no role for back-bonding in aliphatic or aromatic phosphine complexes, such bonding is important for complexes of PF_3 and phosphites[162–165]. In most of the discussion on this topic[13,14], and even some of the more recent ones[162], it is assumed that the appropriate orbitals of the phosphine for any back-donation are the phosphorus d orbitals. Examination of Figure 3 shows clearly that the much more likely acceptor orbitals are the σ^* orbitals $3a_1$ or $2e$.

This question has been studied recently by both theoretical[121,166] and physical[167,168] methods. Xiao *et al.*[121], in the empirical calculations described above (Section II.B.4), found that the LUMO of the phosphines studied consisted mostly of phosphorus p character, consistent with the $2e$ orbitals in Figure 3. In a later study, Marynick[166], using

both empirical and *ab initio* calculations, confirmed that phosphine ligands could be π-accepting without involving d orbitals on phosphorus and that the σ^* orbitals were indeed the acceptor orbitals. This conclusion was confirmed by Tossell *et al.*[167], who examined the LUMO of PH_3 by electron transmission spectroscopy and found it to be of σ type. In an elegant study, Orpen and Connelly[168] examined the metal—phosphorus and the phosphorus—substituent atom bond lengths in the crystal structures of a series of transition metal complexes. The idea was that if the back-bonding is occurring into σ^* orbitals, then the bonds to the phosphorus substituents should be weakened[168], and they found that indeed there was a correlation between M—P bond strengthening and P—X bond weakening as measured by bond length.

F. Hydrogen Bonding in Phosphines

Although atoms of relatively low electronegativity are not expected to participate in hydrogen bonding, there is some structural evidence that P—H linkages can do so[2]. Most studies so far have been by high-level calculation, but there seems no doubt that there would be a weak interaction between PH_3 and hydrogen halides[169–173].

III. MULTIPLY BONDED PHOSPHORUS

It is only in recent years that stable trivalent phosphorus molecules with phosphorus coordination numbers 2 and 1 have been synthesized. This may have been due to the considerations discussed in Section I, which suggested that multiple bonding to phosphorus should be weak. However, with appropriate substituents (sterically demanding groups and/or electron-releasing groups), P=C, P≡C, P=P, P≡P and other multiple bonds to phosphorus may be incorporated into isolable compounds. Since the subject is relatively young, there are a number of useful recent reviews available[174–182].

A. Structure

There are now a large number of single-crystal X-ray crystallographic studies of phospha-alkenes[47,174,176] and it has been shown that the P=C group has the geometry expected for a true phosphorus to carbon double bond. Its σ-skeleton is planar and the P—C bond length can vary between 161 and 171 pm with an average of 167 pm[174], clearly shorter than that of a typical P—C single bond (Table 2). This double-bond nature has been confirmed by other physical measurements such as NMR spectroscopy[175] and especially the isolation of stable *E* and *Z* isomers, which show a substantial barrier to interconversion by rotation about the P—C axis[174]. It is interesting that the bond angles in some phospha-alkenes[176] show similar trends to those in phosphines in that the unsubstituted parent molecule has an H—P—C angle of 97.5°, the mesityl-substituted derivative has a C—P—C angle of 107.5° and the mesityl-substituted nitrogen analogue has a C—N—C angle of 120.8°. Recently, a detailed study of the infrared spectra of simple phospha-alkenes has been reported[183].

The structure of phospha-alkynes has been established mainly by microwave spectroscopy[179], which gives a P—C bond length of approximately 154.4 pm, and this short length is confirmd by the first X-ray crystal structure determination[184], which gave a value of 151.6 pm.

The structures of a limited number of diphosphenes have been determined by X-ray crystallography[180]. The P=P double bond is found to be approximately 200 pm long, which is twice the double bond covalent radius, and the molecules are planar, adopting a *trans* conformation with C—P—P bond angles of 102–108° depending on the steric bulk of the substituents[180].

B. Bonding

It has become clear that there is a remarkable qualitative similarity between multiple bonds to carbon and those to phosphorus in terms of bond length–strength relationships and electron density distributions[174,179,185].

Simple directed valence arguments can be used to rationalize the bonding in these compounds along the same lines as the bonding in alkenes, alkynes, imines and cyanides. Thus the bonding in phospha-alkenes can be described as overlap of an sp^2 hybrid on phosphorus and carbon to form a σ bond, and overlap of two p orbitals to form a π bond, another sp^2 hybrid on phosphorus forming another σ bond and the remaining sp^2 hybrid containing the lone pair of electrons. In this example, the promotion energy necessary to form the sp^2 hybrid is presumed to be offset by the energy of the bonds formed. The bonding in diphosphenes is similarly described by replacement of the trigonal carbon by another phosphorus. Also, the bonding in phospha-alkynes is described in terms of sp hybrids and two π-bonding p orbitals on phosphorus. Even though these arguments are sufficient to account for the bonding, it must be borne in mind that they may be too simplistic given their failure in the case of the phosphines (Section II.B).

1. *Phospha-alkenes*

A number of recent calculations[176,186–195] and a useful photoelectron spectroscopic study[196] have included treatments of the bonding in phospha-alkenes. These studies show that the HOMO is of π type with the phosphorus lone-pair σ orbital only slightly more stable (and in some cases this order may be reversed[176]). The LUMO is the π^* orbital and it is relatively low lying in energy[190,194–196]. Note that this is the opposite order of the occupied valence orbitals from that in imines, where the HOMO is the lone pair[196]. The behaviour of these frontier orbitals in pericyclic reactions has been studied[194,197,198] and shown to be dependent, as expected, on which orbital is the HOMO[194,197].

Some of these calculations[186–190] have also addressed the general problem of why these molecules are stable and have tried develop a common treatment of all multiple bonding, which has required the construction of a framework for the comparison of π bond energies[186,188]. When such comparisons are made, some surprising results can emerge; for example, the π bond strength in $HP{=}CH_2$ is calculated to be 448 kJ mol^{-1}, significantly higher than in either its nitrogen analogue or ethylene[187]. In a significant study, Schleyer and Kost[186] calculated the π bond energies for a wide range of double bond systems using the 6–31G* basis set with electron correlation and zero-point energy correction. The difference in energy between two X—Y single bonds and an X=Y double bond was calculated by means of isodesmic equations and the π bond energy derived by substraction of this difference from the dissociation energies of the single-bond system[186]. The interesting result is that for each series C=X and Si=X, the π bond energies for both first- and second-row substituents correlate with the electronegativities of X[186]. When electronegativity differences between carbon and silicon and among the X groups is taken into account, first- and second-row π bond energies are similar[186].

Finally, an ESCA examination of λ^3-phosphorins supports the theory that these compounds are aromatic[199].

2. *Phospha-alkynes*

A number of phospha-alkynes have been investigated by photoelectron spectrocopy[179]. Once again the first ionization potential corresponds to removal of an electron from a bonding π orbital and the second to the lone pair[179]. There is a strong similarity between the photoelectron spectra of phospha-alkynes and cyanides, except that in the former there

is an increase in the π–n separation attributed to the poorer overlap of the 3p orbitals compared with the 2p orbitals[179].

There have been a few calculations on phospha-alkynes[200–204] and the parent HCP has been the subject of numerous calculations (detailed in ref. 202). In general, these confirm the results of the spectroscopic investigations but some attention is paid to the question of the linearity of the C—C—P unit[200,204].

3. Diphosphenes

The bonding in diphosphenes has been studied by spectroscopic methods[180,205] and by molecular orbital calculations[180]. These confirm the similarity of the P=P bond to the double bond in olefins[205]. Once again the π orbital and the lone pair combination are close in energy and either may be the HOMO[180].

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The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

CHAPTER **3**

Optically active phosphines: preparation, uses and chiroptical properties

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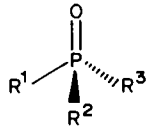
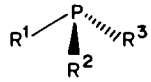
I. INTRODUCTION

The first optically active phosphine oxide (**1**) in which the phosphorus atom is the only asymmetric centre in the molecule was decribed in 1911 by Meisenheimer and Lichtenstadt[1]. It was not until 50 years later that optically active phosphines such as **2** could be prepared, thanks to the efforts of Horner *et al.*[2,3].



(1)



(2)

The driving force in the early 1900s for trying to isolate compounds [phosphorus(III), -(IV) and -(VI)] with asymmetric phosphorus was the need to gain information about the bonding and stereochemistry around phosphorus. Several reviews have given surveys of these early developments, e.g. refs 4 and 5. For the last two decades there has been renewed interest in phosphorus chemistry because (i) many compounds with asymmetric phosphorus atoms [phosphorus(IV) and -(V)] have interesting biological properties closely connected with absolute configuration[4–7] and (ii) chiral phosphines with chiral units at phosphorus and/or in the vicinity of phosphorus have found wide use as ligands for transition metals[8]. Asymmetric catalysis was greatly stimulated by the discovery of new complexes and spectacular results were obtained, leading in some cases to industrial applications.

This chapter focuses on optically active phosphines, although stereochemical problems and preparations involving phosphorus(III), -(IV) and -(V) derivatives are strongly interconnected. In this account we define *phosphines* as compounds in which the phosphorus atom is connected only to carbon or hydrogen atoms [e.g. PhP(alkyl)H, menthylPPh$_2$, *o*-anisylphenylPMe]. This definition excludes phosphorus(III) compounds, in which phosphorus is linked to a heteroatom [e.g. PhP(OMe)Me, PhP(Cl)Me], although many optically active phosphines are prepared from them. Phosphorus(V) compounds such as phosphine oxides are not included in this survey, but they will be occasionally considered when needed for identification or storage of phosphines.

Optically active phosphines can involve one or several sources of chirality. A classification of chiral phosphines is possible if one makes a distinction between phosphines with an asymmetric phosphorus atom and those in which the chiral unit is external to phosphorus (asymmetric carbon atom, axis or plane of chirality). A combination of both substructures is also known.

The chapter is organized in the following manner. First the various classes of chiral phosphines are described, with some examples, then the routes to optically active phosphines are detailed. Chiroptical properties of these compounds and absolute

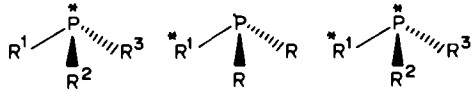
configuration assignments are discussed in Section IV. Methods for measuring enantiomeric excesses of chiral phosphines are reviewed in the next section. Because of their importance, the stereochemical features of reactions occurring at phosphorus or in vicinal positions are considered next. The chapter ends with a description of the uses of chiral phosphines as ligands for transition metals. Many complexes are useful catalyst precursors in asymmetric catalysis (e.g. hydrogenation, C—C bond formation, C—C bond migration).

II. VARIOUS CLASSES OF CHIRAL PHOSPHINES

Chiral phosphines can be divided into two broad classes: monophosphines and polyphosphines. In this section, representative examples of chiral phosphines are illustrated, together with their absolute structures.

A. Monophosphines

There are basically three ways to design chiral monophosphines: the chirality can be located on either the phosphorus atom or a side-chain, or on both (**3–5**, Scheme 1).

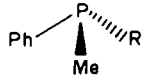


(**3**) (**4**) (**5**)

SCHEME 1. Main types of chiral monophosphines.

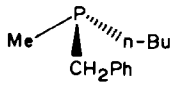
1. Monophosphines with an asymmetric phosphorus centre

Optically active phosphines of type **3** (Scheme 1) were the first to be used in asymmetric hydrogenation[17,18]. Representative P-chiral phosphines are as follows. In these derivatives one finds a phosphorus atom usually surrounded by at least one aryl group. A few trialkylphosphines (e.g. **7**) and triarylphosphines (e.g. **8**) are also known.

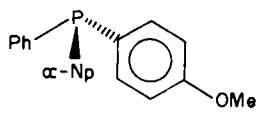


(**6**)

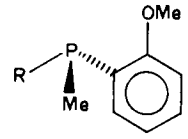
(a) R = Et[3,20]
(b) R = *n*-Pr[20]
(c) R = CH_2Ph[20]
(d) R = CH_2CHCH_2[3,20]
(e) R = β-Np[20]
(f) R = *p*-$OMeC_6H_4$[20]
(g) R = *t*-Bu[21]
(h) R = *o*-EtC_6H_4[22]
(i) R = *o*-$MeS\text{-}C_6H_4$[22]
(j) R = *o*-$Me_2NC_6H_4$[22]



(**7**)[23]



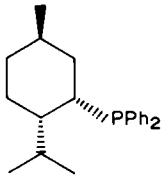
(**8**)[24]



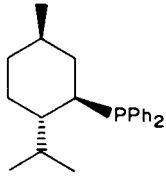
(**9**)[23,25] R = Ph: pamp
(**10**)[24,25] R = *c*-C_6H_{13}: camp

2. *Monophosphines with a chiral side-chain*

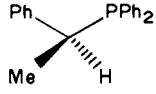
Phosphines of the general formula **4** (Scheme 1) are the easiest to obtain because their synthesis mostly starts from a chiral natural product, as will be described later. Some examples are depicted in structures **11**–**25**.



(11)[26] nmdpp



(12)[26] mdpp



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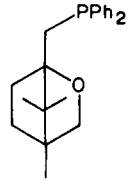

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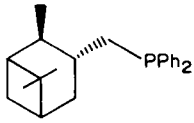
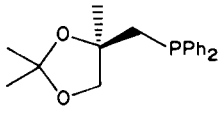
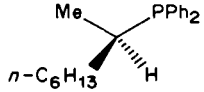


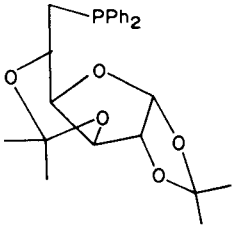
(15)[29]



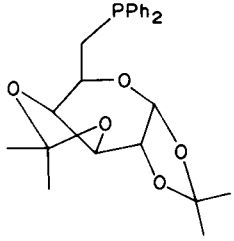
(16)[29] glyphos



(17)[30]



(18)[31]



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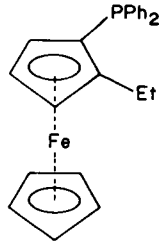
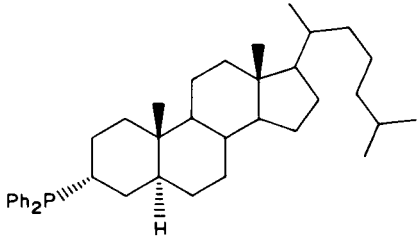
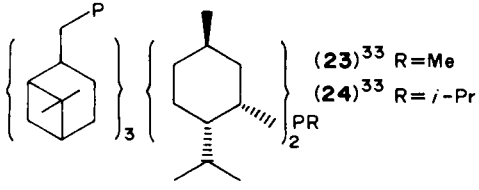


(20)[32] ppef

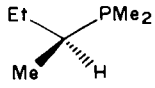


(21)[30] dicol



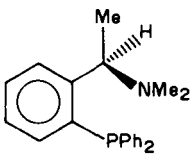
(22)[33]

(23)[33] R=Me
(24)[33] R=*i*-Pr

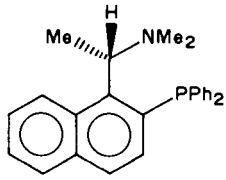


(25)[34]

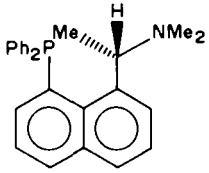
Some monophosphines bearing a functionalized side-chain were synthetized in order to act as a bidentate ligand of a transition metal in a complex (**26–49**).



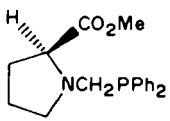
(**26**)[35] amphos



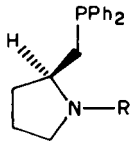
(**27**)[35] 1,2-dpnea



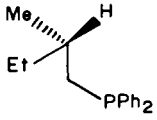
(**28**)[35] 1,8-dpnea



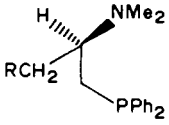
(**29**)[36]



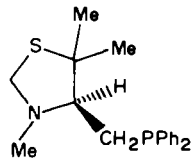
(**30**)[39] R=H pm
(**31**)[39] R=CO_2Bu^t bpm



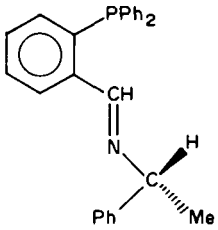
(**32**)[38]



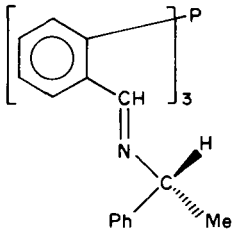
(**33**)[39] R=MeS methylcycphos
(**34**)[39] R=CH_2SMe methphos
(**35**)[39] R= *i*-PrS



(**36**)[39] cyclopenphos



(**38**)[41] iminaphos

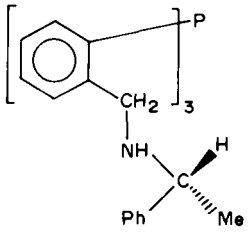


(**39**)[41] trisminphos

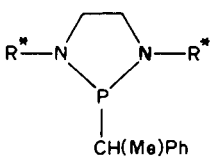
$(EtO_3)Si(CH_2)_nP(menthyl)_2$

n=1–5

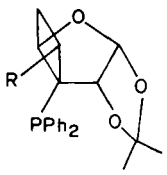
(**37**)[40]



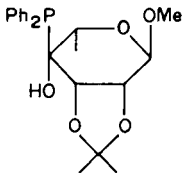
(**40**)[41] aminphos



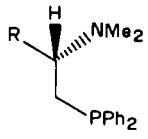
(**41**)[42]



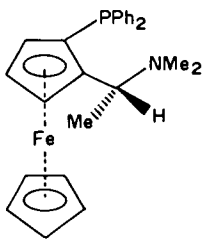
(**42**)[43] R=CN
(**43**)[43] R=CH_2NH_2



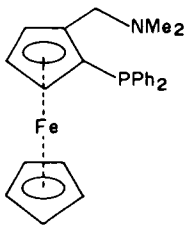
(**44**)[44]



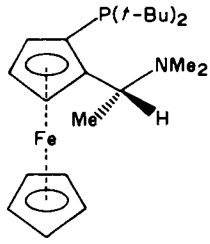
(**45**)[32] R=*i*-Pr valphos
(**46**)[32,45] R=$PhCH_2$ phephos
(**47**)[32] R=*t*-Bu *t*-leuphos



(48a)[32,46] (R,R)-ppfa



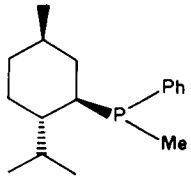
(48b)[32,47] (S)-fepm



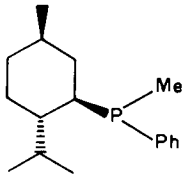
(49)[48]

3. *Monophosphines with chirality both at phosphorus and in a side-chain*

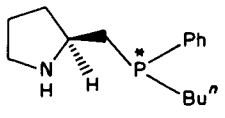
Optically active phosphines of type **5** (Scheme 1) have been reported for a few examples (**50–52**).



(50)[49,50]



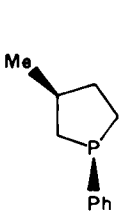
(51)[49,50]



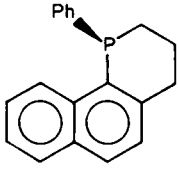
(52)[51]

4. *Monophosphines with a cyclic structure*

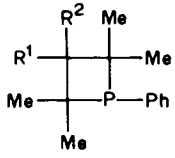
Chiral monophosphines in which asymmetric phosphorus is incorporated in a ring are known, as in **53–55**, and are part of a family that will be fully discussed in Chapter 12. A new type of cyclic monophosphine has been recently synthesized[193] in which the phosphorus atom is bridgehead and cannot be thermally racemized. Phosphine **55′** gives a rhodium complex which acts as an asymmetric catalyst in the homogeneous hydrogenation of *N*-acetyl-α-aminocinnamic acid (ca 50% ee).



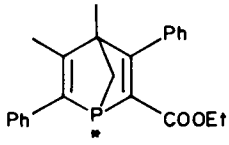
(53)[52]



(54)[54]



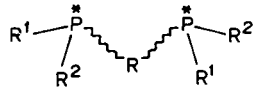
(55)[53]



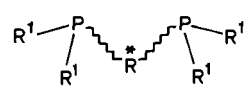
(55′)[193]

B. Polyphosphines

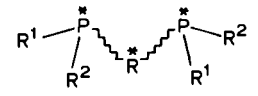
A variety of chiral diphosphines with the general formulae **56–59** have been reported as promising ligands for stereoselective catalysis.



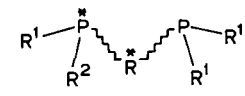
(56)



(57)



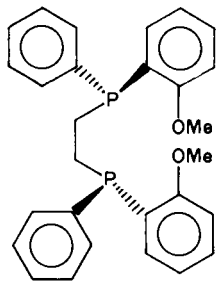
(58)



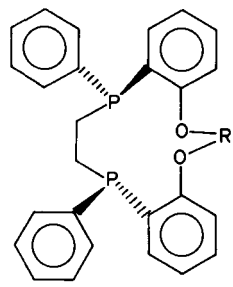
(59)

1. Diphosphines with at least one asymmetric phosphorus

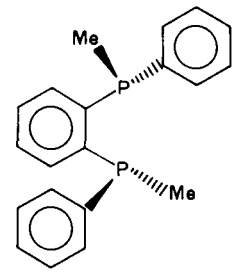
Phosphines **60–65** are examples of diphosphines of type **56**, with two asymmetric phosphorus atoms, and of diphosphines of types **58** and **59**, where chirality can be found both at phosphorus and in the organic framework.



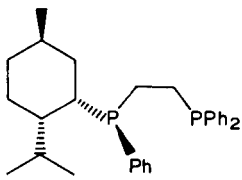
(60)[55] dipamp



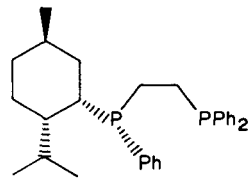
(61)[56] R=$(CH_2OCH_2)_n$



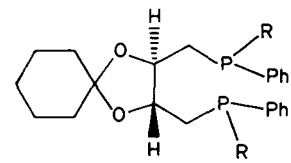
(62)[57]



(63)[58]



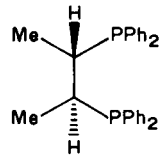
(64)[58]



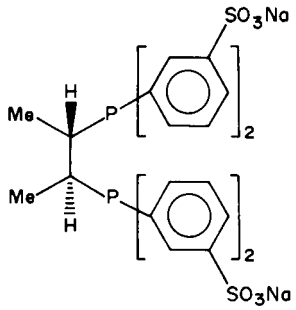
(65)[59] R= *c*-C_6H_{11}, $PhCH_2$

2. Diphosphines with a chiral group connecting two achiral phosphorus atoms

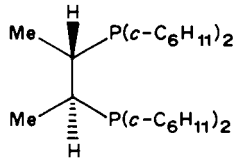
The diphosphines with the general formula **57** have often been used as chelating ligands in asymmetric catalysts.



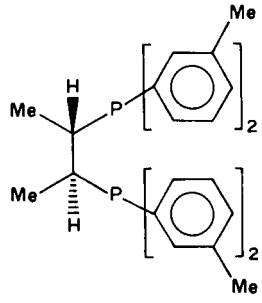
(66)[60] (*S,S*)-chiraphos



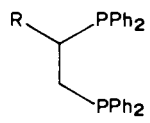
(74)[66]



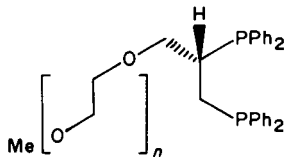
(75)[67]



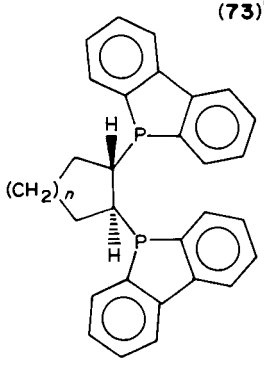
(76)[68]



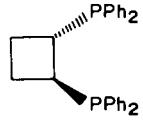
(67)[57] R=Me prophos
(68)[57] R=Ph phenphos
(69)[62] R=*c*-C_6H_{11} ctcphos
(70)[63] R=CH_2OCH_2Ph
(71)[64] R=*i*-Pr valphos
(72)[64] R=CH_2Ph benzphos
(73)[65] R=CH(Me)(NHBoc)



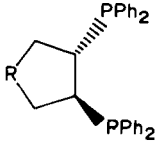
(77)[69] *n*=1–5,16,18



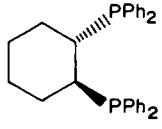
(78)[70] *n*=0,2



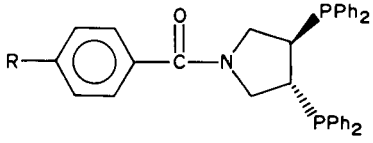
(79)[70] dpcb



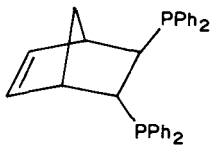
(80)[71] R=CH_2 dpcp
(81)[72,73] R=NH deguphos



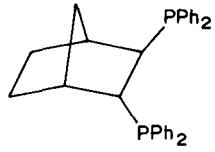
(82)[70]



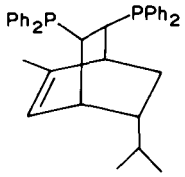
(83)[73] R=H benzoylphos
(84)[73] R=OH
(85)[73] R=OMe



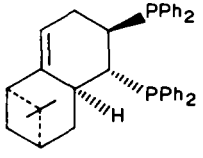
(86a)[74] norphos



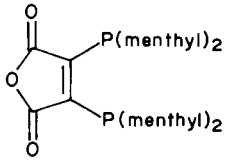
(86b)[75] renorphos



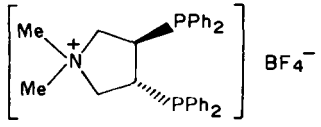
(87)[76] phellanphos



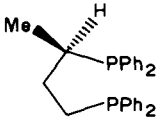
(88)[76] nopaphos



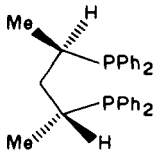
(89)[77]



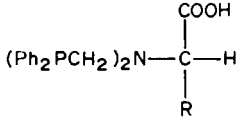
(90)[78]



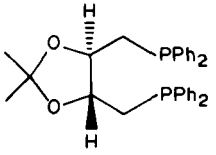
(91)[46,79] chairphos



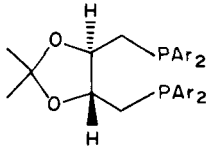
(92)[79] skewphos



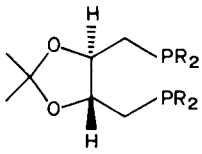
(93)[80] R=CH_2OH
(94)[80] R=Me
(95)[80] R=CH_2COOH
(96)[80] R=CH_2Ph
(97)[80] R=CH_2CH_2COOH
(98)[80] R=$CHMe_2$
(99)[80] R=CH_2CHMe_2



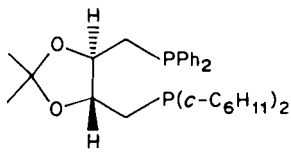
(100)[81,82] (*R*,*R*)-diop



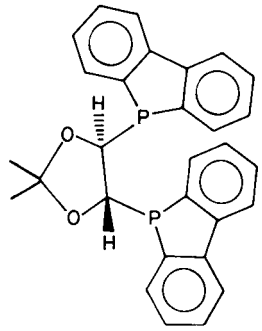
(101)[83] Ar=2-Me, 3-Me or 4-Me-Ph
(102)[84] Ar=2-anisyl
(103)[83] Ar=3,5-dimethylphenyl
(104)[83,84] Ar=3-anisyl
(105)[85] Ar=1 or 2-naphthyl



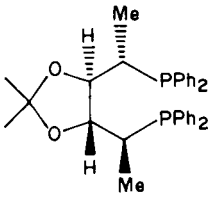
(106)[86] R=Et, *i*-Pr
(107)[67,87] R=*c*-C_6H_{11}



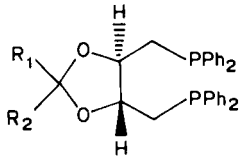
(108)[88] diocp



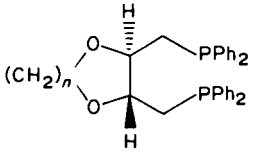
(109)[83,89] dbp-diop



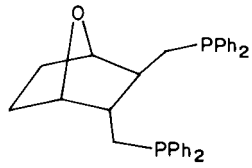
(110)[45]



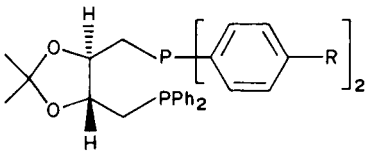
(111)[85] R_1, R_2=Ph
(112)[30] R_1, R_2=3-(5α-cholestanyl) diocol



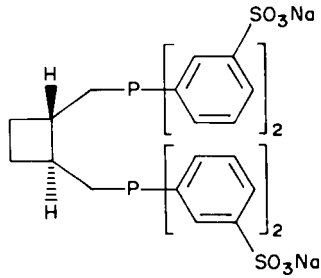
(113)[90,92] *n*=0–2



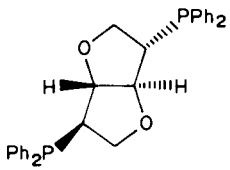
(114)[91]



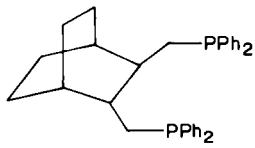
(115)[93] R=Me
(116)[93] R=OMe



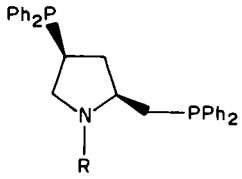
(117)[66]



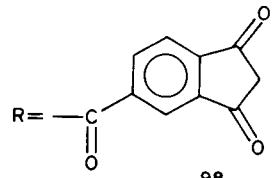
(118)[94]



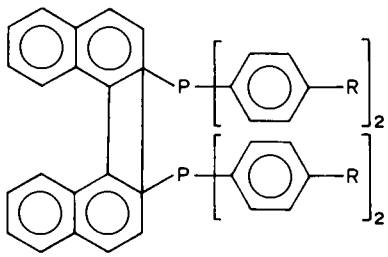
(119)[83]



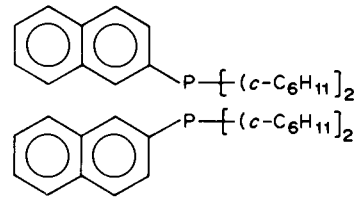
(120)[37] R=CO_2Bu^t bppm
(121)[37] R=$COBu^t$ pppm
(122)[95] R=$CONHR_1$ cap
(123)[96] R=H ppm
(124)[97] R=CONHPh Ph-cap
(125)[99] R=CONHPh-*p*-Br



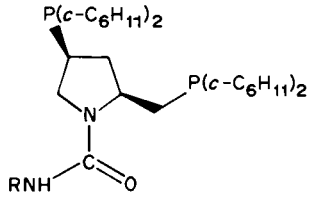
(126)[98]



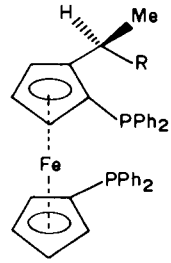
(127a)[49,123] R=H binap
(127b)[123] R=Me
(127c)[123] R=*t*-Bu



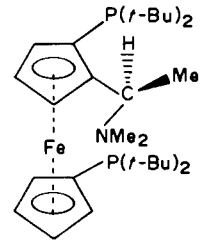
(128)[100] Cy-binap



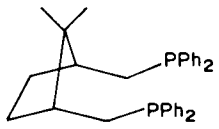
(129)[101] R=*t*-Bu
(130)[101] R=Ph
(131)[101] R=cyclohexyl



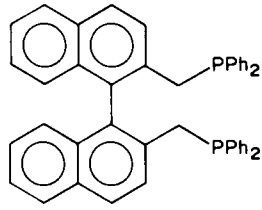
(132)[47] R=NMe_2(*R*,*S*)-bppfa
(133)[32] R=OAc (*R*,*S*)-bppfAc
(134)[102] R=OH bppfOH
(135)[103] R=Me bppfMe



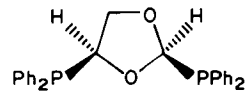
(136)[48]



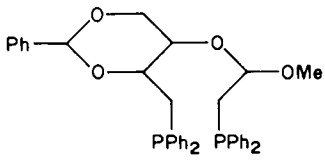
(137)[104] camphos



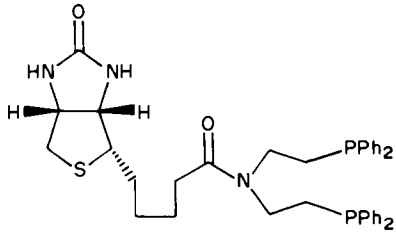
(138)[105] naphos



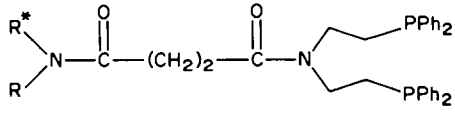
(139)[31] dioxop

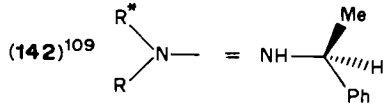


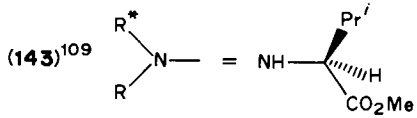
(140)[31] erythritop

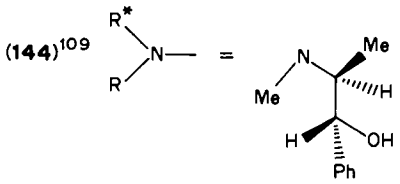


(141)[106]





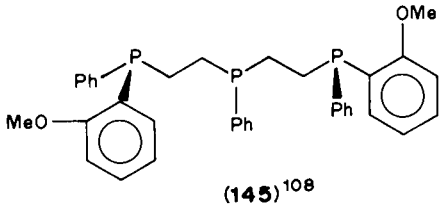




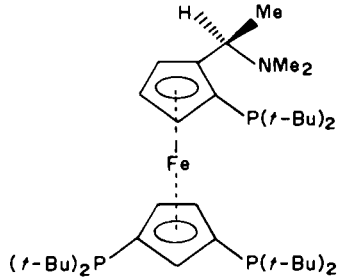
A unique type of chiral phosphine $[(\eta^5\text{-}C_5H_4PPh_3)RePPh_2(NO)(PPh_3)]$ has been recently reported by Zwick *et al.*[192]. Chirality arises from the presence of an asymmetric rhenium atom.

3. Triphosphines

There are a few cases of chiral triphosphines, e.g. **145** and **146**.



(145)[108]

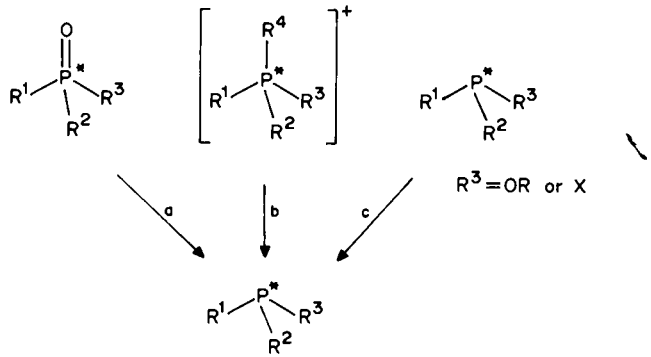


(146)[48]

There seems to be no report of optically active tetra- (or more) phosphines, although tetraphosphines with cyclic structures have been reported[109].

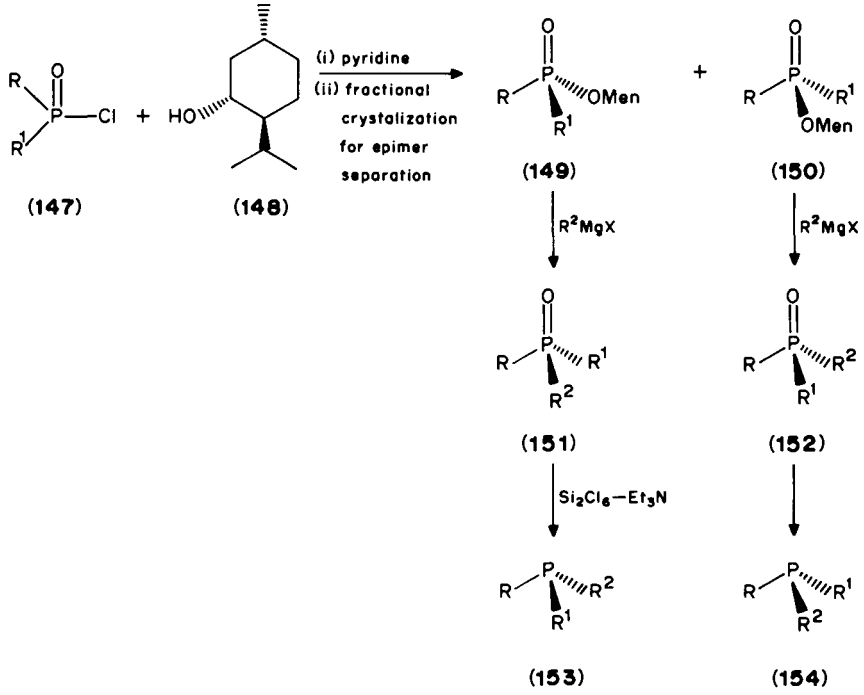
III. PREPARATION OF STEREOCHEMICALLY PURE PHOSPHINES

Methods for preparing optically active phosphines involve either the transformation of a chiral precursor or a resolution step. There are three main transformation methods giving access to P-chiral phosphines: (a) reduction of chiral phosphines oxides by halosilanes, (b) electrolytic hydrogenolysis of chiral phosphonium salts and (c) displacement of chiral phosphinites by organometallic reagents, as shown in Scheme 2.



SCHEME 2. Routes to P-chiral phosphines.

Korpium *et al.*[110] developed a general method for creating asymmetric phosphorus atoms, as illustrated in Scheme 3. Esterification of (−)-menthol with R′(R)P(O)Cl affords

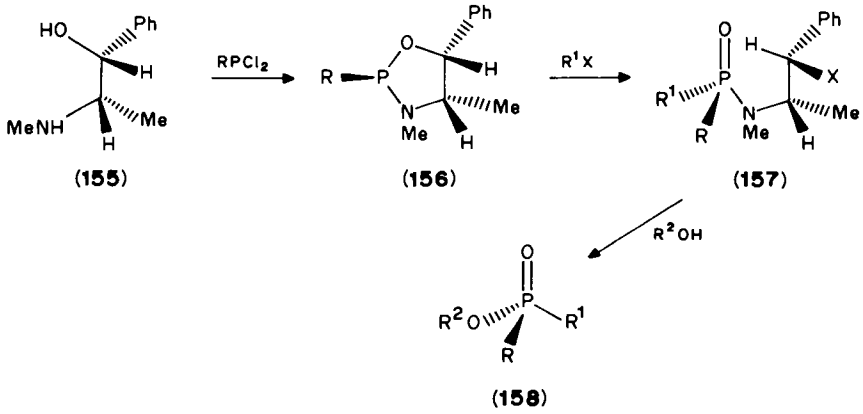


SCHEME 3. Use of Si_2Cl_5 to prepare P-chiral phosphines.

a mixture of the diastereomers of phosphinates, which can be separated by fractional crystallization. Each diastereomer thus obtained is treated with a Grignard reagent to give the corresponding phosphine oxide with inversion of configuration. Reduction of the phosphine oxide by Si_2Cl_6 produces the related optically active phosphine with complete inversion of configuration[20]. It has been observed that the combined reagent $HSiCl_3$–Et_3N is not stereoselective for phosphine oxide reduction whereas $PhSiH_3$ gives mainly retention of configuration[49]. Therefore, Si_2Cl_6 seems to be the most useful reagent for the stereospecific transformation of a phosphine oxide into a phosphine.

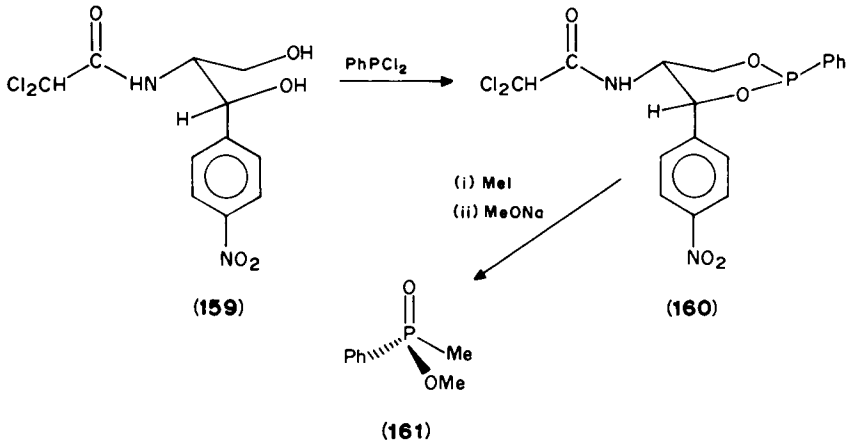
Alternative methods are now available for preparing optically active phosphinates, from which it is possible to make phosphine oxides after reaction with an organometallic reagent. Several approaches have been reported[111]. One approach is to synthesize and to resolve a 1,3,2-oxazaphosphole derivative[111b]. A simple method is first to prepare oxazophospholidine by the action of $RPCl_2$ on (−)-ephedrine (Scheme 4). Only one diastereomer is obtained with the absolute configuration at phosphorus indicated in Scheme 4. Treatment with an organic halide R″X leads (by an Arbuzov reaction) to a phosphinamide. Alcoholysis of **157** gives the phosphinates **158**. The overall yields are good and the phosphinates obtained have more than 80% ee. The same methodology has been applied to readily available 1,3-diol, chloramphenicol (**159**) (Scheme 5).

Use of $PhPCl_2$ leads to a cyclic phosphinite (**160**), and subsequent treatment with sodium methylate results in a methyl phosphinate (**161**) with 74% ee. An asymmetric synthesis of phosphinates involving the Arbuzov reaction using C_2 symmetry compounds has been reported by Kato *et al.*[112] (Scheme 6). The Arbuzov reaction of (5*S*,6*S*)-dimethoxy-2-phenyl-1,3,2-dioxaphosphacycloheptane (**162**) with various alkyl halides



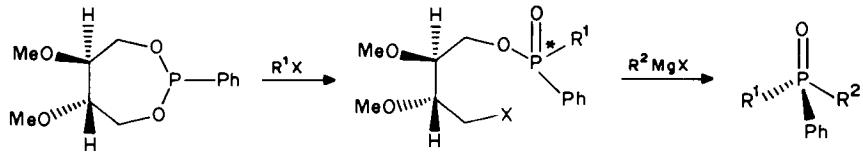
(155) (156) (157) (158)

SCHEME 4



(159) (160) (161)

SCHEME 5

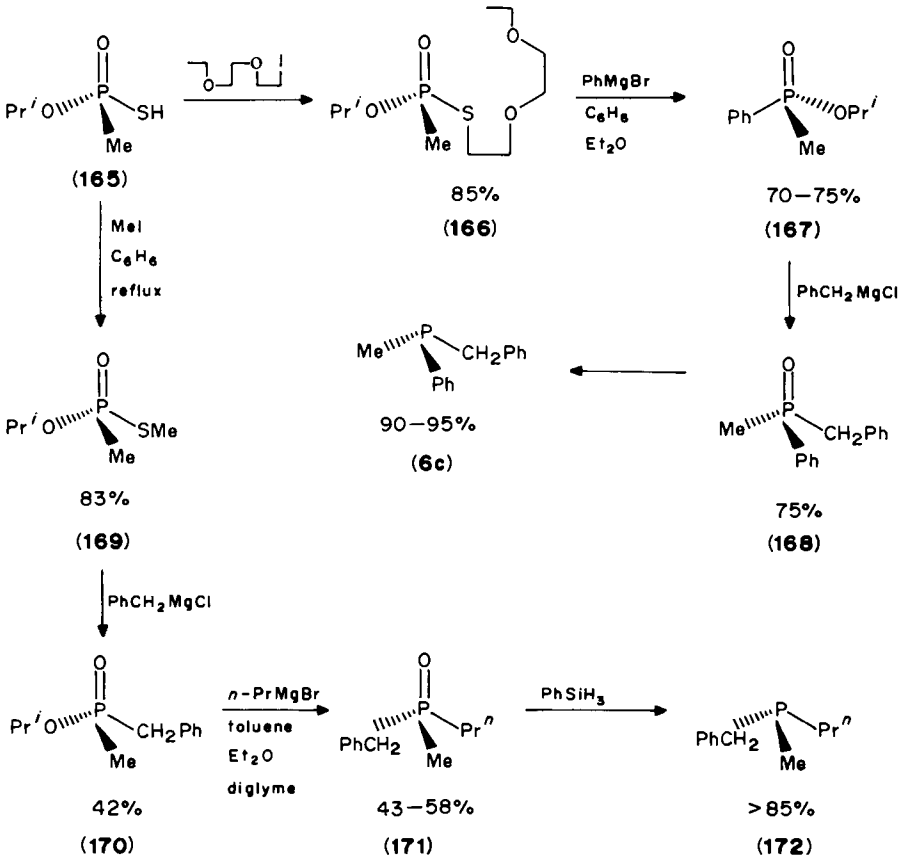


(162) (163) (164)

SCHEME 6

produces acyclic phosphinates (**163**) in a moderate to high diastereomeric excess, which are converted into optically active phosphine oxides (**164**) by Grignard reagents. Moriyama and Bentrude[113] developed a new route to the optically active phosphine

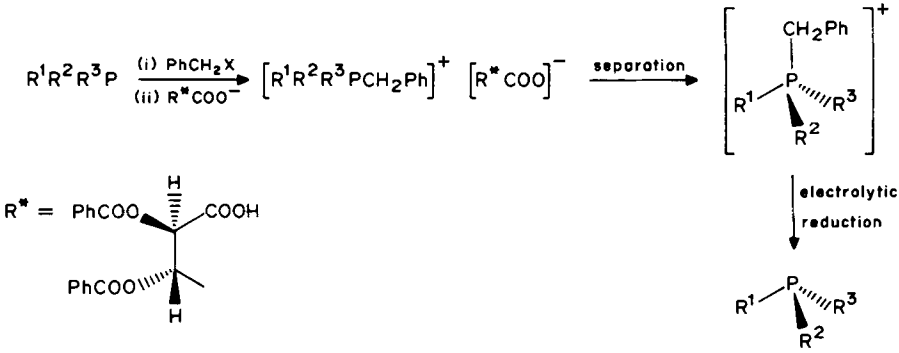
oxides $MePhP(O)CH_2Ph$ (**168**) and *n*-$PrMeP(O)CH_2Ph$ (**171**) from *O*-isopropyl *S*-alkyl methylphosphonothioates (**166** and **169**). Reductions of **168** and **171** with $PhSiH_3$ afford the corresponding optically active phosphines, $MePhPCH_2Ph$ (**6c**) and *n*-$PrMePCH_2Ph$ (**172**) (of optical purities 45–70% and 13–59%, respectively) (Scheme 7).



SCHEME 7

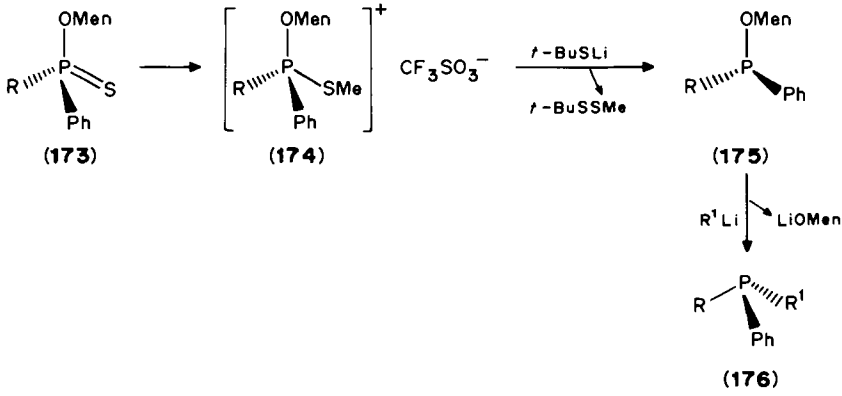
Toda *et al.*[114] reported that some (alkyl-substituted/arene)phosphinates and phosphine oxides can be resolved efficiently by crystallization of molecular complexes with optically active 2,2′-dihydroxy-1,1′-binaphthyl. The method gives 100% optically pure compounds.

A second route to P-chiral phosphines is the electrolytic hydrogenolysis of chiral phosphonium salts. Chiral phosphonium salts are available through various processes, mainly resolutions. Kumli *et al.*[115] introduced the (−)-dibenzoylhydrogentartrate anion as a resolving agent for phosphonium salts. A number of benzylphosphonium salts were resolved and further converted by Horner and Mentrup[116] into the corresponding chiral phosphines through electrolytic reduction to **3**. The electrolytic reduction occurs with retention of configuration at phosphorus. Phosphines **6–8** were prepared in this way (Scheme 8). This pioneer approach has largely been replaced by the other methods described in this section.



SCHEME 8. P-chiral phosphines from benzylphosphonium salts through electrolytic reduction.

A third route to P-chiral phosphines is the displacement reaction on chiral phosphinites by organometallic reagents (the method of Korpium *et al.*[110] described previously). Mikołajczyk[117] developed general methods for the synthesis of chiral phosphinites (Scheme 9). Desulphurization by the two-step sequence depicted in Scheme 9 gave good



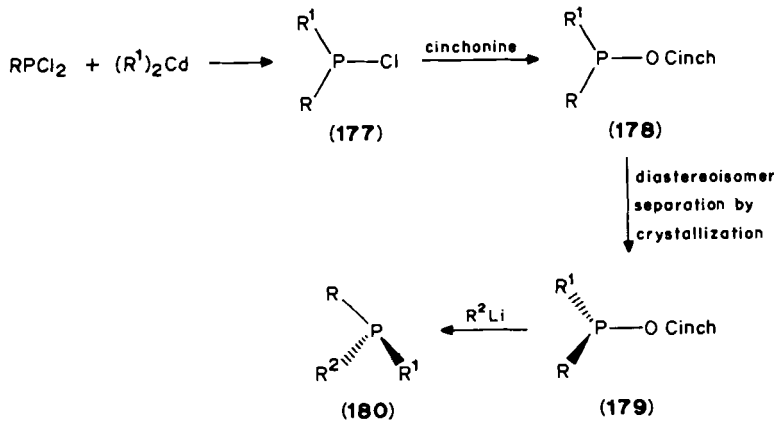
SCHEME 9

yields of menthyl phosphinites (**175**), which were treated with an alkyllithium in diethyl ether at $-50\,^{\circ}C$ to produce phosphines (**176**) with high optical purity. The last step proceeds with inversion of configuration. A similar process was described by Chodkiewicz *et al.*[118], based on the reaction sequence in Scheme 10, starting from $RPCl_2$. A resolution step occurs with help of an alkaloid. The interest in these two last methods lies in the fact that a chiral phosphine (and not a phosphine oxide) is produced directly.

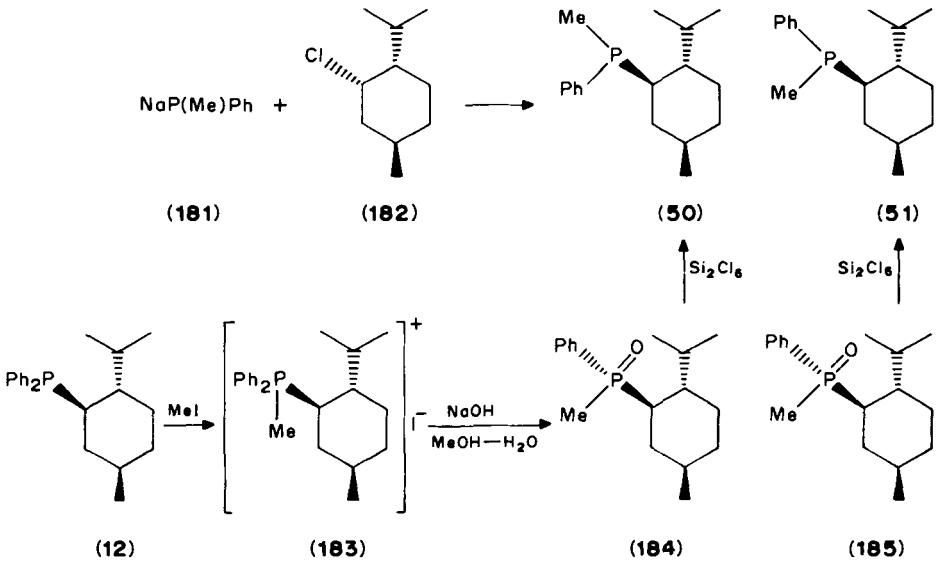
Methyl-*tert*-butylphenylphosphine (**6g**) has been resolved by combination with (+)-η^3-pinenylnickel bromide and subsequent separation of the diastereomeric nickel complexes[165].

Phosphines **50** and **51**, having both a chiral phosphorus and a chiral side-chain, have been prepared using the reactions[50,51] (shown in Scheme 11).

Monophosphines with a chiral side-chain have been easily prepared by treatment of the



SCHEME 10



SCHEME 11

tosylate (or halide) of the optically active compound (available from the chiral pool) with the diphenylphosphide anion:

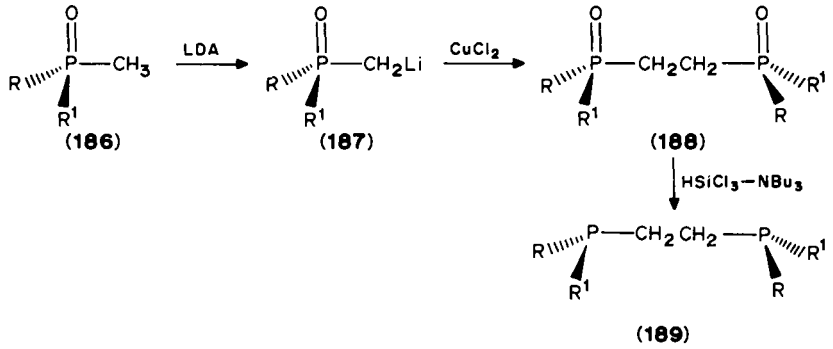
$$R^*X + {}^-PPh_2 \longrightarrow R^*PPh_2 + X^- \qquad (1)$$

Nmdpp (**11**) and mdpp (**12**) were first prepared in this way from menthol and neomenthol, respectively[26]. The reaction proceeds mainly with inversion of configuration at carbon. The alternate reaction has been used to prepare dialkylphosphines such as dimenthylmethylphosphine or dimenthylisopropylphosphine and trismyrtanylphosphine[33]. It is also especially convenient for the introduction of phosphorus on an aromatic ring.

$$R^{*-} + XPPh_2 \longrightarrow R^*PPh_2 + X^- \quad (2)$$

Ortholithiation of $ArCH^*(CH_3)N(CH_3)_2$ (Ar = Ph, 1-naphthyl, ferrocenyl) occurs easily. The resulting organolithium reacts with $XPPh_2$, leading to a phosphine. By using this method, amphos (**24**), 1,2-dpnea (**25**), 1,8-dpnea (**26**) and ppfa (**47**) were prepared[35]. In the last example a planar chirality is stereoselectively created because of the directing effect of the *N,N*-dimethylamino group fixed to an asymmetric carbon, which oriented lithiation on only one of the two *ortho* positions in the ring.

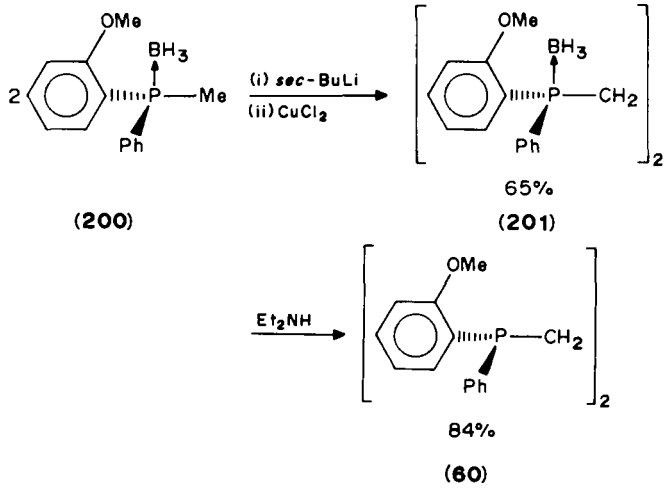
Diphosphines *with at least one asymmetric phosphorus* have been prepared mainly by the following three methods. The most general route to forming chiral 1,2-diphosphines stereoselectively is the oxidative coupling of two chiral phosphine oxides (Scheme 12). By



SCHEME 12

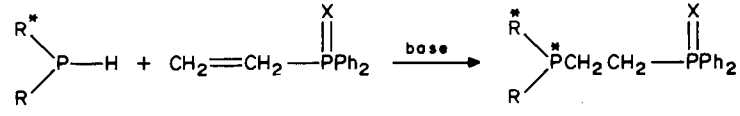
using this method, Vineyard *et al.*[55] prepared (*R,R*)-dipamp (**60**), which gives a very efficient rhodium catalyst for asymmetric hydrogenation and which is used in an industrial asymmetric synthesis of (*S*)-dopa.

On the basis of the unique reactivities of phosphine–boranes, Imamoto *et al.*[119] developed a new route to optically pure **60** (Scheme 13).



SCHEME 13

The 1,4-addition of R*(Ph)PH to $CH_2{=}CHPPh_2$ or $CH_2{=}CHP(S)Ph_2$ in the presence of a base yields 1,2-diphosphines containing only one asymmetric phosphorus atom (Scheme 14). The diastereomeric diphosphines **63** and **64** were prepared by using this

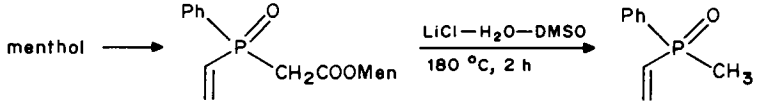


(202) **(203)** **(204)**

SCHEME 14

method[58]. Separation of the pure diastereomer is wasteful, involving extensive fractional crystallization.

Pietrusiewicz *et al.*[120a] introduced a chiral synthon as the key for the synthesis of many mono- or di-phosphines. It is obtained from menthol (Scheme 15). Conjugate addition on



[(−)-(*S*)-**205**] [(−)-(*S*)-**206**]

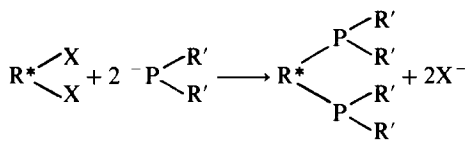
SCHEME 15

optically active vinylphosphine oxides was also achieved very easily in an aqueous medium by the zinc- or copper-promoted reaction of alkyl halides[120b]. Many phosphine oxides (**206'**) could be prepared from the phosphine oxide **206**. The procedure requires ultrasonic irradiation, and fully maintains configurational integrity at the phosphorus centre. This method has also been applied to (menthoxylcarbonylmethyl)phenylvinylphosphine oxide (**205**) to add an isopropyl fragment to the vinyl group.

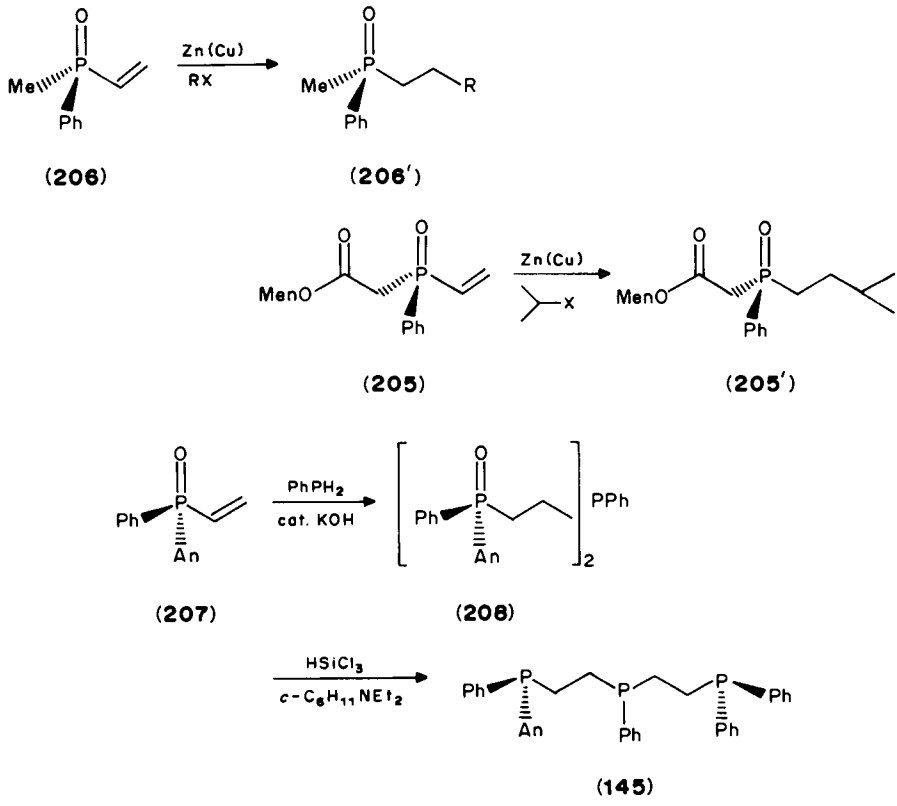
Recently, Johnson and Imamoto[108] utilized a chiral vinylphosphine oxide for the synthesis of various chiral polyphosphine with two asymmetric phosphorus atoms (Scheme 16).

The third method is resolution using a diastereomeric transition metal complex. The chelating *o*-phenylenebis(methylphenylphosphine) (**62**) has been prepared as in Scheme 17[57]. A large-scale resolution of racemic **62** involves the formation of diastereomeric palladium complexes (**211**).

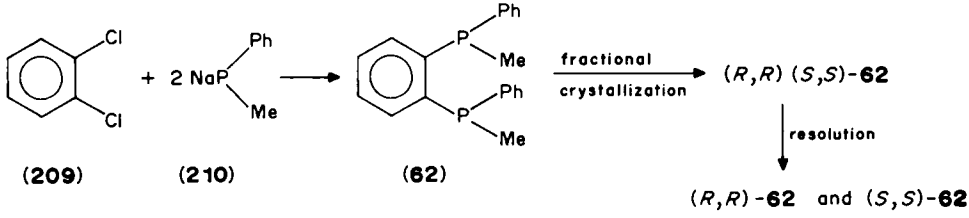
Diphosphines with a chiral group connecting two achiral phosphorus atoms are relatively easy to synthesize. The most widely used reaction to prepare such diphosphines is based on the alkylation of a disubstituted phosphide by a chiral ditosylate or dihalide as shown in reaction 3. By this method, diphosphines such as 1,2-diphosphines (**66–72**), 1,3-diphosphines (**91**, **92**) and 1,4-diphosphines (**100–119**) were synthesized[81]. Typical examples are the preparation of diop (**100**) and related 1,4-diphosphines (Scheme 18).



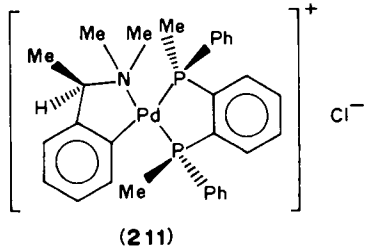
(3)

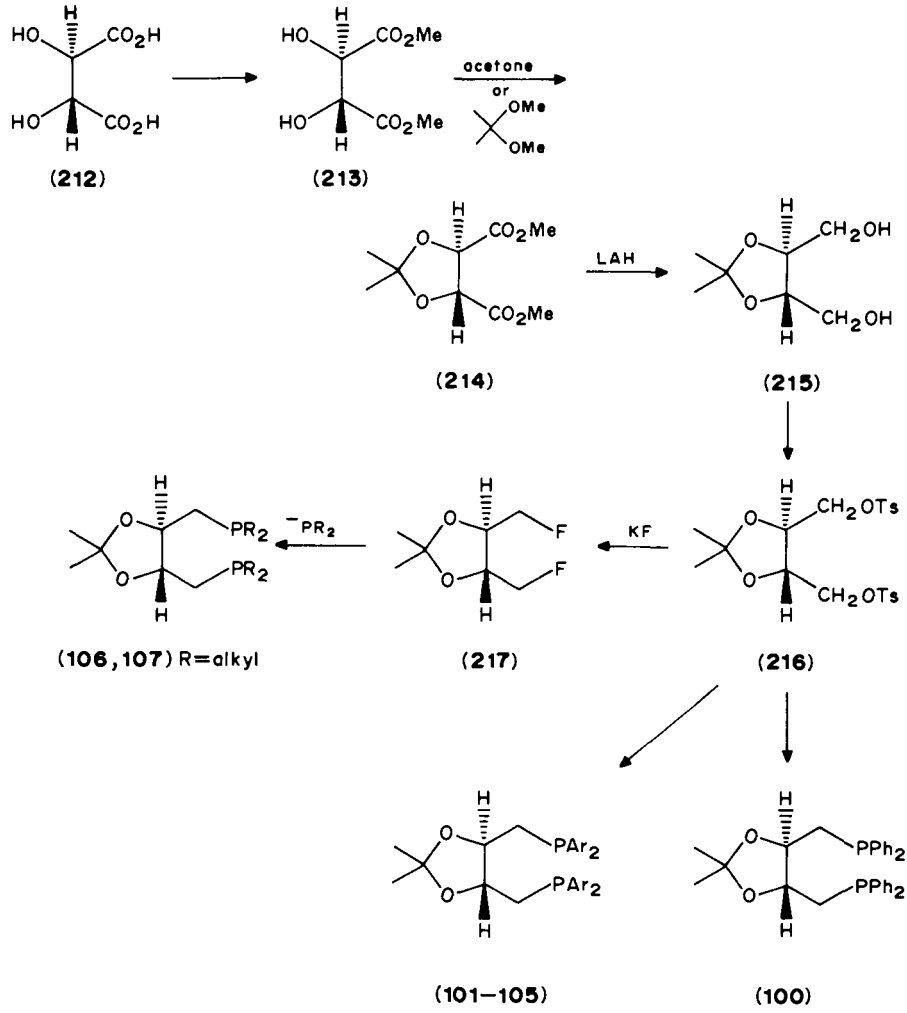


SCHEME 16



SCHEME 17

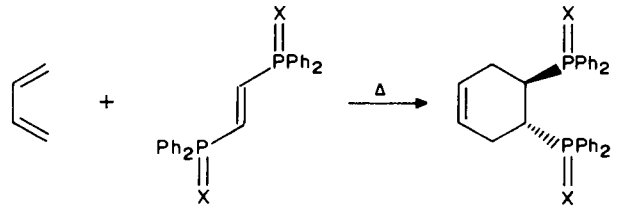




SCHEME 18

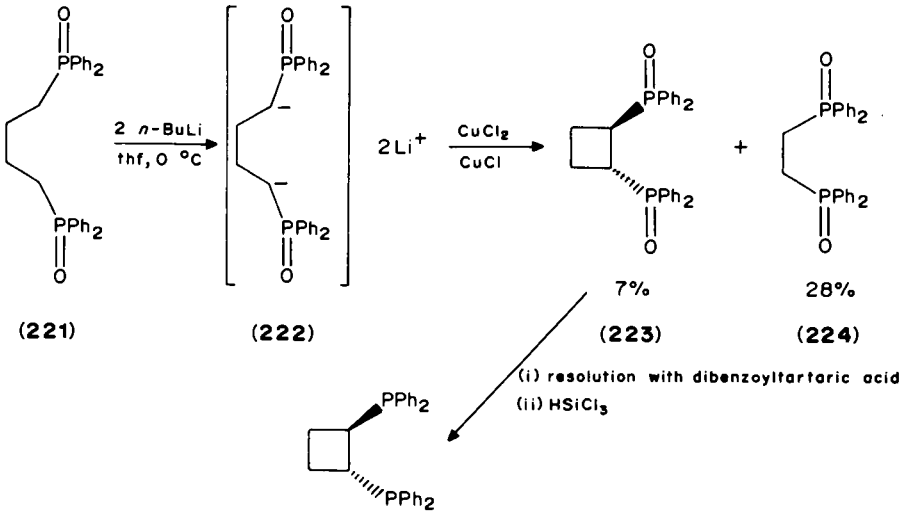
A completely different approach to chiral 1,2-diphosphines is based on the Diels–Alder reaction (Scheme 19). Both enantiomers of norphos (**80a**) were obtained by Brunner *et al.*[74] by this method. Samuel *et al.*[76] carried out a Diels–Alder reaction between 1,2-diphosphinated ethylene (X = S) and chiral dienes available from terpenes. For instance, (*S,S*)-phellanphos (**87**) and (*R,R*)-nopaphos (**88**) were prepared stereoselectively, in two steps, from (−)-phellandrene and (+)-nopadiene. Desulphurization was achieved by heating with sodium in toluene.

The intramolecular cyclization of the dianion of a diphosphine dioxide has been carried out (Scheme 20)[121]. Resolution of the cyclic diphosphine dioxide **223** was performed with dibenzoyltartaric acid and was followed by reduction with trichlorosilane to give dpcb (**79**).



(218) (219) (X=O,S) (220)

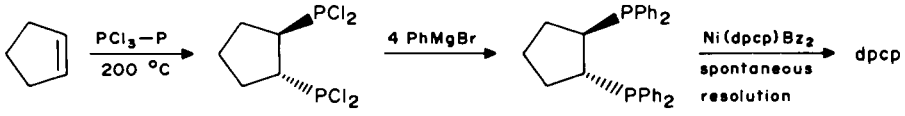
SCHEME 19



(221) (222) (223) (224) (79)

SCHEME 20

Dpcp (**80**) was prepared starting from cyclopentene (**225**) and phosphorus trichloride (Scheme 21)[122].



(226) (80') (80)

SCHEME 21

The rhodium complex of binap (**127**) is a highly efficient catalyst for some asymmetric hydrogenations and asymmetric double-bond migrations, as will be discussed later. Racemic binap was synthesized from 2,2'-dibromo-1,1'-binaphthyl by sequential treatment with *t*-BuLi and $ClPPh_2$. Resolution was then performed through complexation with an optically active palladium complex and fractional recrystallization. A much

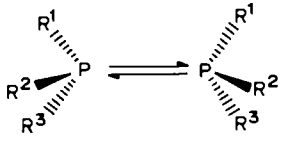
simpler resolution was realized later, on the bisphosphine oxide of binap, through separation of diastereomeric molecular complexes salts with either camphorsulphonic acid or dibenzoyltartaric acid[123].

This section can be summarized as follows. The various preparations of chiral phosphines are now widely based on selective transformations of natural products coming from the chiral pool (terpenes, aminoacids, tartaric acid, etc.). The chemistry is usually easy when there is no asymmetric phosphorus atom in the molecule, otherwise most of the methods involve at some stage separation of epimers at phosphorus. The fortunate and rare case is the one in which asymmetric synthesis at phosphorus occurs.

Resolution still remains of great use when it is easy to perform, since it gives both enantiomers of a compound. Resolution of a phosphine oxide by camphorsulphonic acid was used as early as 1911 by Meisenheimer and Lichtenstadt[1] for the preparation of **1**. This method is much more general than initially believed since Brunner *et al.* resolved the dioxide of norphos (**86a**) with tartaric acid, and Noyori *et al.* resolved the dioxide of binap (**127**) with camphoric acid. Resolution of many phosphine percursors (oxides, phosphinates, etc.) has often been performed by standard methods when a carboxylic group is present in the molecule.

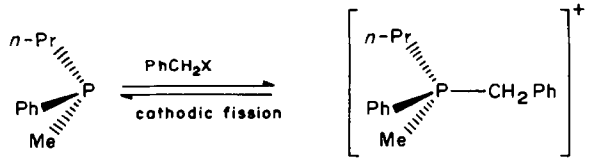
IV. CHIROPTICAL PROPERTIES, ABSOLUTE CONFIGURATION

P-chiral phosphines are relatively stable but they may be racemized at 130 °C with activation energies of *ca* 125.5 kJ mol^{-1} (equation 4)[124]. Therefore, it is necessary to consider carefully the stereochemical stability at phosphorus during the course of the synthesis.



(4)

X-ray crystallography has been used to determine the structures of a wide variety of phosphorus compounds. For instance, the absolute configuration of the phosphonium salt **6b'** was determined by X-ray diffraction, which enabled the absolute configuration of **6b** to be deduced as *S* on the basis of the assumption of retention during quaternization step (equation 5)[125].



(5)

(6b) **(6b')**

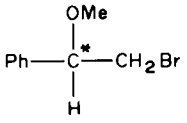
The absolute configuration of chiral phosphines can also be directly determined by X-ray analysis of their metal complexes[99,121,123]. The absolute configuration is confirmed by the Bijvoet method.

NMR analysis may be useful for the determination of the absolute configuration of a phosphorus centre, especially if a chiral centre of known configuration is present in the molecule. For example, chemical shift non-equivalence has been used to determine the configuration at the phosphorus centre in diastereoisomeric *l*-menthyl esters of alkylphosphinates **149** and **150**[126].

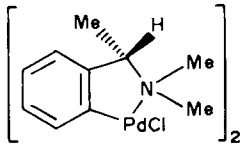
ORD and CD techniques have also been used for the configuration analysis of phosphine oxides. The study of the chiroptical properties of various phosphine oxides and sulphides has led to a direct configurational correlation of sulphoxides and phosphine oxides by intersystem matching of the Cotton effects[127]. The configurations of **127b** and **127c** were substantiated by comparing the CD spectra with those of (*R*) −(+)- and (*S*)-(−)-binap (**127a**), whose configurations have been determined by X-ray analysis[123].

V. METHODS OF MEASUREMENT OF ENANTIOMERIC EXCESSES

Enantiomeric excesses of P-chiral tertiary phosphines have been mainly determined by NMR analysis after derivatization to diastereomeric compounds: (i) quaternization of phosphines using 2-methoxylphenethyl bromide (**A**)[128] and (ii) formation of diphosphine complexes from (−)-bis(μ-chloro)bis[(*R*)-dimethyl(α-methylbenzyl)aminato-C_2,N]-dipalladium(II) (**B**)[129].



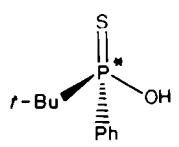
(**A**)



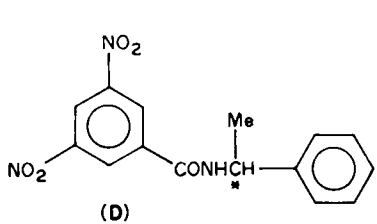
(**B**)

The method described by Pasquier and Marty[151], in which there is no need for a chiral auxiliary, can be applied to phosphines. In this method the sample serves as its own reference. A kinetically labile complex bonds reversibly two molecules of a partially resolved substrate (a phosphine in the present case). To measure the enantiomeric excess of this substrate by NMR necessitates measuring the ratio of *meso* to enantiomeric pair complexes starting from the racemic ligand and from a partially resolved sample. It is also necessary to measure the relative amount of free substrate to complex. From these experimental data, obtained by NMR on a small scale, the enantiomeric excess is easily calculated using an equation given by the authors[151]. The method was used to measure the enantiomeric excess of 1-diphenylphosphino-2-propanethiol with Ni^{2+} as the auxiliary metal centre. The phosphine was prepared by ring opening of partially resolved methylthiirane. η^3-Pinenylnickel bromide has been used as a chiral reagent for measuring the enantiomeric excesses of some P-chiral phosphines[165].

It has been proposed that (−)-*tert*-butylphenylphosphinothioic acid (**C**)[113] and (−)-*N*-(3,5-dinitrobenzoyl)-α-phenylethylamine (**D**)[130] may be used as chiral solvating reagents for phosphine oxides (which are easily obtained by oxidation of phosphines). The chiral shift reagent [(Eu(hfc)$_3$] is also useful for measuring the enantiomeric excess of phosphine oxides and phosphinates[131].



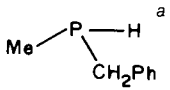
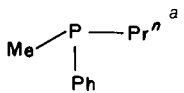
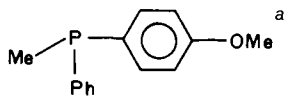
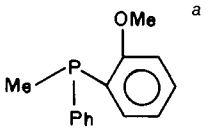
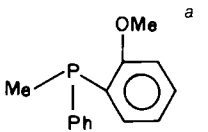
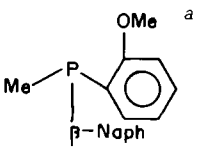
(**C**)

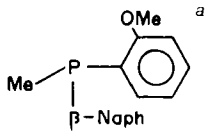
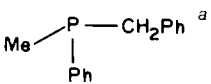
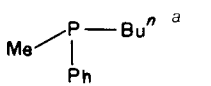
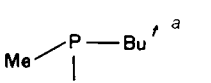
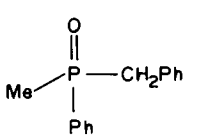
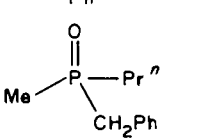
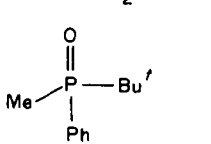


(**D**)

Some examples of enantiomeric excess measurement by the various methods are given in Tables 1 and 2.

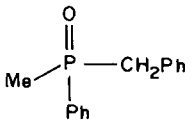
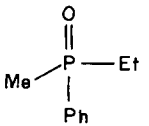
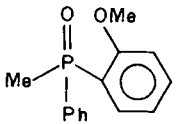
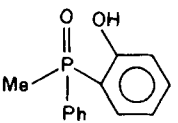
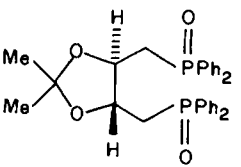
TABLE 1. Measurement of the enantiomeric excesses of monophosphines and derivatives

Reagent	Phosphine or derivative	Solvent	NMR ($\Delta\nu$, Hz)		Ref.
A	 [a]	D_2O	OMe *p*-Me	2.7[b] 0.5	128b
A	 [a]	D_2O	OMe *p*-Me	4.2[b] 9.2	128b
A	 [a]	D_2O	OMe	0.9[b]	128b
A	 [a]	D_2O	OMe *p*-Me Anisyl OMe	2.2[b] 5.5 3.3	128b
A	 [a]	$(CD_3)_3CO$	OMe *p*-Me Anisyl OMe	6.0[b] 3.5 2.3	128b
A	 [a]	$CDCl_3$	OMe Anisyl OCH_3	1.5[b] 1.9	128b

A		C_6H_5CN	Anisyl OCH_3	4.2[c]	128b
A		$CDCl_3$	OMe	0.23 ppm	132
A		$CDCl_3$	OMe	0.11 ppm	132
A		$CDCl_3$	OMe	0.22 ppm	132
C		$CDCl_3$	*p*-Me	6.0–10.3[c]	113
C		C_6D_6	*p*-Me	10.6[d]	113
D		$CDCl_3/CCl_4$ (9:1)	*p*-Me *p*-Bu^t	4.5[e] 2.5	130

(*continued*)

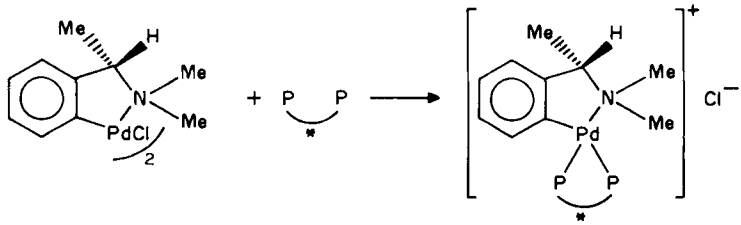
TABLE 1. (*continued*)

Reagent	Phosphine or derivative	Solvent	NMR ($\Delta\nu$, Hz)		Ref.
D		$CDCl_3$	*p*-Me	6.0[e]	130
D		$CDCl_3/CCl_4$ (9:1)	*p*-Me	5.5[e]	130
D		$CDCl_3/CCl_4$ (9:1)	*p*-Me OMe	4.0[e] 3.0	130
D		$CDCl_3$	*p*-Me	5.0[e]	130
D		$CDCl_3$	Me CH CH_2	6.0[e] 7.0 7.0	130

[a]As phosphonium salt, $[R^1R^2P^3PCH_2-\underset{H}{\overset{OCH_3}{\overset{|}{\underset{|}{C}}}}-Ph]^+Br^-$.

[b]60 MHz.
[c]100 MHz
[d]300 MHz
[e]500 MHz

TABLE 2. Measurement of the enantiomeric excesses of diphosphines[a]



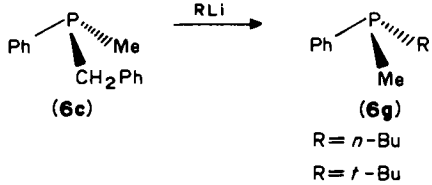
	^{31}P, δ (ppm) (J)[b]		^{1}H, δ (ppm)			
			R,R[c]		S,S[c]	
Diphosphine	R,R[c]	S,S[c]	NMe	CMe[d]	NMe	CMe[d]
diop **100**	33.6(*S*)[e]	33.7(*S*)[e]	2.70	1.80	2.73	1.95
62	44.725)	47.6(26)	2.63	1.53	2.90	1.48
	29.3(25)	31.0(26)	2.88[f]			
dipamp **60**	48.4(29)	45.3(25)	2.83	1.63	2.91	1.90
	32.1(29)	32.8(25)				
norphos **86a**	48.4[e,g]	46.7(5)[e]		1.85		1.89
		44.9(5)				
renorphos **86b**	42.6(7)[e]	45.5(8)[e]		1.93		1.96
	42.0(7)	44.2(8)				

[a]0.1 M solutions in $CDCl_3$.
[b]The absorptions for **62**–**86b** are pairs of doublets with coupling constant in Hz in parentheses.
[c]Configurations of the chiral centres in the free diphosphine ligand.
[d]All signals are doublets, $J = 6$ Hz.
[e]It is important to use a 1:1 ratio of **B** to diphosphine to obtain this spectrum.
[f]The two NH_2 groups are magnetically different in this complex.
[g]Narrow, unresolved multiplet.

HPLC analysis is useful for the measurement of enantiomeric excesses of phosphine oxides and phosphinates. Guyon *et al.*[133] reported the HPLC analysis of diastereoisomers of *O*-menthyl methylphenylphosphinates. It is also possible to determine the optical purity of phosphine oxides and phosphinates by HPLC on a chiral column[19,114,141,142,194,195].

VI. STEREOCHEMISTRY OF CHEMICAL REACTIONS ON PHOSPHORUS OR IN VICINAL POSITIONS

Nucleophilic substitution at phosphorus in tertiary phosphines with alkyllithium reagents proceeds with predominant inversion of configuration (equation 6)[132]. The reaction is drastically affected by the medium, as shown in Table 3.



(6c) **(6g)**

R = *n*-Bu
R = *t*-Bu

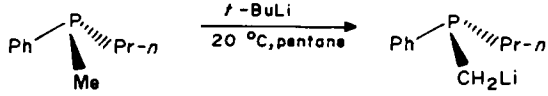
(6)

TABLE 3. Yields of nucleophilic substitution by butyllithium at phosphorus in (+)-(*R*)-*p*-**6** as a function of reaction medium[a] (ref. 132)

Medium	Yield (%)	
	n-BuLi	*t*-BuLi
thf	39	14
thf–tmeda	28	16
Et_2O	21	3
Et_2O–tmeda	50	73
C_6H_{14}	0	2
C_6H_{14}–tmeda	77	76

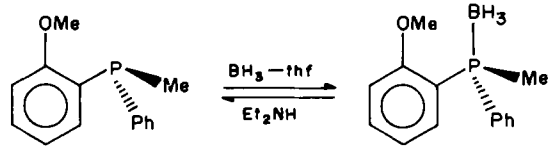
[a]The following standard conditions were used: [**6**] 0.05–0.1 M; *n*-BuLi introduced as a 1.7 M solution in hydrocarbon solvent in nine- to ten-fold excess; the reaction was run for 0.5 h at room temperature, quenched with water and analysed by GLC, using *n*-$C_{16}H_{24}$ as internal standard; tmeda: *n*-BuLi mole ratio = 1:1.

It has been observed that the stereochemical integrity of methylphosphines is preserved when they are converted into the α-carbanion (equation 7)[134].



(**6b**) (**6b'**) (7)

Imamoto *et al.*[119] reported a stereospecific interconversion between **9** and **9'**. It is interesting that the BH_3 group of phosphine–boranes is mildly removed by the reaction with an amine such as diethylamine.

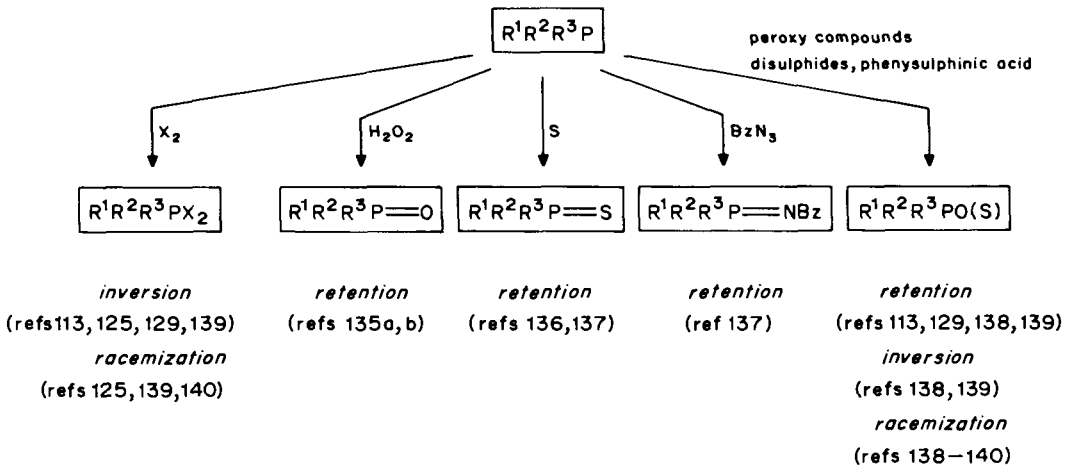


(**9**) (**9'**) (8)

Both reactions have been found to proceed with complete retention of configuration. As discussed previously, removal of oxygen from phosphine oxides with asymmetric phosphorus is possible with Si_2Cl_6 (full retention of configuration) or $PhSiH_3$ (largely inversion of configuration). The reaction requires prolonged heating above 100 °C. This contrasts with the mild removal of the BH_3 moiety from phosphine–boranes.

The stereochemical courses of the transformation of P-chiral phosphines into phosphorus(IV) and -(V) compounds are summarized in Scheme 22.

Dimethyl selenoxide, SeO_2, reacts under mild conditions with compounds such as methyl-*n*-propylphenylphosphine (**6b**) to give the corresponding phosphine oxide with full


R1R2R3P
peroxy compounds
disulphides, phenysulphinic acid
X2
H2O2
S
BzN3
R1R2R3PX2
R1R2R3P=O
R1R2R3P=S
R1R2R3P=NBz
R1R2R3PO(S)
inversion
(refs113, 125, 129, 139)
racemization
(refs 125, 139, 140)
retention
(refs 135a, b)
retention
(refs 136, 137)
retention
(ref 137)
retention
(refs 113, 129, 138, 139)
inversion
(refs 138, 139)
racemization
(refs 138–140)

SCHEME 22

inversion of configuration at phosphorus[135c]. A mechanism involving a phosphorane intermediate was proposed.

VII. USES IN ORGANOMETALLIC CHEMISTRY AND ASYMMETRIC CATALYSIS

A. Introduction

Chiral phosphines are widely used as ligands for transition metals. Structural studies have been carried out on many isolated complexes. Usually these studies were intended to provide models for the interpretation of the steps occurring in asymmetric catalysis. Because asymmetric catalysis developed rapidly through empirical experiments, the main results obtained will first be analysed. In Section 3.VII.G some coordination chemistry is detailed. Phosphines have to be considered as soft ligands[143] (or of Chatt class a[144]) and are well adapted for coordination to soft metals, essentially metals which have d orbitals (transition metals). The main asymmetric catalytic systems are based on phosphine–metal complexes with metals such as nickel, cobalt, rhodium, ruthenium, platinum and palladium. Many chiral phosphines have been devised in order to find the best fit between the chiral catalyst and the substrate for a given reaction.

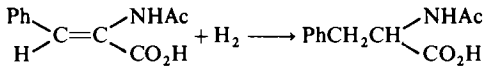
B. Asymmetric Catalysis with Rhodium Complexes

1. Asymmetric hydrogenation

Wilkinson's complex [$RhCl(PPh_3)_3$] was the first catalyst precursor for the homogeneous hydrogenation of olefins. Its discovery in 1966 greatly stimulated research into homogeneous catalysis in general, especially with rhodium complexes. In 1968, two attempts to use a chiral modification of Wilkinson's complex appeared simultaneously: Horner *et al.*[17] and Knowles and Sabacky[18] (at Monsanto) replaced triphenylphosphine by methyl-*n*-propylphenylphosphine (**6b**) and obtained up to 15% ee in the asymmetric reduction of unsaturated compounds such as α-ethylstyrene or α-phenylacrylic acid. In 1974 Morrison and Masler[26] prepared the chiral phosphines R^*PPh_2, where R* is a chiral group such as neomenthyl or menthyl (e.g. **11** and **12**); 60% ee was obtained in the asymmetric reduction of (*Z*)-$Ph(Me)C{=}C(H)CO_2H$. In 1971–72 an important class of chiral ligands was discovered by Kagan and Dang[81,145]. This family, of general formula $Ph_2PR^*PPh_2$, includes diop (**100**) as the prototype. Diop–rhodium complexes (diop:Rh = 1:1) are excellent catalysts for the hydrogenation of many C=C double bonds. For example, *N*-acetylphenylalanine was obtained in 82% ee by hydrogenation of (*Z*)-$PhCH{=}C(NHAc)CO_2H$. Ligands having asymmetric phosphorus atoms were used by the Monsanto group successfully: camp (**10**)[25a] and dipamp (**60**)[55] gave, for example, 90% and 95% ee, respectively, in the asymmetric synthesis of *N*-acetylphenylalanine. The industrial production of (*S*)-dopa, a useful drug against Parkinson's disease, has been operated since 1974 by Monsanto. It is based on asymmetric hydrogenation with a rhodium–dipamp catalyst.

Most of the chiral ligands developed for rhodium complexes avoided the preparation of asymmetric phosphorus atoms and were chelating diphosphines, $Ph_2PR^*PPh_2$. Many analogue of diop, a 1,4-diphosphine, have been synthesized and are often very efficient. Other types of 1,4-diphosphines such as binap (**129**)[99], bppm (**120**)[37] and bppfa (**132**)[47], and also 1,3- or 1,2-diphosphines, have been found to be very useful in asymmetric hydrogenation. Some results for the hydrogenation of dehydroamino acids are given in Table 4. Enantiomeric excesses close to 100% are now not unusual, especially with 1,2-diphosphines.

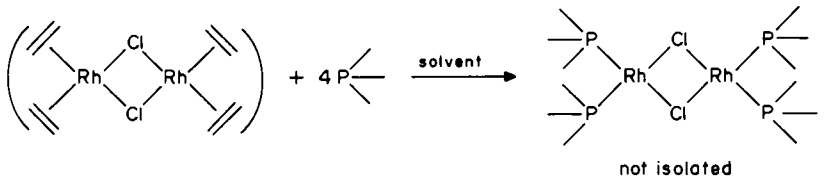
TABLE 4. Asymmetric hydrogenation with various phosphines as ligand of the rhodium catalyst



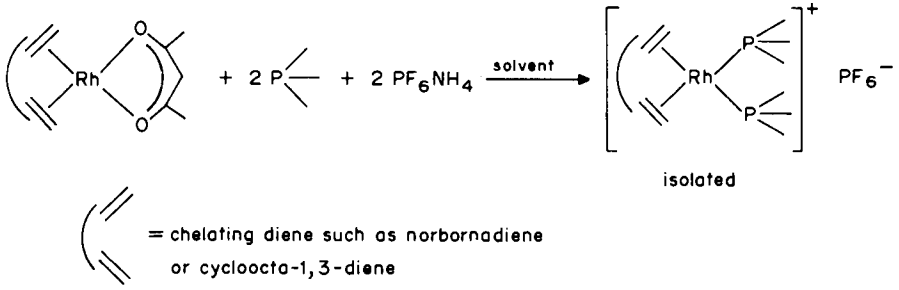
Ligand[a]	ee (%) (configuration)	Ref.
(*R*,*R*)-diop **100**[b]	80(*R*)	81,150
(*S*,*R*)-bppfa **132**[b]	93(*S*)	47
(*S*,*S*)-bppm **120**	91(*S*)	37
(*R*)-binap **127a**[d]	99(*S*)	99
(*R*,*R*)-dioxop **139**[d]	78(*S*)	31
(*S*,*S*)-skewphos **92**	92(*R*)	79
(*R*,*R*)-dipamp **60**	94(*S*)	55
(*R*)-prophos **67**	90(*S*)	57
(*S*,*S*)-chiraphos **66**	99(*R*)	60
(*R*,*R*)-norphos **26a**[b]	96(*S*)	74
(*S*,*S*)-phellanphos **87**	95(*R*)	76
(*S*,*S*)-dpcp **80**	99(*R*)	71
(*S*,*S*)-deguphos **81**	99(*R*)	73
(*S*)-camp **10**	89(*S*)	25

[a]Cationic complex, unless stated otherwise.
[b]*In situ* neutral complex.
[c]Addition of triethylamine.
[d]Reaction on *N*-benzoyldehydrophenylalanine.

The rhodium–phosphine complexes are usually *in situ* catalysts and are generated as in Scheme 23. The substrate and hydrogen are subsequently introduced. This procedure is very convenient for initial screening of a small amount of a chiral phosphine. If it is necessary to store a chiral catalyst, a cationic rhodium complex can be prepared from a neutral rhodium precursor. as in Scheme 24.



SCHEME 23



SCHEME 24

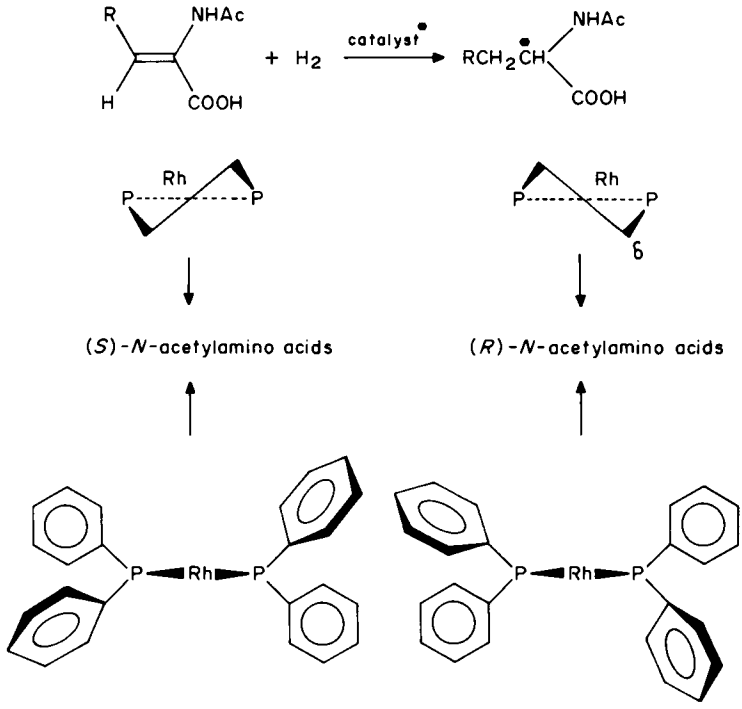
Mechanistic details of the asymmetric hydrogenation of dehydroamino acid derivatives are known owing to the efforts of many groups, especially those of Halpern[146] and Brown[147]. By a combination of ^1H, ^{13}C and ^{31}P NMR spectroscopy in solution and of X-ray crystallography on various isolated complexes the following conclusions can be drawn:

(i) *N*-Acyldehydroamino esters coordinate both by the double bond and by the amide group. Usually the two diastereomeric complexes (differing by the prochiral face which is coordinated) are detectable in solution, one complex being predominant.

(ii) Oxidative addition of hydrogen occurs on the above complex, in what is considered as the turnover-limiting step. The dihydride complexes could not be detected because of the fast subsequent insertion reaction of the double bond into the Rh–H bond. The resulting alkylrhodium complex was observed by Chan *et al.*[146] by lowering the temperature. The global stereochemistry is always a *cis* addition of two hydrogens[148,149].

(iii) The major diastereomeric olefin rhodium complex formed at the beginning of the reaction is not the one leading to the final product.

A correlation between the arrangement of the *P*-phenyl rings and the absolute configuration of the α-amino acid which is produced has been proposed by Vineyard *et al.*[55]. An edge-to-face array as shown in Scheme 25 consistently induces (*S*)-*N*-acylamino acid synthesis. The correlation could be obtained by X-ray analysis of various complexes. Fryzuk and Bosnich[60] pointed out that good correlations are also found for chiral 1,2-diphosphines by considering the chirality of the five-membered chelate ring. A λ conformation (Scheme 25) is always associated with asymmetric synthesis of (*S*)-amino



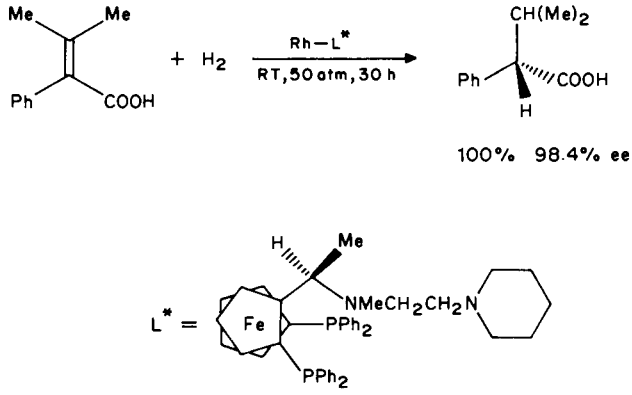
SCHEME 25

acids. The mechanistic picture of how the chiral recognition occurs during the first hydrogen transfer on prochiral double bond is still missing.

Iridium–phosphine complexes are not very efficient for the homogeneous hydrogenation of olefins unless the phosphine is a *trialkylphosphine* such as P(cyclohexyl)$_3$[152]. However, Oro *et al.*[153] used a cationic iridium complex, [Ir(cod)(PhCN)(nmdpp)]$^+$, where nmdpp represents neomenthyldiphenylphosphine, at room temperature and with 1 atm of hydrogen. This complex catalyses the hydrogenation of *N*-acetyldehydroamino esters, even when there is a tetrasubstituted double bond, but the enantiomeric excesses are low ($\leqslant 27\%$).

The inactivity of many iridium–phosphine complexes allowed Alcock *et al.*[154] to prepare chiral rhodium complexes starting from a racemic phosphine. They found that menthyl(*Z*)-*N*-acetyldehydrophenylalaninate can give rise to an isolatable cationic iridium complex, [Ir(PhCH=C(NHAc)CO$_2$menthyl)$_2$]$^+$. When two equivalents of *racemic* chiraphos (**66**) are mixed with this complex at $-78\,^\circ C$ and the temperature is raised to 20 °C, 1 mol of (*S,S*)-chiraphos displaces 1 mol of dehydroamino ester. Then [(nbd)$_2$Rh]$^+$BF$_4^-$ (0.8 equiv.) was added. The free (*R,R*)-chiraphos chelated to the rhodium complex. This chiral rhodium complex was the usual catalyst for asymmetric hydrogenation; for example, methyl (*Z*)-α-acetamidocinnamate was reduced to the corresponding amino ester with 89% ee (the same enantiomeric excess was observed with optically pure chiraphos). The *in situ* resolution of the chiral diphosphine for homogeneous catalysis was applied successfully to racemic chiraphos (**66**), to *rac-trans*-1,2-bis(diphenylphosphino)cyclopentane (**80**) and to *rac-trans*-1,2-bis(diphenylphosphino)-cyclohexane (**82**). This last compound was resolved for the first time.

Asymmetric hydrogenation of conjugated acids with a fully substituted double bond is very difficult with most rhodium catalysts and various diphosphines [e.g. bppfa (**132**) or chiraphos (**66**)]. Hayashi *et al.*[155] found that the introduction of a tertiary amino group into a side-chain in some ferrocenylphosphines results in an efficient rhodium catalyst (Scheme 26). The terminal amino group forms a salt with the substrate and consequently



SCHEME 26

attracts it to the coordination sphere of the complex. This attractive interaction between the ligand and the substrate enhances both the catalytic activity and the enantioselectivity given by the chiral diphosphine. This approach should be of wide application in asymmetric catalysis with chiral phosphines.

Rhodium–phosphine complexes are not very active for ketone reduction. Heil *et al.*[156]

were able to reduce acetophenone to PhCH(OH)Me with 80% ee by using the combination $[RhCl(nbd)]_2$ + diop + NEt_3. The reaction works at 50 °C and 70 atm hydrogen. Milder experimental conditions are possible when an ester group is close to the ketone group. Thus $CH_3COCO_2Bu^i$ was converted into $CH_3CH(OH)CO_2Bu^i$ (70% ee) using [RhCl(bppm)] as the catalyst[157]. The same catalyst was used in an asymmetric hydrogenation of α-ketolactone into pantolactone (80% ee)[158].

A ferrocenyldiphenylphosphine bearing a free hydroxyl (bppfOH, **134**) seems to be one of the most useful ligands for the asymmetric reduction of ketones[159]. Pyruvic acid was converted into lactic acid with 83% ee, acetophenone gave carbinol with 40% ee, $Ph(Me)C{=}NCH_2Ph$ was reduced to an amine (48% ee) and epinephrine (95% ee) could be obtained by hydrogenation of an α-amino ketone[160].

2. Hydrosilylation

Asymmetric hydrosilyation of ketones or imines is an alternative method to asymmetric hydrogenation, since alcohols or amines are produced after hydrolysis of the intermediate ROSi or RR'NSi. The Rhodium–diop catalyst allows the asymmetric hydrosilylation of simple ketone (e.g. acetophenone ⟶ PhCHOHMe, 58% ee[25a]) or a keto esters [e.g. $MeCO(CH_2)_2CO_2Bu^i \rightarrow MeCHOH(CH_2)_2CO_2Bu^i$, 84% ee[161]]. In these experiments, α-$NpPhSiH_2$ was the reagent. Diphenylsilane and Rh–diop catalyst is also a good combination for the asymmetric reduction of imines (≤ 50% ee)[162].

3. Hydroformylation

Asymmetric hydroformylation of olefins catalysed by rhodium complexes containing chiral phosphines has been a topic of intense investigation. The formation of hydratropaldehyde from styrene is the model reaction that has been most widely investigated (equation 9).

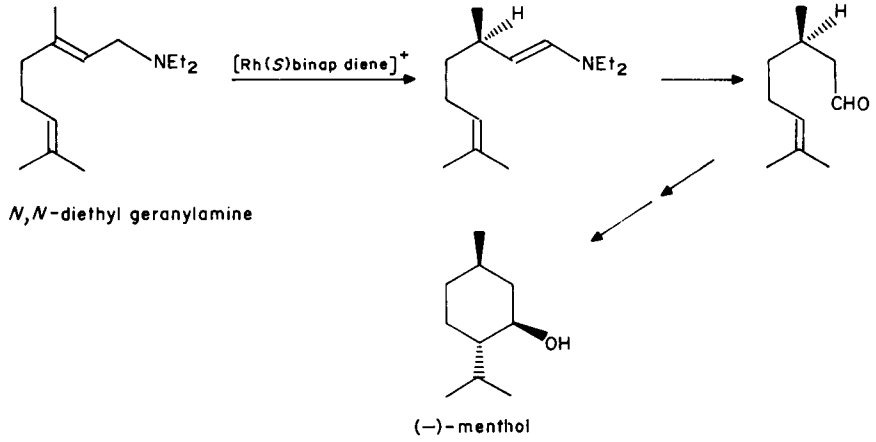
$$PhCH{=}CH_2 + CO + H_2 \longrightarrow PhCH\begin{matrix}\diagup CHO \\ \diagdown CH_3\end{matrix} + PhCH_2CH_2CHO \qquad (9)$$

Pino and Consiglio[163] found that the combination $[HRh(CO)(Ph_3)_3]$–diop (1:4) catalyses the formation of aldehydes in 25% ee. Two Japanese groups have also found enantiomeric excesses of up to 20% using nmdpp (**11**) or benzyl(methyl)phenylphosphine (**6c**). Butyl(methyl)phenylphosphine and $[RhCl(cod)]_2$ gave hydratropaldehyde with 40% ee (BASF)[164]. Chiral monophosphines or diphosphines and rhodium complexes were not able to achieve enantiomeric excesses above 40%, even with substrates other than styrene. However, platinum–tin complexes gave spectacular improvements.

4. C=C bond migration

The migration of a double bond is sometimes a competitive reaction in catalytic homogeneous hydrogenation. It is possible in some systems to take advantage of C=C bond migration for performing asymmetric syntheses from an achiral precursor. A necessary condition is that the reaction is strictly irreversible, in order to avoid racemization.

A major achievement in this area was the work of Tani *et al.*[87]. They found that the complex [Rh(cod)(binap **127a**)]$^+BF_4^-$ is an excellent catalyst at 40 °C for the asymmetric transformation of geranylamine to an enamine (> 90% ee), which is easily hydrolysed into citronellal (Scheme 27). Citronellal can be transformed in two steps into optically pure menthol. The Takasago Company in Japan is now producing (−)-menthol in hundred-



SCHEME 27

ton quantities by this Scheme. Binap **127b** is unique amongst the various chiral diphosphines which were tried.

C. Asymmetric Catalysis with Nickel–Phosphine Complexes

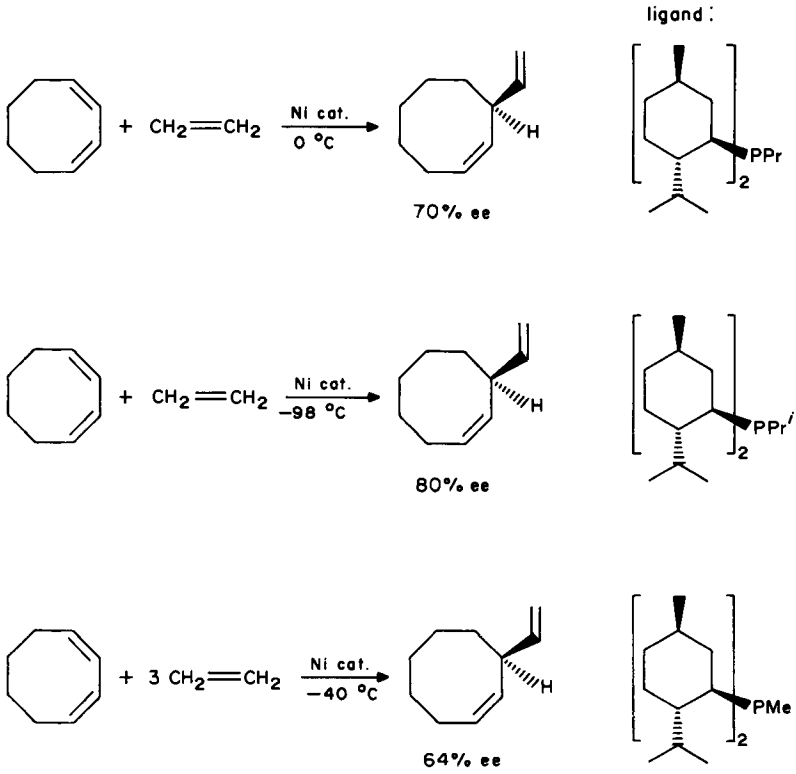
One of the earliest reports of asymmetric catalysis by phosphine transition metal complexes was provided by Bogdanovic[33] and Wilke[165]. They had previously shown that Ziegler–Natta-type complexes (such as a combination of η^3-alkylnickel chloride, $Al_2Et_3Cl_3$ and a phosphine) were excellent catalysts for the addition of simple olefins to olefins or conjugated dienes. By using chiral trialkylphosphines some codimerizations of ethylene on cycloocta-1,3-diene or norbornene gave products with enantiomeric excesses of up to 80% (Scheme 28).

These are amongst the best cases of asymmetric C—C bond formations. An intermediate in the catalytic cycle seems to be a nickel(II) hydride of the type [HNiX(Ph_3)(olefin)]. A model was proposed to explain the high enantioselectivities[33]. More recently, a French group[166] has shown that the catalyst precursor [Ni(cod)$_2$]–$AlClEt_2$–aminophosphine is also able to perform the transformation of cyclohexa-1,3-diene and ethylene into 3-vinylcyclohexene (73% ee at $-70\,^{\circ}C$). The chiral aminophosphines R,R′NPPh_2 are phosphorus ligands which are outside the scope of this chapter and which will be not discussed.

Asymmetric coupling reactions with Grignard reagents were found to be catalysed by nickel–phosphine complexes. The first positive results of asymmetric coupling were reported almost simultaneously by two groups[167,168a]. [$NiCl_2$(diop)] was the catalyst, the reaction being the formation of PhCH(Me)CH=CH_2 ($\leqslant 17\%$ ee) (equation 10).

$$\begin{matrix} \text{Me} \\ | \\ \text{PhCHMgCl} \end{matrix} + \text{BrCH=CH}_2 \xrightarrow{\text{Ni cat.}} \begin{matrix} \text{Me} \\ | \\ \text{PhCHCH=CH}_2 \\ * \end{matrix} \qquad (10)$$

This reaction was extensively studied by Kumada's group with a wide variety of chiral phosphines, including ferrocenylphosphines and β-dimethylaminoalkylphosphines. Very high enantioselectivity (up to 94%) could be achieved in the coupling reaction[168b]. Most of the reactions involved a Grignard reagent which cannot give rise to easy β-elimination (e.g.



SCHEME 28

$$\underset{\text{Et}}{\text{MeCHMgX}} + \text{PhY} \xrightarrow{\text{Ni cat.}} \underset{\text{Et}}{\text{MeCHPh}} \qquad (11)$$

ArMgX). However, *sec*-butylmagnesium halides are also able to react (equation 11)[169]. The catalyst is [$NiCl_2$(prophos **67**)]. The reaction depends strongly of the nature of X and Y. The highest enantiomeric excess was 44% (when X = Y = Br) with an isolated yield of 80%. Prophos is better than diop for reducing the formation of by-products owing to the rearrangement of the of the Grignard reagents.

The mechanistic details of these coupling reactions are not known. It was proposed that the reaction goes through a nickel(0) complex which undergoes oxidative addition of vinyl bromide. The resulting complex [$LNi(CH{=}CH_2)Br$](L = chiral diphosphine) reacts selectively with one enantiomer of the racemic Grignard reagent with nucleophilic substitution of bromine. The reaction ends with a reductive elimination which gives the coupling product, while the Grignard reagent simultaneously racemizes.

D. Asymmetric Catalysis with Platinum–Phosphine Complexes

The main use of platinum–phosphine complexes in asymmetric catalysis is in hydroformylation. It was discovered that the combination [$PtCl_2L_2$]–$SnCl_2$ (L_2 = chiral

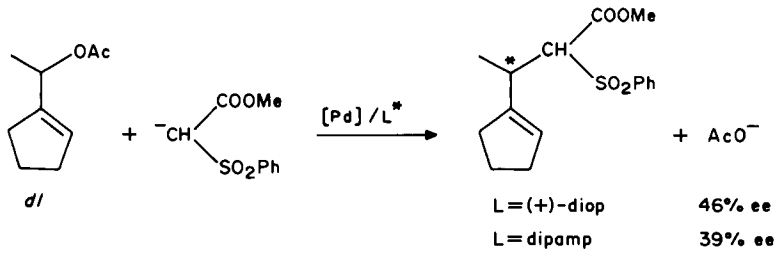
diphosphine) allows a low reaction temperature and gives fairly high enantiomeric excesses. With diop as ligand, atropaldehyde with an enantiomeric excess of up to 80% has been obtained from styrene[170]. The active complex is presumably [PtCl($SnCl_3$)diop]. A breakthrough in that area came recently from the work of Stille[171] with $PtCl_2$–$SnCl_2$–bppm (**120**). When the hydroformylation of styrene was carried out in the presence of triethyl orthoformate, which acts as trapping agent of atropaldehyde and prevents its racemization, almost enantiomerically pure diethyl acetal of hydratropaldehyde was obtained. Many examples of high enantioselectivities have been described, but a chiral diphosphine giving a high branched to normal ratio in asymmetric hydroformylation combined with a high optical yield remains to be discovered.

E. Asymmetric Catalysis with Palladium–Phosphine Complexes

Palladium complexes with chiral diphosphines have been widely used for coupling reactions and allylic substitution. Some examples of olefin hydrogenation have also been described.

1. Asymmetric allylic substitution

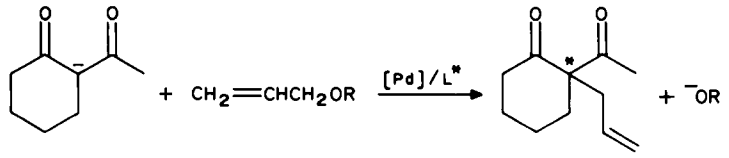
Palladium-catalysed allylic substitution has been successfully applied to organic synthesis[172,173]. The reaction can be used in asymmetric synthesis by replacing the achiral ligands of the catalyst (PPh_3, diphos, etc.) by chiral phosphines. For example, Scheme 29



SCHEME 29

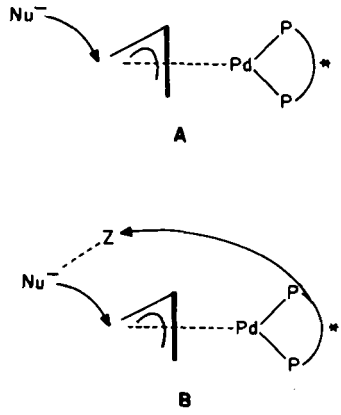
has been described by Trost and Strege[174]. The chiral catalyst was prepared from [$Pd(PPh_3)_4$] and bidentate diphosphines (diop or dipamp) which displace triphenylphosphine. The steric course of the reaction and the role of chiral diphosphines is difficult to discuss because the starting material is a racemic mixture.

A simpler system, where an asymmetric centre is created on the nucleophile, was studied by Fiaud *et al.*[175] (Scheme 30). With L* = diop and R = Ph the allylated product was isolated with only 10% ee. This was ascribed to the reaction mechanism, which involves a *trans* nucleophilic attack of an η^3-allyl Pd intermediate A (Scheme 31). The creation of an



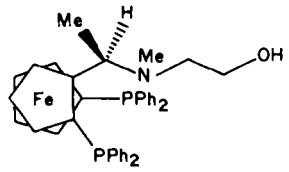
SCHEME 30

asymmetric centre on the nucleophile is then not controlled by the chiral diphosphine, which is too far away. A solution to that problem was proposed by Hayashi *et al.*[176], by the adjunction of a side-chain on a chiral diphosphine able to interact attractively by a group Z with the nucleophile as in intermediate **B** (Scheme 31). This approach was investigated in the area of chiral ferrocenyldiphosphines such as bppfa (**132**).



SCHEME 31

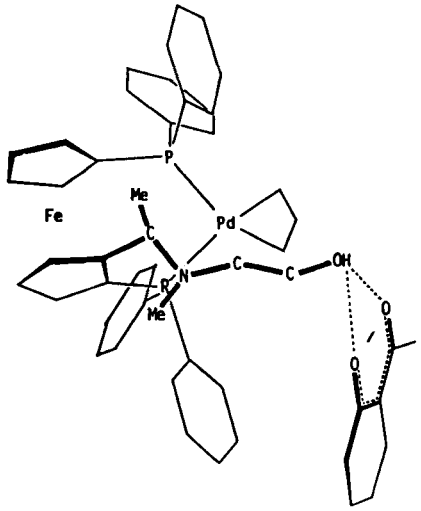
Functionalized ferrocenylphosphines with side-chains of various lengths bearing an OH or amino group in the terminal position have been prepared. One of the best ligand is **C**. It gives about 80% enantiomeric excess in the alkylation of 2-acetylcyclohexanone.



Scheme 32 was proposed to explain how the chiral diphosphine interacts with the enolate and helps to the chiral recognition. This scheme takes into account conformation of bppfa as given by the crystal structure of [$PdCl_2$(bppfa)].

Attractive interaction between nucleophile and hydroxy groups[172] on the side-chain of a chiral ligand has also been very beneficial in allylic alkylations where the asymmetric centre is created on the allylic compound (enantiomeric excess up to 90%)[177].

The molecular engineering of chiral phosphines for providing additional interactions (attractive or repulsive) with the reactants seems a very promising field for improving enantioselectivity and reactivity. It is especially valuable when one knows some mechanistic details because the rational development of 'second generation' ligands becomes possible.



SCHEME 32

2. Asymmetric hydrocyanation

The asymmetric addition of HCN to alkenes in the presence of a Pd(0)–diop catalyst has been reported[178]. 2-*exo*-Cyanonorbornane (30% ee) was produced from norbornene.

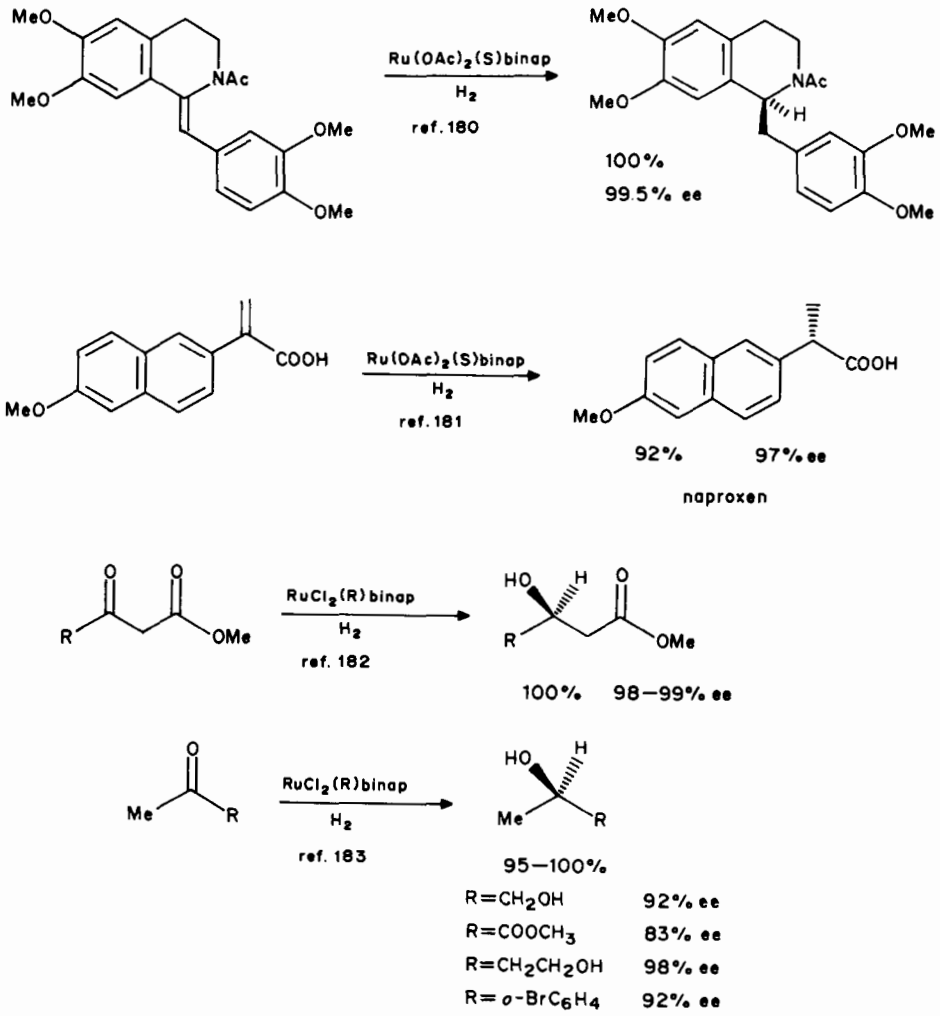
F. Asymmetric Catalysis by Ruthenium–Phosphine Complexes

Some ruthenium–diop complexes have been investigated as hydrogenation catalysts; enantiomeric excesses of up to 70% were found in the asymmetric hydrogenation of conjugated acids[179]. A breakthrough came recently with the discovery by Noyori and coworkers that $[RuX_2(binap)](X = OAc$ or Cl) complexes are superior catalysts for the asymmetric hydrogenation of many substrates. A few representative examples[180–183] are given in Scheme 33. The reactions are performed under pressure but are highly efficient (yield and enantiomeric excess).

One can expect a renewed interest in catalysis with ruthenium chiral phosphine complexes. The coordination chemistry of ruthenium complexes involving binap, compared with other chelating diphosphines, seems very specific[184].

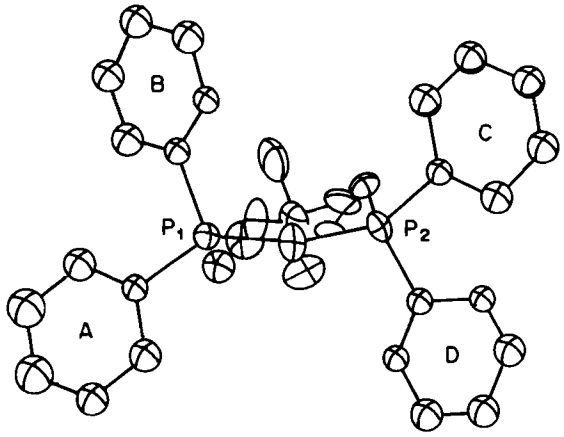
G. Coordination Chemistry of Chiral Phosphines

Many studies have been carried out in solution or in the solid state in order to elucidate the mechanistic details of catalytic asymmetric reactions. X-ray crystal structures of many complexes involving chiral phosphine ligands have been described. Chelate bisphosphine rhodium complexes were especially investigated in the hope of elucidating the origin of the high enantioselectivity occuring in asymmetric hydrogenation of dehydroamino acids (see discussion in Section 3.VII.B.1). The *P*-phenyl edge-to-face array hypothesis[55,185] (Scheme 25) was based on the X-ray structures of various rhodium complexes. Some selected structures are reproduced in Scheme 34 for ligands such as diop (**100**) chiraphos (**66**), dipamp (**60**) and cycphos (**69**).

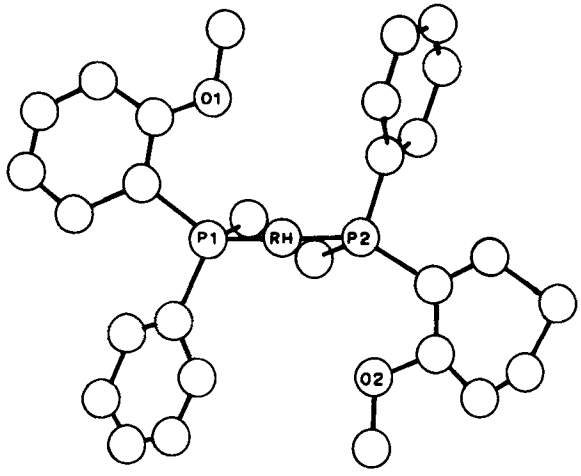


SCHEME 33

With a 1,2-diphosphine such as chiraphos the five-membered (twist conformation) is chiral because the two methyl groups take a pseudoequatorial orientation. It was found that the general rule 'a λ chelated ring induces synthesis of (*S*)-*N*-acylamino acids' does not seem to have any exception[57,76]. Moreover, some kind of correlation exists between λ or δ configuration and the chirality of the edge-to-face array (see Scheme 25). However, the 'edge-to-face' rule does not to seem very general, as pointed out first by Oliver and Riley[186], who studied the X-ray structures of three polymorph crystals of the cationic complex [Rh((*R*)-cycphos **69**)(nbd)]$^+$. The phenyl arrays are sensitive to the crystal packing. Scheme 34 shows one structure with a face-to-face array. Recently, Brown and Evans[187] made a careful comparison of all the available X-ray structures of chelate bisphosphine rhodium complexes (17 examples). It appears that for 1,2-diphosphines



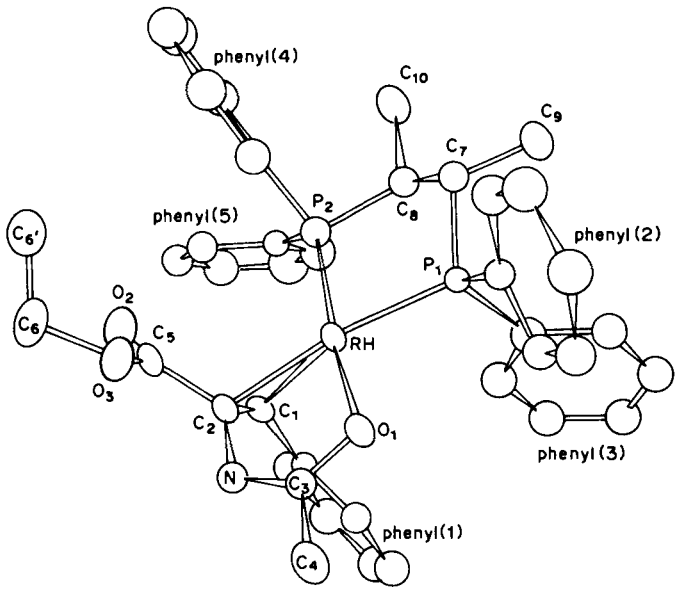
(185) $[Rh(diop)nbd]^+$



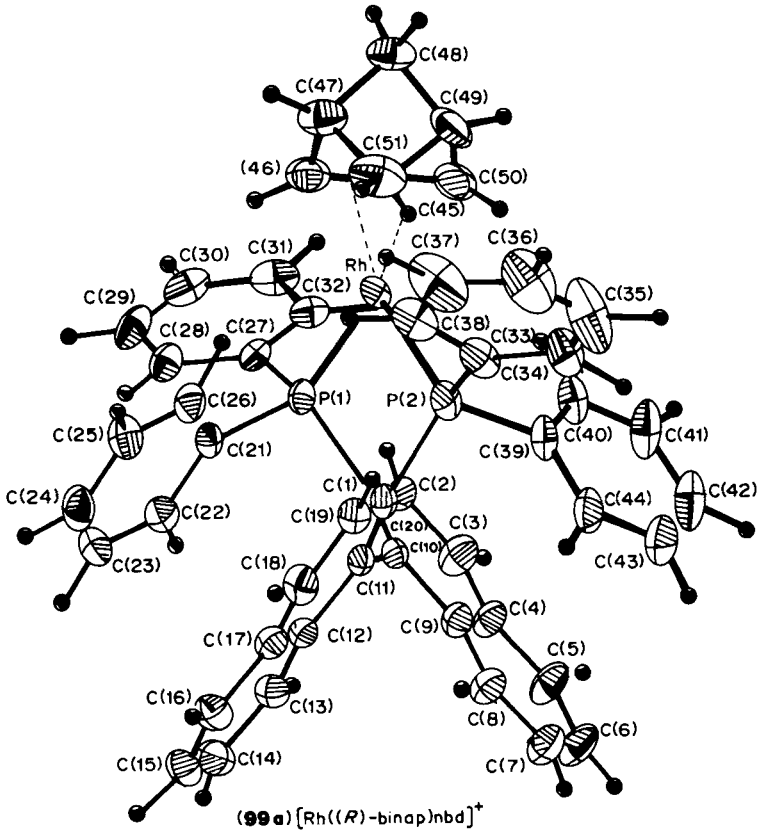
(185) $[Rh(dipamp)(cod)]^+$

SCHEME 34

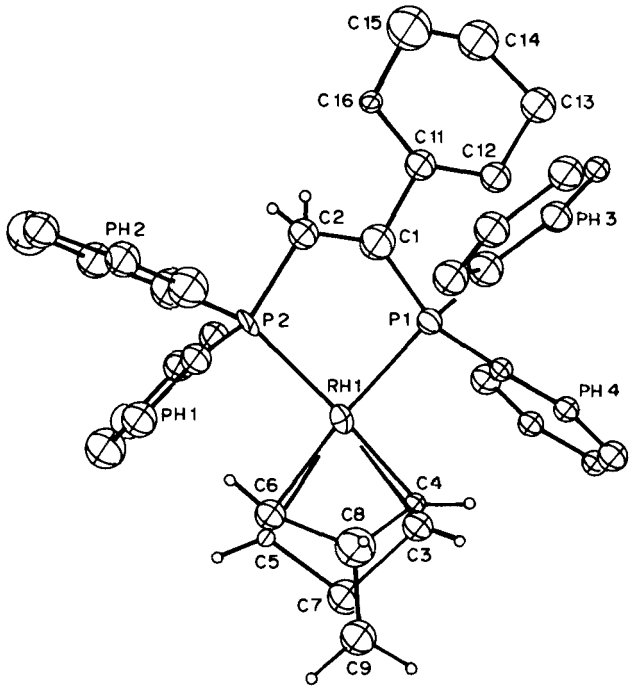
(continued)



(**146**) [Rh(*S*,*S*)-chiraphos(*Z*)-ethyl α-acetamidocinnamate]$^+$



(**99a**) [Rh((*R*)-binap)nbd]$^+$



(**186**) [Rh((*R*)-cyphos **69**)nbd]$^+$

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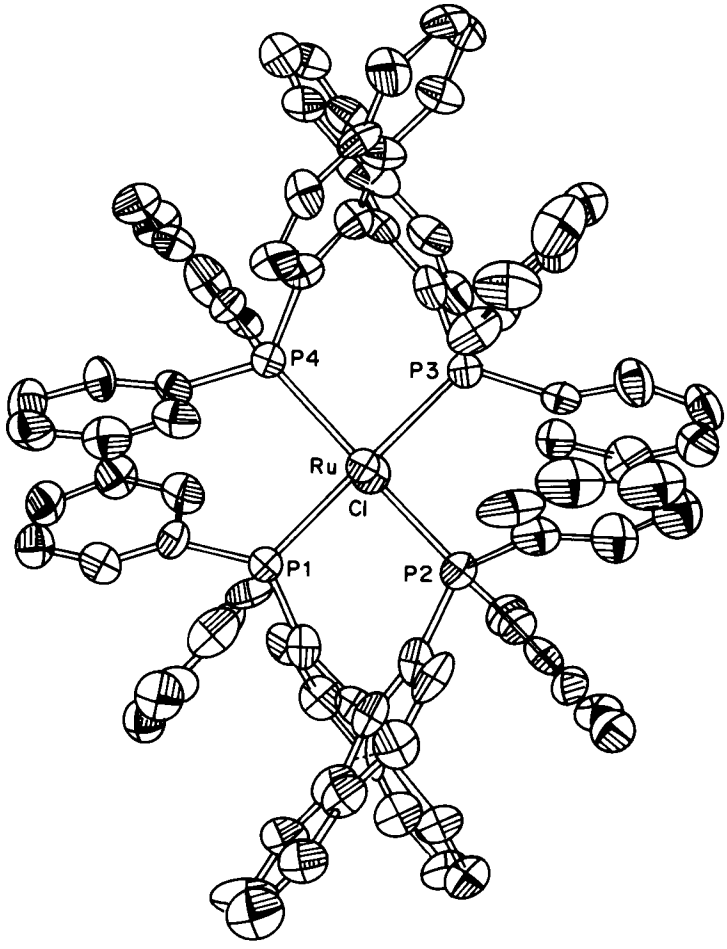
SCHEME 34

when the chelate backbone possesses equatorial substituents forcing the conformation towards a C_2 twist conformation, that in turn predisposes the *P*-aryl rings towards the C_2 edge-to-face array. Then the edge-on ring is always pseudoaxial and the face-on ring pseudoequatorial. For 1,4-diphosphines leading to a seven-ring chelate only diop or binap complexes give a C_2 conformation of the chelate ring giving the C_2 edge-face array of *P*-aryl rings. A molecular graphics analysis was performed by the authors to help to understand the relation between structure and reactivity in asymmetric hydrogenation. A combination of crystallographic data and molecular mechanics allowed them to analyse the origin of enantioselectivity in catalysis by rhodium complexes of chiraphos or analogues[187].

Even if X-ray crystallography is unable to explain fully the stereochemistry of catalytic reactions, it is a useful tool to see how the chiral ligand bonds to the metal. Thus ruthenium–binap complexes were investigated[180,188], because of the spectacular results given in asymmetric hydrogenation. An example is [RuHCl((*R*)-binap)$_2$] (**188**)[188]. This complex surprisingly gives opposite results to the rhodium–(*R*)-binap complexes in asymmetric hydrogenation of C=C bonds. However, the binap conformation is very similar in both complexes (compare with the structure of a Rh–binap complex in Scheme 34).

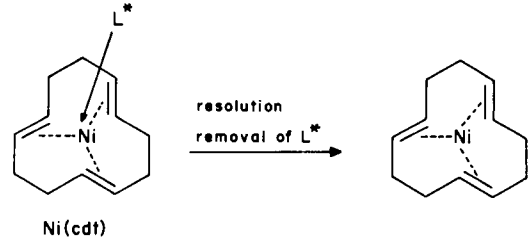
Nickel or palladium ferrocenylphosphines are useful catalysts for asymmetric catalysis, especially for asymmetric C—C bond formation [189] (as discussed above). In order to



(188) $RuHCl((R)\text{-binap})_2$

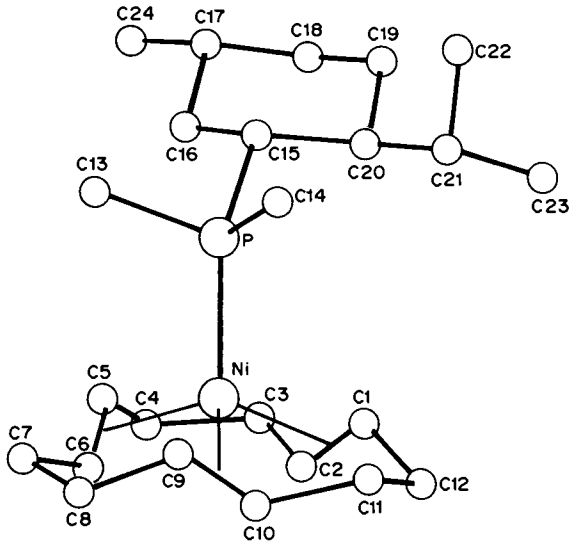
analyse ferrocenylphosphinepalladium-catalysed asymmetric allylation (Scheme 32)[176], the crystal structure of $[PdCl_2(bppfa)]$ was elucidated[190]. X-ray crystallography was also used to obtain some insight into catalytic reactions involving chiral monophosphines. A mechanism has been proposed to explain the asymmetric hydrovinylation reaction using a nickel dimenthylalkylphosphine[33]. One basis of this mechanism lies in the crystal structure of [Ni(η^3-1-methyl-2-butenyl)methyl(dimenthylmethylphosphine)].

Crystal structures of complexes with chiral phosphines as ligands are also useful for stereochemical studies. As an illustration two recent results are considered. Cyclododecatrienylnickel (0) was resolved by the use of menthyldimethylphosphine[165]. This remarkable chiral organometallic owes its chirality to the helicity of its conformation. The absolute configuration was established by X-ray structural analysis of complex (Scheme 35). The crystal structures of complexes are also useful for elucidating the steric course of



Ni(cdt)

L* = menthyldimethylphosphine



(165)Ni(cdt)((−)-menthyldimethylphosphine

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SCHEME 35

reactions around a metal when this is a chiral centre. Consiglio and Morandini[191] synthesized many chiral ruthenium complexes of the structure $[CpRuL_2R]$ (R = halide, H, Alkyl and L_2 = chelating diphosphine such as prophos, additional cycphos or phenphos). In these complexes ruthenium is an additional asymmetric centre. The sterechemistry of the chiral complexes was determined by X-ray diffraction, chiroptical methods and multinuclear NMR spectroscopy.

VIII. CONCLUSION

A wide variety of chiral phosphines are now available. There are many structural types of chiral phosphines, with a centre, axis or a plane of chirality. A computer-based literature survey of chiral phosphines has been made[10,16]. Chemical transformations of phosphines, either chiral at phosphorus or in a side-chain, are now well understood. Only a few data

could be found on the chiroptical properties of phosphines. The methods for measurement of enantiomeric excesses are multiple, permitting work on a small scale. Resolution of phosphines through complex formation between phosphine oxides and chiral acids seems to be a fairly general and simple procedure. However, most of the chiral phosphines are prepared by chemical transformations of optically active natural products available from the chiral pool. Phosphines, because of their unique bonding properties, are excellent ligands in many transition metal complexes. Coordination chemistry involving chiral phosphines has been greatly expanded because of the direct application to asymmetric catalysis. One can expect in the future to see the appearance of new generations of chiral phosphines, specially devised to fulfil the need for more stereoselective catalytic reactions.

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The Chemistry of Organophosphorus Compounds
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CHAPTER 4

Electrochemistry of organophosphorus(III) compounds

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I. INTRODUCTION

Ever since the discovery of the toxicity of organophosphorus compounds there has been immense interest in understanding the intermediates in the chemistry of that toxicity. This has led to a spate of investigations on these compounds using electrochemical techniques. The detailed exploration of this chemistry started only in the late 1960s when modern electrochemical techniques had started to invade the field. Further impetus for this study has grown from the use of the organophosphorus compounds (a) in warfare as paralysing agents (b) as fungicides and (c) as pesticides. Phosphorus in relation to its Group V partner nitrogen differs in the production of toxic compounds, nitrogen compounds being less toxic as their chemical reactivity is considerably weaker; this is further substantiated by phosphonium compounds discharging at more positive potentials than their nitrogen analogues as the phosphorus atom has the imate ability to expand its octet, making its reactivity higher. As a consequence, other electrode reactions tend to occur in the electrode–solution interface. The complex nature of electrode reactions such as C—P bond cleavage has limited the growth of this field, although the potential for developing reactive intermediates is higher.

Organophosphorus compounds are also biologically important. Phosphorylation thermodynamics and energy-transfer schemes might be helpful in manipulating new reaction schemes for creating biological potency. An exhaustive recent review[1] of the enthalpy, free energies and standard potentials of their reactions revealed the possibilities of developing such new schemes. Organophosphorus electrochemistry gained popularity after the establishment of physical techniques for the product identification, such as ESR, GC, TLC and NMR.

This chapter is intended to describe the work carried out on phosphorus(III) compounds, together with a few phosphorus(V) compounds, to indicate the differences in the reaction mechanisms arising from the different oxidation states; however, it does not attempt to discuss the vast amount of work that has been carried out on organophosphorus(V) compounds. The first part of the chapter discusses the value of electrochemical techniques for investigating reaction mechanisms, followed by extensive discussions of organophosphorus(III) compounds.

A. Electrochemical Techniques

The transient intermediates generated during an electro-organic process can be monitored only if the time window of the selected electrochemical technique allows the observation of the process. The reaction schemes postulated by using slow techniques such as controlled-potential coulometry cannot provide this information, as the time window for this technique is large; other techniques such as polarography and cyclic voltammetry allow the characterization of the transients. Electrochemical techniques provide a time window from several minutes down to 10^{-4} s. Hence the history of the complete evolution of the stable product can be successfully obtained by combining the results of all the three techniques[2-4]. Bard and Faulkner[3] gave an excellent introduction to electrochemical methods in their review.

1. Polarography

This technique, introduced by Heyrovsky, paved the way for the discovery of a host of other powerful electrochemical techniques. It employs a reproducible electrode surface area through the dropping mercury electrode in the electrochemical cell. This electrode is used as the working electrode; the counter electrode is either a pool of mercury of a large platinum mesh (100 times the area of the working electrode). The reference electrode

employed is a saturated calomel electrode (SCE). The electrodes are introduced into an electrochemical cell that contains the deaerated supporting electrolyte solution. The electrodes are connected to the polarographic instrument for varying the potential of the working electrode and for determining the resulting current. The current–voltage curve is S-shaped and can yield the characteristic half-wave potential and the diffusion-limited current[2]. The diffusion current is related to the number of electrons transferred in the electrochemical process:

$$i_d = 607nm^{2/3}t^{1/6}D^{1/2}C^* \quad (1)$$

where n is the number of electrons transferred at the electrode, m is the mass of mercury flowing through the capillary, t is the drop time, D is the diffusion coefficient of the molecule or ion and C^* is the bulk concentration of the species. The slope of the wave, defined by $E_{3/4} - E_{1/4}$ (referring to the potentials at three quarters and one quarter of the value of i_d, respectively), in a reversible one-electron reduction will equal 56 mV[3]. This criterion has been used in the analysis of the polarographic waves of several organophosphorus compounds to determine the number of electrons transferred at the electrode to attain the diffusion plateau. The time window of this technique is defined by the lifetime of the mercury drop, i.e. 2–3 s.

2. *Cyclic voltammetry*

Cyclic voltammetry employs a triangular sweep applied to the electrochemical cell. The electrodes generally employed are a stationary mercury or platinum working electrode, a large platinum counter electrode and a saturated calomel electrode. Unlike the case in polarography, where a constant renewal of the electrode area (dropping mercury electrode) results in the periodic destruction of the diffusion layer, here the continuous growth of the diffusion layer results in the current–voltage curve taking a peak-shaped pattern. The peak potential and peak current values are used as diagnostics of the process occurring at the electrode[3,5–7]. The chemical reactions following the charge transfer at the electrode can be well monitored and the kinetic constants can be evaluated. The stability of the electrochemical reduction product can be conveniently followed by this technique. By varying the sweep rate of the experiment, it is possible to evaluate the rate of the chemical reaction that is scavenging the electroactive product. In addition, the formation of new electroactive species by the scavenging reaction can be followed by this technique. The time window for this technique extends to a lower limit of 10^{-4} s; the upper limit of a few seconds is limited by the convection caused by density gradients. As a result, unstable free radicals formed during the electrode reaction can be detected by this technique.

3. *Controlled-potential electrolysis*

The evaluation of the number of electrons transferred in the overall reaction scheme and the large-scale preparation of the end product can be effected by using controlled-potential coulometry. A general treatment of a variety of cases encountered in electrochemical investigations may be found in the review by Bard and Santhanam[4]. As the time window of this technique ranges from a few seconds to several minutes, the knowledge gained by this technique can provide an insight into the intermediates in electrochemical reductions if the product is studied by a spectrophotometric or ESR technique.

II. AROMATIC PHOSPHINES

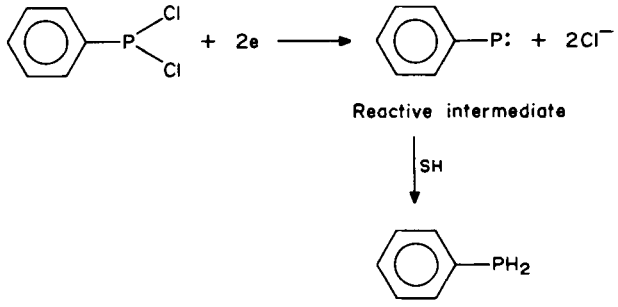
The early investigations on the polarographic reduction of Group V organocompounds started in 1954[8,9]. However, the mechanistic understanding did not develop

until about 1968; this development became possible through modernization of instrumentation.

Several substituted phosphines have been investigated[10-16] using electrochemical techniques; the initial investigations[13] were carried out polarographically, but did not give the complete mechanism. Hence faster techniques such as cyclic voltammetry were used in later investigations.

A. Monophenylphosphines

Phenylphosphorus dichloride was examined by polarography[10]; it undergoes reduction, consuming 2e with $E_{1/2} = -2.5$ V vs $Ag/AgClO_4$:



(2)

The charge transfer is irreversible as the reduction is followed by a cleavage reaction where SH represents the solvent (monoglyme). As a result of the fast cleavage, cyclic voltammetric examination did not exhibit a complementary anodic peak even at sweep rates of 100 V s^{-1}. Phenylphosphine reduction was not observed, suggesting that it is not reduced in the available potential range.

The mechanism indicated above operates with other organometallics containing arsenic, antimony and bismuth (i.e. $PhAsCl_2$, $PhSbCl_2$ and $PhBiCl_2$); the electrolytic method provides a method for preparing and studying the properties of the subvalent organometallics.

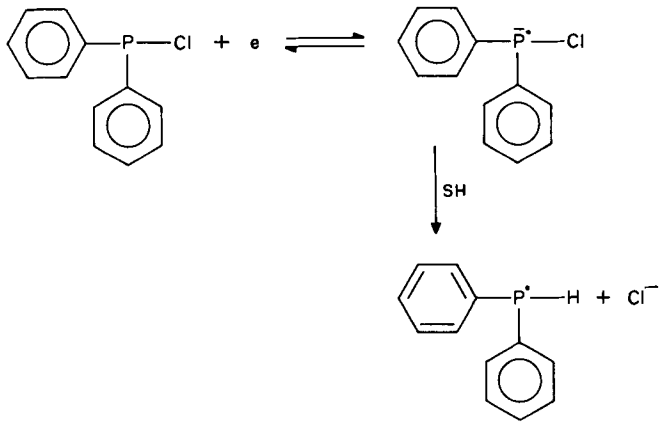
B. Diphenylphosphines

The electrochemical reduction of halogenated diphenylphosphine has been investigated[10]; the polarographic half-wave potential occurs at $E_{1/2} = -3.3$ V vs $Ag/AgClO_4$ in monoglyme. This reduction has also been examined using cyclic voltammetry; the complementary anodic peak was not observed even at a sweep rate of 100 V s^{-1}. The lifetime of the 1e reduction product is estimated at less than 10 ms. The reaction mechanism in equation 3 has been postulated for chlorodiphenylphosphine.

The electrochemical reduction of 1 occurs at 200 mV more positive than triphenylphosphine owing to reduced conjugation.

C. Triphenylphosphine

The electrochemistry of arylphosphines has received wider attention owing to the chemical reactivity of the 1e product. This had led to products of varying nature being formed, depending on the solvent employed in the electrochemical studies. The importance of the electrochemistry of arylphosphines arises from the fact that they are intermediates in the reduction of several phosphonium salts.



(3)

(1)

1. Polarography

Triphenylphosphine shows a characteristic wave with $E_{1/2} = -2.70$ V vs SCE. Figure 1 shows a typical polarogram of triphenylphosphine in dmf. On the basis of Tomes criterion for reversibility ($E_{1/4} - E_{3/4} = 56$ mV), it has been concluded that it undergoes a one-electron reversible or quasi-reversible transfer[11]. Assuming that the reduction of triphenylphosphine consumes 1e, the diffusion coefficient of triphenylphosphine is calculated to be 0.54×10^{-5} cm^2 s^{-1} at 25 °C.

2. Cyclic voltammetry

The stability of the 1e reduction product of triphenylphosphine has been followed by cyclic voltammetry[11]. The cyclic voltammetric curve of triphenylphosphine in dmf is shown in Figure 2. The cathodic peak appears at -2.75 V vs SCE and the complementary peak at -2.68 V. The 1e reduction product is stable, as shown by the peak current ratio, $i_{pa}/i_{pc} = 1.0$, where i_{pa} and i_{pc} are the anodic and cathodic peak currents, respectively.

Table 1 gives data for the cyclic voltammetric reduction of triphenylphosphine. The current function (proportional to $i_p/v^{1/2}$, v is the sweep rate) for the cathodic peak showed constancy with sweep rate, suggesting that the process is diffusion controlled. These observations were confirmed by later studies by Saveant and Binh[17], who investigated the electrochemical reduction of triphenylphosphine in hexamethylphosphoramide. In this medium, a slow catalytic process (see Figure 3) was observed, which was attributed to the regeneration of triphenylphosphine. This catalytic process was completely absent in dmf[11]. As a result, distinctly different products were obtained in large-scale controlled-potential electrolysis. This may have been caused by the presence of BF_4^- in the medium.

It has been demonstrated that triphenylphosphine is protonated in the presence of a proton donor; the protonated species undergoes a 4e reduction. As the protonated species is more difficult to reduce than the unprotonated species, the reduction occurs at $E_{pc} = -2.76$ V. The protonation scheme is represented as in equilibrium 4[11].

$$(C_6H_5)_3P + H^+ \rightleftharpoons (C_6H_5)_3PH^+ \tag{4}$$

This mechanism differs from the conventional protonation of the anion radical produced

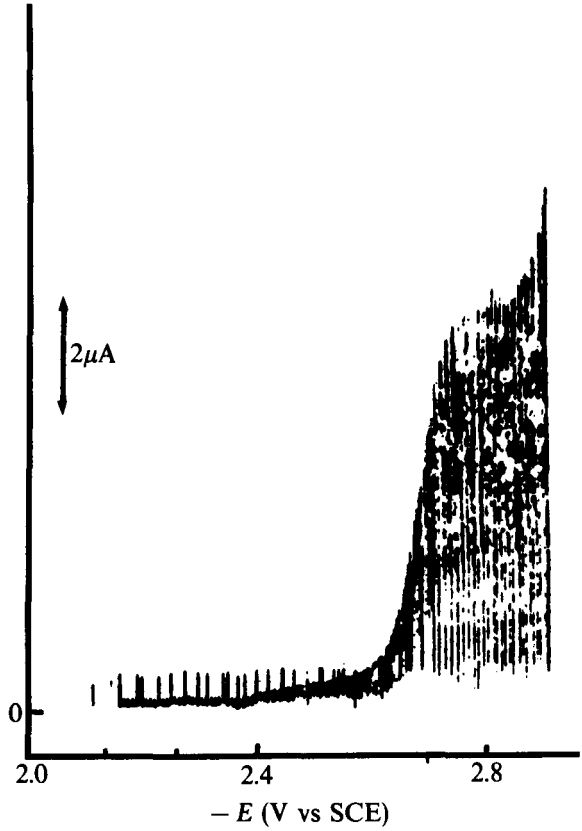


FIGURE 1. Polarogram for the reduction of triphenylphosphine. The solution contained 0.1 M tetrabutylammonium iodide and 2.38 mM triphenylphosphine in dmf. Reprinted with permission from Santhanam and Bard, *J. Am. Chem. Soc.*, **90**, 1118 (1968)[11]. Copyright 1968 American Chemical Society.

by the 1e reduction of aromatic hydrocarbons. This situation produces a shift of the cyclic voltammetric peak towards positive potentials.

3. Controlled-potential coulometry

Complexities in large-scale controlled-potential electrolysis develop when the polarographic plateau region is close to the background electrolysis. Thus, by conducting electrolysis at -2.80 V vs SCE with $(C_4H_9)_4NI$ as the supporting electrolyte, Santhanam and Bard[11] observed a catalytic process occurring during the electrolysis; as a result, the electrolysis current decreased to a steady-state value that was higher than the background current. The catalytic scheme obscures an unambiguous evaluation of the number of electrons consumed in the initial reduction. By using $(C_4H_9)_4NBF_4$ as the supporting electrolyte[17] in hexamethylphosphoramide, a similar catalytic process was also observed,

TABLE 1. Cyclic voltammetric data for reduction of triphenylphosphine

Sweep rate ($mV\,s^{-1}$)	i_{pc} (μA)	i_{pa}[a] (μA)	i_{pa}/i_{pc}[b]	E_{pc} (V vs SCE)	E_{pa} (V vs SCE)
		Without proton donor			
67.1	5.3	5.0	0.90	−2.75	−2.68[c]
153	7.8	9.0	0.97	−2.75	−2.68[c]
222	9.1	11.0	1.01	−2.75	−2.68[c]
312	11.2	12.9	0.99	−2.75	−2.68[c]
476	13.4	15.7	1.00	−2.76	−2.68[c]
712	15.6	18.4	1.06	−2.76	−2.66[c]
222	20.0	20.0	1.00	−2.75	−2.68[c]
		With proton donor			
222	86.0	—	—	−2.76	—[e]
222	142.0	—	—	−2.82	—[f]

[a]Estimated by using extrapolation of cathodic current as base line.
[b]Calculated using Nicholson's semiempirical method to obtain i_{pa}.
[c]The solution contained 0.1 M tetrabutylammonium iodide and 0.59 mM triphenylphosphine in dmf. The working electrode was a hanging mercury drop electrode and the auxiliary electrode was silver wire. Potentials vs SCE may include some uncompensated iR drop.
[d]The concentration of triphenylphosphine was 2.28 mM.
[e]The solution contained 2.28 mM triphenylphosphine and 0.014 M hydroquinone.
[f]The solution contained 2.28 mM triphenylphosphine and 0.03 M hydroquinone.

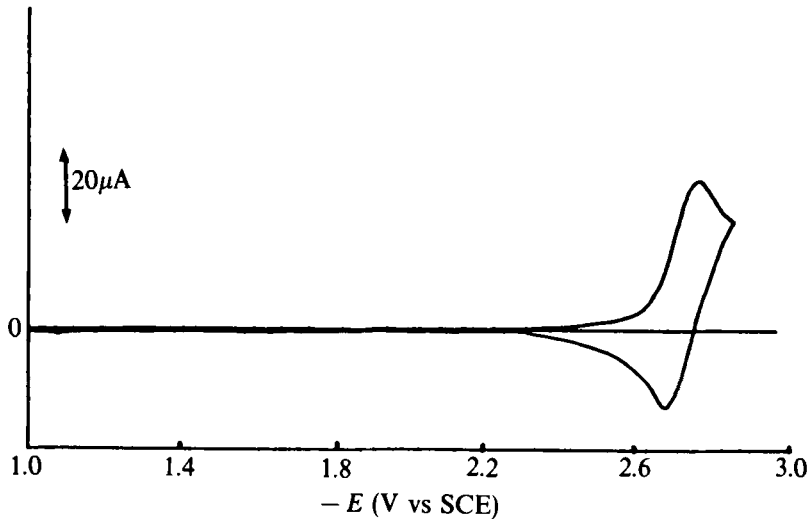


FIGURE 2. Typical cyclic voltammetric curve of 2.38 mM triphenylphosphine in dmf containing 0.1 M tetrabutylammonium iodide. Working electrode, hanging mercury drop electrode. Sweep rate for the experiment, 67.1 $mV\,s^{-1}$. Reprinted with permission from Santhanam and Bard, *J. Am. Chem. Soc.*, **90**, 1118 (1968)[11]. Copyright 1968 American Chemical Society.

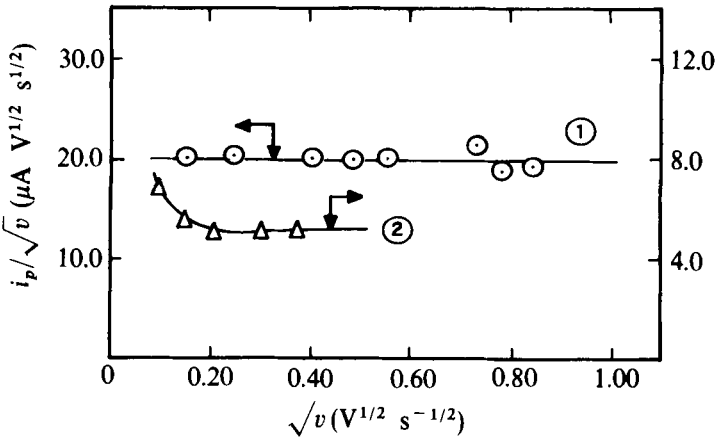
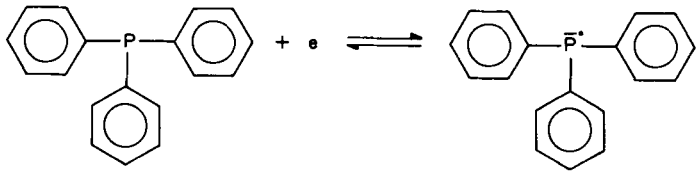


FIGURE 3. Plot of current function ($i_{pc}/v^{\frac{1}{2}}$) (i_{pc} = cathodic peak current, v = sweep rate) vs square root of sweep rate in (1) dmf and (2) hexamethylphosphoramide.

as indicated in Section II.C.2; the catalytic process is faster when $(C_4H_9)_4NBF_4$ is used as the supporting electrolyte. The suggested products of controlled-potential electrolysis vary from butyldiphenylphosphine, tributylamine and benzene to diphenylphosphinic acid and biphenyl[11].

4. Reaction mechanism

The first step in the electrochemical reduction of triphenylphosphine has been proved unequivocally[11] to be the formation of the free radical anion, as shown in equation 5.



(2) (3) (5)

As the radical anion **3** is unstable, it decomposes to give a variety of products, depending on the experimental conditions. Thus Britt and Kaiser[18] obtained the ESR spectrum shown in Figure 4, which has been attributed to the diphenylphosphine. The mechanism proposed for the chemical reduction (equations 6 and 7):

$$(C_6H_5)_3P + 2M \rightleftharpoons (C_6H_5)_2PM + C_6H_5M \quad (6)$$

$$(C_6H_5)_2PM + M \rightleftharpoons (C_6H_5)_2PM^- + M^+ \quad (7)$$

involves phenyl cleavage producing small amounts of biphenyl. The ESR spectrum is composed of hyperfine splittings arising from one P atom (two equal-intensity lines), one K atom (four equal-intensity lines) and the proton splittings from the protons present in two benzene rings. The coupling constants were determined as $a_o = a_p = 2.0$ G and

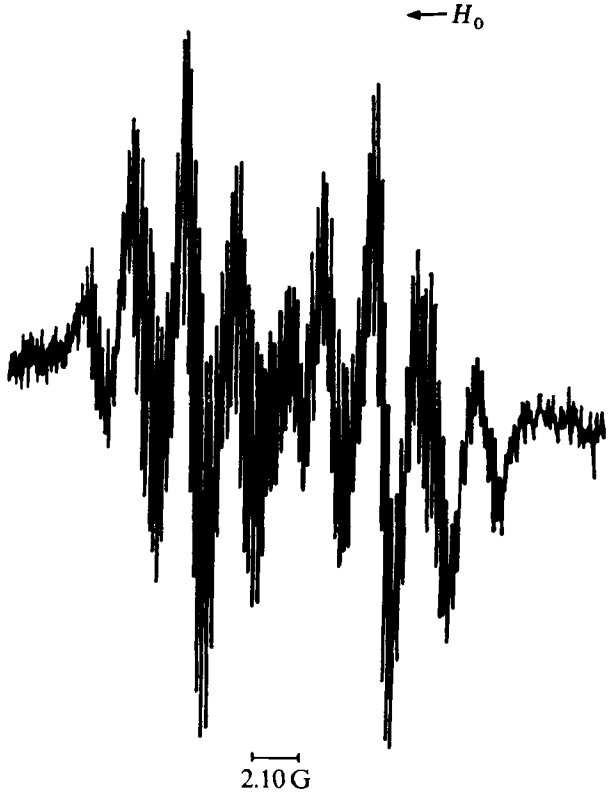


FIGURE 4. ESR spectrum of diphenylphosphine radical generated by chemical reduction. Reprinted with permission from Britt and Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965)[18]. Copyright 1965 American Chemical Society.

$a_m = 0.80$ G. The ESR spectrum showed two lines of equal intensity separated by 8.4 G, which were split into five lines separated by 2 G. The spectral features under high resolution showed 10–12 lines separated by about 0.2 G.

The instability of the free radical anion formed during the electrochemical reduction of triphenylphosphine has also been observed[15,19]; a fast-disappearing unresolved ESR spectrum was obtained. Consistent with this discussion is the observation of ESR signal corresponding to the biphenyl during the reduction of triphenylphosphine by sodium–potassium alloy in dimethoxyethane[19b].

The decomposition products of the free radical anion depend on the experimental conditions such as the water content in the medium, oxygen and the supporting electrolyte (equations 8–10).

$$(C_6H_5)_3P^- \underset{}{\overset{SH}{\rightleftharpoons}} (C_6H_5)_2PH + C_6H_5^{\cdot} + S^- \tag{8}$$

$$2C_6H_5^{\cdot} \longrightarrow C_6H_5{-}C_6H_5 \tag{9}$$

$$C_6H_5{-}C_6H_5 + e \longrightarrow C_6H_5{-}C_6H_5^- \tag{10}$$

TABLE 2. Half-wave potentials of fluorine-substituted triphenylphosphines[a]

compound	$-E_{1/2}$ (V)	$E_{3/4}-E_{1/4}$ (mV)
Tris(pentafluorophenyl)phosphine	1.68	110
Diphenyl(pentafluorophenyl)phosphine	1.88	95
Unsubstituted	2.70	62

[a]Medium: dmf containing $(C_4H_9)_4NI$. Taken from Ref. 20.

The mechanism in equations 8, 9 and 10, where SH = solvent, is in conformity with the observed ESR features[18,19a] and the electrochemical results[8,11]. Large quantities of butyldiphenylphosphine were also obtained in hexamethylphosphoramide (hmpa) which has a lower dielectric constant ($\varepsilon = 30$)[a] than dmf ($\varepsilon = 37$). The $C_6H_5^{\bullet}$ radical also undergoes hydrogen atom abstraction to give the hydrocarbon (equation 11):

$$C_6H_5^{\bullet} + SH \longrightarrow C_6H_6 + S^{\bullet} \tag{11}$$

with a possibility of

$$S^{\bullet} + e \longrightarrow S^{-} \tag{12}$$

and

$$S^{\bullet} + (C_6H_5)_3P^{-} \longrightarrow (C_6H_5)_3P + S^{-} \tag{13}$$

The reactivity of the triphenylphosphine anion radical with $(C_4H_9)_4N^{+}$ has also been observed in hmpa solvent[a]:

$$(C_6H_5)_3P^{-} + (C_4H_9)_4N^{+} \longrightarrow (C_4H_9)P(C_6H_5)_3 + N(C_4H_9)_3 \tag{14}$$

D. Substituted Triphenylphosphines

The effect of fluorine substitution on the electrochemical reduction of triphenylphosphine has also been investigated[20]. Tris(pentafluorophenyl)phosphine shows a polarographic wave with $E_{1/2} = -1.68$ V vs SCE in dmf. The wave is irreversible with a slope of 90–100 mV. The electrochemical reductions of the fluoro compounds are diffusion controlled. The half-wave potentials are given in Table 2.

The stability of the one-electron reduction wave of tris(pentafluorophenyl)phosphine has also been examined by cyclic voltammetry[20]. The lack of the complementary anodic peak for the wave suggested the reduction product was an unstable species. The cyclic voltammetric data obtained[20] are given in Table 3; the results strongly suggest that the process of electrochemical reduction is diffusion controlled. The cyclic voltammetric behaviour of diphenyl(pentafluorophenyl)phosphine compares well with that of tris(pentafluorophenyl)phosphine.

Controlled-potential coulometric analysis of the fluorine-substituted compounds revealed a process of decomposition of the anion radical with the elimination of fluorine[20]. This mechanism of fluorine elimination is characteristic of the reduction of several organic halides[20–26]; most of these reductions lead to the corresponding hydrocarbons.

[a]Hmpa is selectively adsorbed at the electrode, thus providing a layer of low proton activity near the electrode[32].

TABLE 3. Cyclic voltammetry of tris(pentafluorophenyl)phosphine[a]

Sweep rate ($mV\,s^{-1}$)	$-E_p$ (V)	$-E_{\frac{1}{2}}{}^{b}$ (V)	i_p (μA)	$i_p/v^{\frac{1}{2}}$ ($\mu a\,mV^{-\frac{1}{2}}\,s^{\frac{1}{2}}$)
14.0	1.70	1.65	2.4	21
33.8	1.72	1.66	3.5	19
72.2	1.73	1.68	4.1	18
123	1.74	1.68	6.1	18
203	1.75	1.70	8.0	18
430	1.77	1.71	11.0	17
657	1.79	1.72	14.0	17

[a]0.80 mM of tris(pentafluorophenyl)phosphine in dmf–0.1 M Bu_4NI solution. Area of the electrode, $4.14 \times 10^{-2}\,cm^2$. Taken from Ref. 20.

E. Catalytic Activity of Phosphines

The electrochemical behaviour of phosphine and substituted phosphines has been examined in aqueous medium[27–29] with special reference to catalytic hydrogen evolution. The phosphines are not electrochemically reducible in the aqueous medium. Carboxyalkylphosphines in buffered acid solutions is significantly influenced by the presence of cobalt(II) and cobalt(III) ions. Figure 5 shows the catalytic currents in the presence of various concentrations of $CoCl_2$. The catalytic currents increase with increasing cobalt ion concentration, as shown in Table 4.

The catalytic hydrogen wave is indicative of a diffusion-controlled reaction; it serves as a method for the ultramicro determination of cobalt ions and for the qualitative and

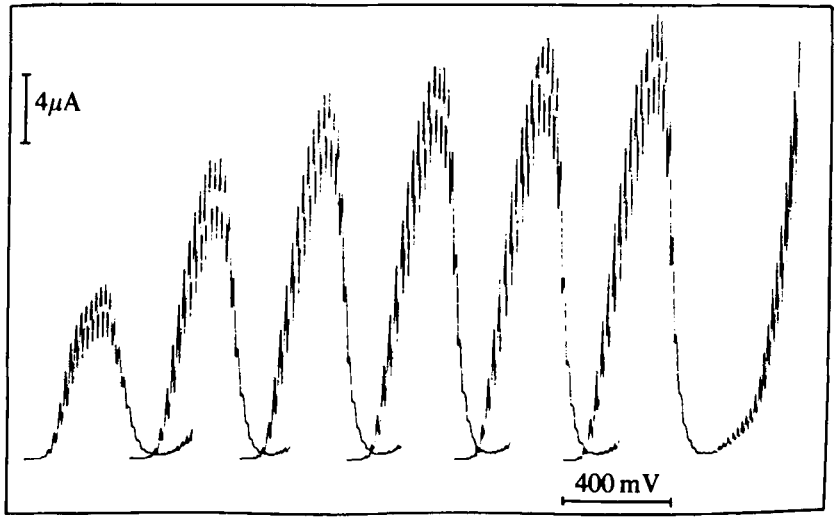


FIGURE 5. Catalytic currents observed in the presence of diphenylphosphinbenzoic acid [O-$P(C_6H_5)_2C_6H_4COOH = 2 \times 10^{-5}$ M] at various $CoCl_2$ concentrations: (a) 2.44×10^{-6}; (b) 4.76×10^{-6}; (c) 9.62×10^{-6}; (d) 1.18×10^{-5}; (e) 1.66×10^{-5} M. Solution pH = 5.5. Scan started at −0.90 V. Reproduced by permission of Elsevier Science Publishers from Ref. 28.

TABLE 4. Influence of cobalt(II) ion on the catalytic current of carboxyalkylphosphine[a]

Co^{2+} (M)	i_K/i_H	$-E_{\frac{1}{2}}$ (mV)	$i_K/i_{H^\bullet}$	$-E_{\frac{1}{2}}$ (mV)
0.088	0.204	1.29	0.573	1.29
0.177	0.366	1.28	0.815	1.29
0.263	0.505	1.28	0.93	1.27
0.350	0.725	1.28	0.96	1.02

[a]Concentration of $H_2PCH_2COOH = 1.78 \times 10^{-4}$ M; $[H^+] = 0.89$ mM. i_K/i_H represents the catalytic current in the presence and absence of Co^{2+}. $i_K/i_{H^\bullet}$ represents the catalytic current in the presence and absence of Co^{2+} containing 0.0022% gelatin. Reproduced by permission of Elsevier Science Publishers from Ref. 28.

quantitative determination of (a) RP(H)CH(R') COOH, where $R = C_6H_5$, C_6H_{11} or H and $R' = H$, CH_3 or C_2H_5, (b) $RP(H)(CH_2)_nCOOH$ where $R = C_6H_5$ or C_6H_{11}, (c) $C_6H_4PR_2COOH$ or $C_6H_4PHRCOOH$, where $R = C_6H_5$, and (d) R_3P, R_2PH, RPH_2 and PH_3, where $R = C_6H_5$.

Phosphorus compounds have a significant effect on the overpotential of hydrogen[28]; by coordination with the metal ion in solution, the overpotential of hydrogen at the mercury electrode is decreased[28].

Organophosphorus compounds show a pronounced inhibitiory effect on the electrochemical reduction of copper(II) and thallium(I)[27,28,30]. The polarograms of copper(II) in the presence of surface-active organophosphorus compounds of the type R^1R^2 and R^3PO, where R is an aromatic ring, show a kinetically controlled limiting minimum current[30].

III. ALIPHATIC PHOSPHINES

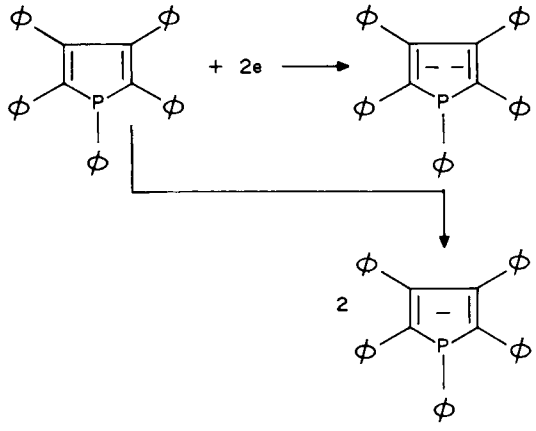
The aliphatic groups in tertiary phosphines are polarographically not reducible[16] and hence have not been investigated.

IV. RING PHOSPHORUS COMPOUNDS

A phosphorus-containing heterocyclic compound (substituted phosphole) has been investigated in detail by Dessy and coworkers[31] using cyclic voltammetry and ESR. Pentaphenylphosphole undergoes a 2e reduction in monoglyme with a half-wave potential at $E_{\frac{1}{2}} = -2.6$ V vs $Ag/AgClO_4$. On controlled-potential exhaustive electrolysis, the free radical anion is formed which exhibits a two-line ESR spectrum with $g = 2.0021$; the doublet has a phosphorus coupling constant of $a_p = 15$ G. The odd electron is localized in the five-membered ring with no hyperfine splitting generated from the phenyl protons. The phosphole anion radical is stable as the reverse electrolysis at the mercury pool (i.e. oxidation of the anion) produces phosphole quantitatively. The corresponding arsenic analogue also produces a blue anion radical but has a half-life of only 1 min. The postulated reduction mechanism[31] is given in equation 15 or 16.

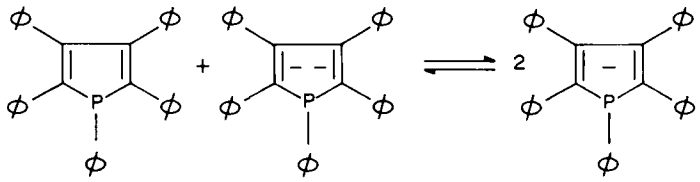
Phosphole differs from its nitrogen analogue in electron density distribution. Pyrrole is therefore not reducible polarographically in the available potential range[32]. However, pyrrole is easily oxidized in acetonitrile, producing a highly conducting polymer on the electrode surface[33-42].

The electrochemistry of pentaphenylphosphole has generated a model for the understanding of organometallics. While the organophosphorus metallics generally fall



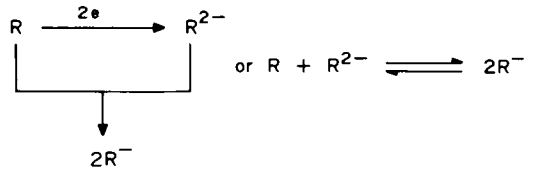
(15)

or alternatively



(16)

into the quadrivalent category, which is outside the scope of this review, it is briefly discussed here to show the contrast behaviour in comparison with trivalent phosphorus compounds. The general mechanism of the organometallic reduction is given in equation 17, in which R represents the organometallic (bridged bimetallic)[31].



(17)

The compounds listed in Table 5 follow the mechanistic scheme (equation 17) proposed for phosphole.

These compounds also give ESR signals with phosphorus splittings; the coupling constants are dependent on the nature of the species. Compound 1 shows a triplet spectrum with an intensity ratio of 1:2:1 and $a_p = 9$ G. Compound 2 gives $a_p = 20$ G, 3 gives $a_p = 13$ G, 4 gives $a_p = 15$ G and 9 gives $a_p = 7$ G. What is striking between the bridged bimetallics and phospholes is the stability of the reduced product and the chemical reversibility, i.e. the fact that the radical anion can be quantitatively oxidized to the parent by controlled-potential electrolysis in both categories. Deviations from this behaviour have been noticed with compounds 6 and 9; this has been attributed to the lack of metal–metal bonds in these compounds.

TABLE 5. Electrochemical behaviour of selected organometallics containing phosphorus

No.	Compound	$-E_{\frac{1}{2}}$ (V)	n	g
1	$[(\pi\text{-}C_5H_5)CoPPh_2]_2$	0.30	1	2.003
2	$[(NO_2)_2FePPh_2]_2$	1.70	1	1.937
3	$[Cr(CO)_4PMe_2]_2$	1.85	2	—
4	$[W(CO)_4PMe_2]_2$	1.90	2	1.994
5	$[C_6H_5MoPPh_2(CO)]_3$	Ill-defined		
6	$[Mn(CO)_4PPh_2]_2$	2.2		—
7	$[(\pi\text{-}C_6H_5)Fe(CO)PPh_2]_2$	0.20	1	1.977
8	$[(CO)_3FePMe_2]_2$	2.1	2	1.999
9	$[(CO)_3Ni \leftarrow PPh_2]_2$	2.4		—
10	$[(\pi\text{-}C_6H_5)NiPPh_2]_2$	2.3	1	2.060

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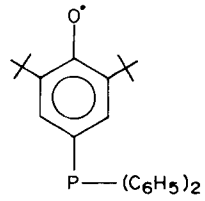
V. NITROAROMATIC PHOSPHORUS COMPOUNDS

Gulick and Geske[43] examined the spin density distribution in the radical **4** in comparison with the distribution in phenoxy radical. The phosphorus coupling constant in the radical ion of **4** is $a_p = 6.8$ G; this value in smaller than for the heteroaromatic phosphorus ($a_p = 14.7$–16.8 G). Muller *et al.*[44] considered a parallel increase in $a_{H(m)}$ and a_p when phosphorus is oxidized to the pentavalent state and attributed this to the positive (electrophilic) nature of the substituent. The question arises as to what extent the phosphorus-containing substituent has perturbed the spin density distribution in the phenoxy ring. The results indicated that $a_H = 1.6$ G in the phosphorus-substituted compound and $a_H = 1.8$ G in the phenoxy radical, indicating that the spin density is not grossly perturbed in the phosphorus-substituted compounds. A similar trend occurs in nitroaromatics substituted with phosphorus. A possible explanation is that the mechanism of transmission of the spin density to the phosphorus atom and further transmission to the phenyl rings may play a role; apparently these rings are twisted out of the plane in the above molecule. A remarkable support for the above argument has been obtained in the electrochemistry of nitroaromatic phosphorus compounds such as tris(*p*-nitrophenyl)phosphate[45,46].



(4)

The first unambiguous ESR spectra of phosphorus-containing free radicals were obtained by Muller and coworkers[47–49] and Lucken[50]. The derivatives of diphenyl(4-hydroxy-3,5-di-*tert*-butylphenyl)phosphine and phosphobetaines yielded ESR spectra giving ^{31}P hyperfine splittings. However, several phosphonohydrazines[45,46] do not yield the ^{31}P hyperfine splitting. Tris(nitrophenyl)phosphate on 2e electrochemical reduction yields a 4,4′-dinitrobiphenyl by cleavage of the oxygen–carbon bond. The

ESR spectrum arising out of this cleavage consists of a 16 G wide spectrum with $a_N = 2.69$ G, $a_H = 1.21$ G and $a_H = 0.21$ G. This analysis of carbon—oxygen cleavage is consistent with the results obtained with bis(nitrophenyl)phosphate, which exhibits an ESR spectrum with the coupling constants $a_N = 2.69$ G, $a_H = 1.21$ G and $a_H = 0.21$ G. The cyclic voltammetric peak potential of bis(nitrophenyl)phosphate is $E_p = -1.02$ V vs SCE and that of 4,4′-dinitrobiphenyl is $E_p = -1.04$ V vs SCE, and hence the cleaved product is reduced at the same potential. The mechanism proposed involves the cleavage of both nitrophenyl rings from each reduced molecule of bis(nitrophenyl)phosphate, which requires 3 Faradays per mole[46].

VI. GENERATION OF ORGANOPHOSPHORUS(III) COMPOUNDS VIA REDUCTIVE CLEAVAGE

The reductive cleavage of phosphorus(V) compounds generates electroactive phosphorus(III) compounds. The electrochemical behaviour of compounds of the type $(C_6H_5)_3P^+(CH_2)_nCN\ X^-$, where $n = 1$–4, has been studied[52–56]. When $n = 1$,

$$(C_6H_5)_3P^+CH_2CN \overset{2e}{\rightleftharpoons} (C_6H_5)_3P + (CH_2CN)^- \qquad (18)$$

(5) **(6)**

$$(CH_2CN)^- + (C_6H_5)_3P^+CH_2CN \rightleftharpoons (C_6H_5)_3P{=}CHCN + CH_3CN \qquad (19)$$

As a result of reductive cleavage, three polarographic waves are observed with $E_{\frac{1}{2}} = -1.48$, -2.68 and -2.56 V. The second wave is due to species **7** and the third to species **6**. Table 6 shows the observed characteristics of the phosphonium compounds. The formation of triphenylphosphine has been proved by controlled-potential electrolysis and product analysis[52].

The polarographic reductions of phosphonium salts are irreversible in comparison with the trivalent phosphorus compounds and the half-wave potentials depend on (a) the drop-time, (b) the concentration of the electroactive compound and (c) the temperature. An examination of about 60 phosphonium compounds reported in the literature[54] showed that only eight of them exihibit only one wave, the remainder showing multiple waves. The latter situation arises when organophosphorus(III) compounds are formed by reaction 20, in which R represents the substituent which varies from methyl to tri-*p*-tolyl or *p*-cumyl.

$$\begin{array}{ccccc} R_4P^+ & \xrightarrow{+e} & R_4P^{\cdot} & \xrightarrow{+e} & R_4P^- \\ & & \downarrow & & \\ & & R_3P + R^{\cdot} & \xrightarrow{+e} & R_3P + R^- \\ & & \downarrow & & \downarrow + H^+ \\ & & R_3P + \tfrac{1}{2}RR & & R_3P + RH \end{array} \qquad (20)$$

VII. P—O BOND FISSION

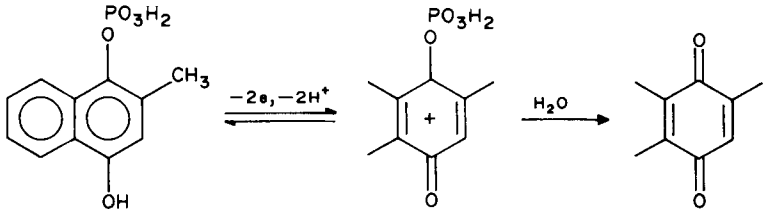
P—O bond fission plays a significant role in biological phosphorylation reactions. As an example, quinol phosphates have the potential to be used as phosphorylating agents in oxidative phosphorylation in biological systems. The oxidation proceeds via P—O bond fission; the oxidation produces a metaphosphate intermediate[57,58]. A general reaction sequence may be written as in equation 21.

Allen and Bond[59] generated semiquinone phosphate radicals by chemical oxidation.

TABLE 6. Polarographic data for the phosphonium compounds $(C_6H_5)_3P^+(CH_2)_nCN\,X^-$ in dmso (taken from Ref. 52)

n	Leaving group	X	$-E_{\frac{1}{2}}$ (V)[a]	Supporting electrolyte
1	$(C_6H_5)_3P$	Br	−1.48 −2.26 −2.56	Tetrabutylammonium Bromide
2	$(C_6H_5)_3P$	Tolyl	−1.74 −2.65	*p*-Toluenesulphonate
			−1.76 −2.70	Tetraheptylammonium iodide
3	$(C_6H_5)_3P$	Br	−1.80 −2.50	Tetrabutylammonium bromide
			−1.81 −2.52 −2.74	Tetraheptylammonium iodide
4	$(C_6H_5)_3P$	Br	−1.83 −2.50	Tetrabutylammonium bromide
			−1.84 −2.60 −2.77	Tetraheptylammonium iodide

[a]V vs SCE.



(21)

The electrochemical oxidation occurs at $E_p = 0.60$ V vs SCE (pH = 0.59), with the wave shifting by 60 mV per pH unit. It is not yet clear in the overall final conversion whether an organophosphorus(III) intermediate is formed as in the case of quaternary phosphonium salts described in Section VI.

VIII. ANODIC OXIDATION OF ORGANOPHOSPHORUS COMPOUNDS

The anodic behaviour of large numbers of tertiary phosphines, secondary phosphines and compounds containing P—P bonds has been studied voltammetrically and polarographically with a carbon paste electrode[60]. The half-wave potentials were related to the σ^* constant of the organic substituent for the biphosphines (see Table 7 and Figure 6).

IX. BASICITY OF PHOSPHORUS COMPOUNDS

Potentiometric titration of phosphines in nitromethane[61] has enabled the basicity of phosphorus compounds to be determined. Table 8 summarizes the pK_a values. A linear

TABLE 7. Electrochemical oxidation of tertiary phosphines in acetonitrile[a]

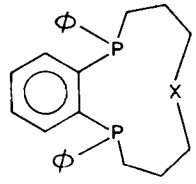
Compound	$E_{\frac{1}{2}}$ V	$E_{\frac{1}{2}}$[b] V
$(C_6H_5)_3P$	1.00	0.93
$(C_6H_5)_2PCH_2C_6H_5$	0.99	0.90
$(C_6H_5)_2PC_{10}H_7$	0.98	—
$(C_6H_5)_2PCH_3$	0.95	0.85
$(C_6H_5)P(C_2H_5)_2$	0.89	0.83
$(C_2H_5)_3P$	0.88	0.84
$(i\text{-}C_3H_7)_3P$	0.88	0.87
$(n\text{-}C_4H_9)_3P$	0.88	0.87
$(C_6H_5)_2PCH_2CH_2CH_2OH$	0.85	0.79
$(C_6H_5)P(CH_2CH_2CH_2OH)_2$	0.80	0.79
$C_6H_{11}P(CH_2CH_2CH_2OH)_2$	0.87	0.82
$n\text{-}C_8H_{17}P(CH_2CH_2CH_2OH)_2$	0.85	0.80
$C_6H_5CHCH_2C(O)C_6H_5$ | $P(C_6H_5)_2$	0.95	—
$C_6H_5CHCH_2C(O)C_6H_5$ | $P(C_6H_5)_2$	0.95	—
$(C_6H_5)_2PH$	0.99	—
$n\text{-}C_4H_9\text{-}C_6H_5PH$	0.91	—
$(C_2H_5)_2PH$	0.84	—
$(C_6H_5)_2PP(C_6H_5)_2$	0.91	—
$C_6H_5(C_6H_5CH{=}CH)PP$ | $(CH{=}CHC_6H_5)C_6H_5$	0.86	—
$C_6H_5(C_2H_5)PP(C_6H_5)C_2H_5$	0.84	—
$(C_2H_5)_2PP(C_2H_5)_2$	0.76	—
$(n\text{-}C_4H_9)_2PP(n\text{-}C_4H_9)_2$	0.73	—
$(i\text{-}C_3H_7)_2PP(i\text{-}C_3H_7)_2$	0.77	—
$(t.\text{-}C_4H_9)_2PP(t.\text{-}C_4H_9)_2$	0.68	—

[a]Supporting electrolyte, 0.1 M $NaClO_4$; working electrode, carbon paste.
[b]Medium, acetonitrile–water (1:1); supporting electrolyte, 0.1 M $NaClO_4$. Reproduced from Ref. 60 with permission of VEB J. A. Barth Verlag.

relation is observed between basicity constants in water and nitromethane; $pK_a(H_2O) = 0.76$, $pK_a(CH_3NO_2) = -2.82$.

X. PHOSPHINO MACROCYCLES

A series of metal tricarbonyl complexes of 11-membered tridentate macrocycles have been investigated[62,63]; these macrocycles have interesting redox properties. In a pioneering study, Fox *et al.*[62] synthesized tridentate coordinating ligands **8**.



X=NMe
X=S
X=Φ

(**8**)

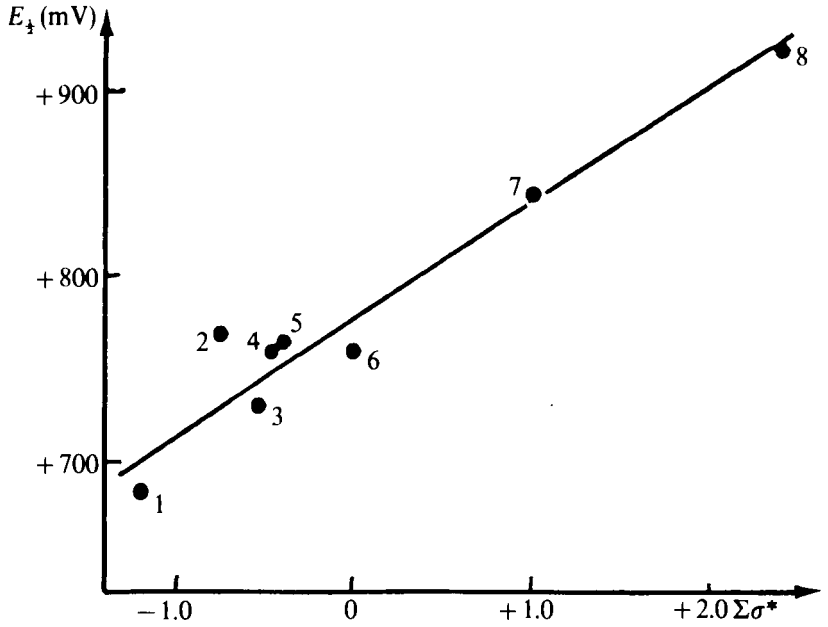


FIGURE 6. Plot of half-wave potential vs Hammet constant for a series of triphenylphosphine in acetonitrile. 1, $(t\text{-Bu})_4P_2$; 2, $(\text{i-Pr})_4P_2$; 3, $(n\text{-Bu})_4P_2$; 4, $(n\text{-Pr})_4P_2$; 5, Et_4P_2; 6, Me_4P_2; 7, $(PhEt)_2P_2$; 8, Ph_4P_2. Reproduced by permission of VEB J. A. Barth Verlag from Ref. 60.

TABLE 8. Basicity of organophosphorus compounds in nitromethane

Compound	pK_a
$(C_2H_5)_3P$	15.49
$(CH_3)_2PC_6H_5$	12.62
$(C_2H_5)_2PC_6H_5$	12.81
$(C_6H_5)_3P$	8.00

Electrochemical studies carried out in CH_2Cl_2 containing tetra-*n*-butylammonium perchlorate at $-78\,^{\circ}C$ revealed the features shown in Table 9. The cyclic voltammetric experiments were carried out with sweep rates ranging from 100 to 1000 mV s^{-1}. The reversibility of the cyclic voltammetric peaks disappeared when nucleophilic anions were present in the medium; one example is the absence of reversibility when tetra-*n*-butylammonium bromide was used as the electrolyte[62]. The phosphorus macrocycles produce the most easily oxidizable complexes, as can be seen from the Table 9.

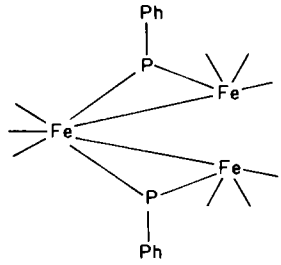
Transition metal clusters are another class of compounds where the electrochemical behaviour of organophosphorus(III) compounds is revealed. Electrochemical reduction of the triiron cluster $[Fe_3(PPh)_2(CO)_9]^-$ occurs reversibly with $E_{\frac{1}{2}} = -1.30$ V vs SCE by reaction 22. The anion is believed to have structure **9** or **10**.

$$[Fe_3(PPh)_2(CO)_9]^- \rightleftharpoons [Fe_3(PPh)_2(CO)_9]^{2-} \qquad (22)$$

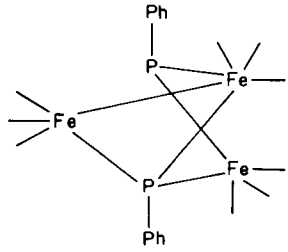
TABLE 9. Redox properties of metals coordinated by macrocycles[a]

	$M_0 \rightarrow M'$			$M' \rightarrow M''$		M → ligand oxidation	
Compound	E_{pa} (V)	E_{pc} (V)	W (mV)	E_{pa} (V)	W (mV)	E_{pa} (V)	W (mV)
(8-P_2NCr)	−0.22	−0.46	50	0.70	100	1.10	180
(8-P_2NMO)	+0.11	−0.15	70	0.80	205		
(8-P_2NW)	−0.09	−0.30	70	0.49	150	0.92	220

[a]Potentials are referred to quasi-reference Ag; its potential is 0.10 V vs SCE; medium, CH_2Cl_2; temperature of the experiment, −78 °C; the various electrochemical transitions are represented as $M_0 \rightarrow M' \rightarrow M''$; W = cyclic voltammetric peak width.



(9)



(10)

The anion radical in acetonitrile solution exhibits the spectrum shown in Figure 7. It can be electrochemically generated from $[Fe_3(PPh)_2(CO)_9]$ and has $E_{\frac{1}{2}} = -0.79$ V. A typical cyclic voltammetric curve is shown in Figure 8. The reactivity of the anion radical of $[Fe_3(PPh)_2(CO)_9]^-$ towards nucleophiles has been well demonstrated[63]. Thus reaction of $[Fe_3(PPh)_2(CO)_9]^-$ with various phosphorus-centred nucleophiles generates a series of anion radicals (reaction 23) having the open structure **11**.

$$[Fe_3(PPh)_2(CO)_9]^- + Et_3P \longrightarrow [Fe_3(PPh)_2(CO)_8PEt_3]^- + CO \qquad (23)$$

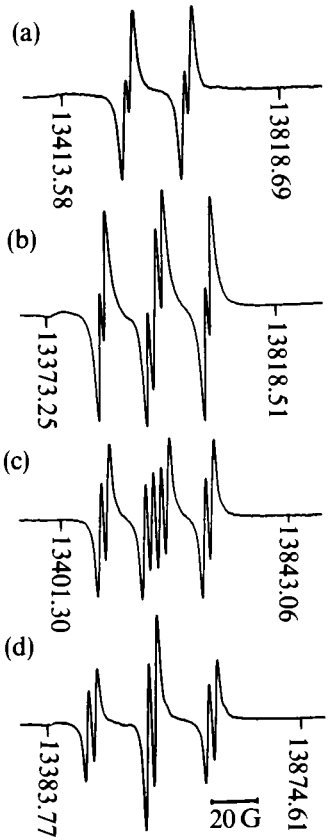
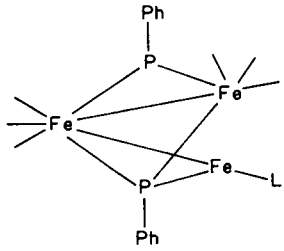


FIGURE 7. ESR spectra of the opened anion radicals $Fe_3(\mu_2\text{-PPh})(\mu_2\text{-PPh})(CO)_8L^-$ in acetonitrile at 25 °C. (a) L = CO; (b) L = PEt_3; (c) L = PPh_3; (d) L = $(O\text{-}i\text{-}Pr)_3$. Proton field markers in kHz. Reprinted with permission from Ohst and Kochi, *Inorg. Chem.*, **25**, 2066 (1986)[63]. Copyright 1986 American Chemical Society.



(11)

Similar reactions with triphenylphosphine and triisopropyl phosphite have been observed. The ESR spectra of the substituted open-structure anion radicals are also shown in Figure 7. The ^{31}P splitting of the triiron clusters is summarized in Table 10.

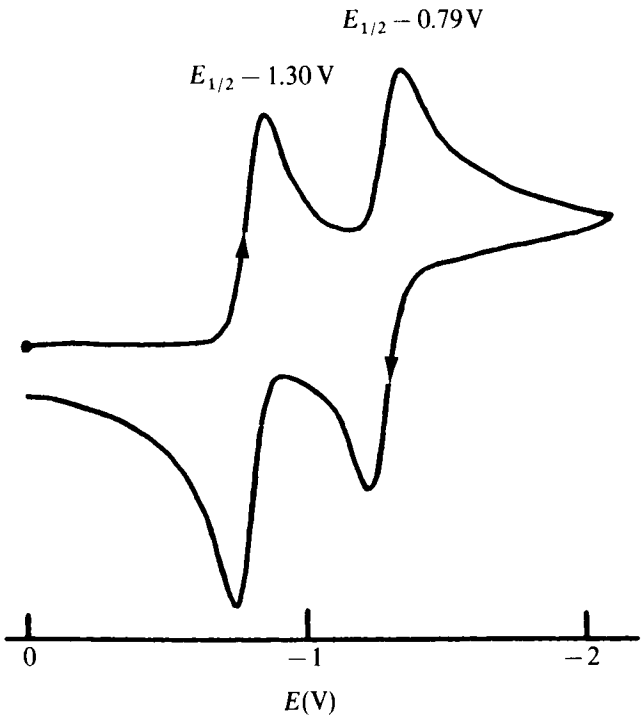


FIGURE 8. Cyclic voltammetric curve of $Fe_3(PPh)_2(CO)_9$ in thf containing 0.3 M tetra-*n*-butylammonium phosphate at 0.50 V s^{-1}. Reprinted with permission from Ohst and Kochi, *Inorg. Chem.*, **25**, 2066 (1986)[63]. Copyright 1986 American Chemical Society.

TABLE 10. ^{31}P splitting for the triiron clusters of $[Fe_3(CO)_8(\mu_3 - PPh)_2L]^{-a}$

	a_G(G)			
L	μ_3 – P	P(L)	g	ΔH_{PP}(G)
PEt_3	18.3	18.3	2.027	4.5
$P(OMe)_3$	17.8	36.0	2.023	6.5
PPh_3	17.5	79.5	2.021	4.0
$(PPh_2CH_2)_2$	12.0	81.0	2.020	3.5

[a] P(L) represents the phosphorus splitting of the ligand; ΔH_{PP} refers to the peak-to-peak line width; g = spectroscopic splitting factor.

XI. ACKNOWLEDGEMENT

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The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

CHAPTER 5

Thermochemistry of phosphorus(III) compounds

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I. INTRODUCTION

An excellent review of the thermochemical properties of phosphorus compounds was produced 25 years ago by Hartley *et al.*[1] and although since that time more experimental data have become available, many of their conclusions remain valid. Tabulations of thermochemical data for organophosphorus compounds have been given by Cox and Pilcher (1970)[2], Pedley and Rylance (1977)[3] and Pilcher and Skinner (1982)[4]. Data for inorganic phosphorus compounds have been listed in a Russian compilation of thermochemical data (1968)[5], by Head (1972)[6] and in the NBS Tables of Chemical Thermodynamic Properties (1982)[7]. Since these tables were produced there has been very little improvement in the quality and quantity of the thermochemical data for phosphorus compounds, and there are several good reasons for this situation. Organophosphorus compounds can be difficult to purify and to handle in air, and application of the classical methods for determining enthalpies of formation are the most difficult when phosphorus is present in the molecule. As successive measurements have been made, more of these difficulties have become apparent. Such problems have discouraged thermochemists from studying organophosphorus compounds when there are interesting problems in other areas requiring solution. It is hoped that a critical survey of the present position may

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encourage some experimenters who have the appropriate techniques available to consider seriously the value of presenting chemists with some reliable data in this area.

II. EXPERIMENTAL METHODS

A. Combustion Calorimetry

Measurement of the enthalpy of combustion is the basic method for determining the enthalpy of formation of an organic compound, but when phosphorus is present in the compound some major problems arise, the most serious of which are:

(i) the formation of phosphorus oxides and oxy acids in the surface layer of the burning sample tends to hinder the achievement of complete combustion; combustion experiments in 30 atm of oxygen unaccompanied by soot formation are rare and in fact some phosphorus derivatives have applications as flame retardants;
(ii) the combustion products can include a mixture of the various phosphorus oxy acids which will require analysis and gives rise to some uncertainties in thermal corrections;
(iii) the phosphorus oxy acids have large energies of dilution and because they can be deposited in various parts of the combustion bomb in differing concentrations, this will make difficult the precise definition of the final system in the bomb;
(iv) most of the usual materials used for crucibles are attacked by the products of the combustion reaction.

Investigators who have applied the combustion method have been aware of the difficulties and have made several attempts to overcome them. Long and Sackman[8] measured $\Delta_c H^\circ$ (Me_3P, l) and allowed the water added to the static-bomb to condense on the walls of the bomb prior to combustion in an attempt to obtain a phosphoric acid solution of uniform concentration. Neale *et al.*[9] placed 10 cm^3 of water in the bomb, a larger quantity than usual to achieve the same effect, and found that 93–96% of the phosphorus oxy acids was orthophosphoric acid and that the thermal correction to correspond to 100% H_3PO_4(aq.) was negligible. They also tested various crucible materials and found that silica, alumina, zirconia and nickel were attacked, but platinum did not seem to be chemically attacked although it developed cracks in its surface. Bedford and Mortimer[10] made careful analyses of the combustion products for several phosphorus compounds and found complete conversion to $H_3PO_4.nH_2O$(l); however, Nikolaev *et al.*[11] found 12–24% of pyrophosphoric acid in the combustion products, including those from one of the compounds studied by Bedford and Mortimer. The Russian workers also investigated crucible materials and found stainless steel, titanium, silica, porcelain and platinum to be unsatisfactory and corundum to be the least corroded. The above account makes clear some of the problems that must be overcome in order to study successfully organophosphorus compounds by the combustion method; those who have applied static-bomb calorimetry have done their best, but their results must be treated with caution.

The development of a rotating-bomb method is essential and the first such measurement was by Head and Lewis[12] of the enthalpy of formation of orthophosphoric acid. White phosphorus enclosed in a polyethylene ampoule was ignited on a gold dish in a gold-lined rotating bomb. Paper chromatographic methods were used to analyse the mixture of phosphorus oxy acids and, together with the orthophosphoric acid, 10% pyrophosphoric acid with 1% triphosphoric acid were found after rotation of the bomb during the combustion experiment; the bomb initially contained 10 cm^3 of water. The value obtained, $\Delta_f H^\circ(H_3PO_4 \text{ in } 40\ H_2O, \text{ l})/(\text{kJ mol}^{-1}) = -1295.4 \pm 1.0$, is completely convincing. Subsequently, Head and Harrop[13] measured the energy of combustion of triphenylphosphine oxide and found that with an initial bomb solution of 10 cm^3 of 60 mass-% $HClO_4$,

after rotation only orthophosphoric acid was present in the combustion products. The use of $HClO_4$(aq.) as the initial bomb solution complicates the experimental procedure, but this work showed that the rotating-bomb method has the potential for the satisfactory solution of the problems arising from the combustion of organophosphorus compounds. The method has so far been applied to only one organophosphorus(III) compound, triphenylphosphine[47].

B. Reaction-solution Calorimetry

Measurement of enthalpies of reaction in solution constitutes an important route to the determination of enthalpies of formation. In many cases, however, the results are not independent of combustion measurements, e.g. $\Delta_f H^\circ[(n\text{-Bu})_3\text{P, l}]$ can be derived from the enthalpy of the reaction

$$(n\text{-Bu})_3\text{P(l)} + \text{H}_2\text{O}_2\text{(l)} = (n\text{-Bu})_3\text{PO(c)} + \text{H}_2\text{O(l)} \quad (1)$$

$\Delta_r H^\circ/(\text{kJ mol}^{-1}) = -442.2 \pm 8.4$,[14] provided we accept $\Delta_f H^\circ[(n\text{-Bu})_3\text{PO, c}]/(\text{kJ mol}^{-1}) = -461.9 \pm 32.6$ derived from its enthalpy of combustion,[15] to be $\Delta_f H^\circ[(n\text{-Bu})_3\text{P, l}]/(\text{kJ mol}^{-1}) = -123.9 \pm 33.7$. Occasionally the inclusion of the combustion measurement is remote but its presence should not be overlooked, e.g. $\Delta_f H^\circ(\text{EtPCl}_2\text{, l})$ was derived from the enthalpy of the reaction[16]

$$\text{EtPCl}_2\text{(l)} + \text{SO}_2\text{Cl}_2\text{(l)} = \text{EtPOCl}_2\text{(l)} + \text{SOCl}_2\text{(l)} \quad (2)$$

but $\Delta_f H^\circ(\text{EtPOCl}_2\text{, l})$ was in turn derived from the enthalpy of the reaction[9]

$$\text{EtPOCl}_2\text{(l)} + 4\text{PhNH}_2\text{(l)} = 2\text{PhNH}_3\text{Cl(c)} + \text{EtPO(NHPh)}_2\text{(c)} \quad (3)$$

requiring $\Delta_f H^\circ[\text{EtPO(NHPh)}_2\text{, c}]$ obtained from its enthalpy of combustion[9]. In all such cases the uncertainty arising from the combustion measurements must be transferred to the result of the reaction-solution measurements and, unfortunately, for organophosphorus compounds this extends greatly the number of thermochemical data that must be regarded with suspicion.

There are, however, some organophosphorus compounds for which the enthalpies of formation derived from reaction-solution calorimetry are independent of combustion measurements, e.g. $\Delta_f H^\circ[(\text{MeO})_3\text{P, l}]$ was determined from the enthalpy of the reaction

$$\text{PCl}_3\text{(l)} + 3\text{MeOH(l)} + 3\text{PhNMe}_2\text{(l)} = (\text{MeO})_3\text{P(l)} + 3\text{PhNMe}_2\text{HCl(c)} \quad (4)$$

by Chernick *et al.*[17], $\Delta_r H^\circ/(\text{kJ mol}^{-1}) = -308.4 \pm 4.2$, giving $\Delta_f H^\circ[(\text{MeO})_3\text{P, l}]/(\text{kJ mol}^{-1}) = -741.0 \pm 4.6$, i.e. with a high precision.

By photoacoustic calorimetry, Burley *et al.*[18] determined $\Delta_f H^\circ[t\text{-BuOP}(n\text{-Bu})_2\text{, l}]$ from the enthalpy of reaction in solution:

$$t\text{-BuO}^\bullet + (n\text{-Bu})_3\text{P} = t\text{-BuOP}(n\text{-Bu})_2 + n\text{-Bu}^\bullet \quad (5)$$

A solution containing the photolabile substrate, di-*tert*-butyl peroxide, was irradiated by a pulsed laser. The reaction of the t-BuO$^\bullet$ radical with $(n\text{-Bu})_3\text{P}$ in solution deposited heat and the sudden deposition of this heat produced shock waves recorded by a piezoelectric transducer. The amplitude of the shock wave was proportional to the heat deposited and from the enthalpy of reaction $\Delta_f H^\circ[t\text{-BuOP}(n\text{-Bu})_2\text{, l}]/(\text{kJ mol}^{-1}) = -439.3 \pm 35.0$ was derived, where the large uncertainty arises from that in $\Delta_f H^\circ[(n\text{-Bu})_3\text{P, l}]$.

For most inorganic phosphorus(III) compounds, the experimental methods that have been used to determine $\Delta_f H^\circ$ are straightforward and require little comment. $\Delta_f H^\circ(\text{P}_4\text{O}_6\text{, c})$ was determined from its enthalpy of combustion in oxygen[19] and $\Delta_f H^\circ(\text{H}_3\text{PO}_3\text{, c})$ from the enthalpy of oxidation in solution using Br_2–H_2O to form H_3PO_4(aq.)[20]. $\Delta_f H^\circ(\text{PF}_3\text{, g})$ was determined from its enthalpy of combustion in fluorine[21]

to produce $PF_5(g)$ coupled with the enthalpy of combustion of phosphorus in fluorine[22] to produce also $PF_5(g)$. The enthalpies of formation of $PCl_3(l)$, $PBr_3(l)$[23] and $PI_3(c)$[24] were determined from their enthalpies of hydrolysis to produce phosphorus acid and the hydrogen halide acid. The determination of $\Delta_f H°(PH_3, g)$ and $\Delta_f H°(P_2H_4, g)$ by Gunn and Green[25] was remarkable both in respect of the elegance of the method used and in the accuracy of the final result. Stibine can be completely decomposed explosively and this explosion can be triggered by passing a current through a platinum wire suspended in the gas. Gunn and Green exploded mixtures of SbH_3 and PH_3 in a reaction vessel placed in a calorimeter. The decomposition of SbH_3 was complete but that for PH_3 was incomplete; the amount of PH_3 decomposed was determined from the total hydrogen produced and the vapour pressure of the condensable gas was shown to equal that for PH_3. From the enthalpy of decomposition, $\Delta_f H°(PH_3, g)/(kJ\,mol^{-1}) = 5.4 \pm 1.7$. From the photoionization measurements of Berkowitz *et al.*[26], the three successive dissociation energies of PH_3 were determined and the summation of these yields the enthalpy of atomization at 0 K:

$$PH_3(g, 0\,K) \rightarrow P(g, 0\,K) + 3H(g, 0\,K) \qquad (6)$$

from which $\Delta_f H°(PH_3, g, 0\,K)$ can be derived, giving $13.49 \pm 2.0\,kJ\,mol^{-1}$. This can be corrected to 298.15 K using the thermodynamic functions for PH_3 given by Stephenson and Giaque[27] to give $\Delta_f H°(PH_3, g)/(kJ\,mol^{-1}) = 5.5 \pm 2.0$, in precise agreement with the result of Gunn and Green[25].

C. Mass Spectrometric and Related Studies

Although calorimetry remains the main source of thermochemical data, non-calorimetric measurements have been making an increasing contribution, especially for species which are unstable or are not accessible in the quantities needed for calorimetric measurements. Studies of equilibria using the Knudsen cell are made more effective when the composition of the effusate is analysed by mass spectrometry. Binneweis[28] studied the reaction carried out inside a Knudsen cell, and made appearance potential measurements on the equilibrium gas mixture effusing from the cell and derived $\Delta_f H°(POCl, g)/(kJ\,mol^{-1}) = -215.1 \pm 5.0$. Similar measurements were made to derive $\Delta_f H°(POF, g)$[29].

$$POCl_3(g) + 2Ag(c) \rightleftharpoons POCl(g) + 2AgCl(c) \qquad (7)$$

Photoionization measurements of the appearance potentials of the fragment ions formed from PH_3[26] and from PF_3[30] have yielded the following successive dissociation energies, $D_0°/(kJ\,mol^{-1})$: $H_2P—H$, 345.0 ± 1.9; $HP—H$, 310.5 ± 8.4; $P—H$, 295.0 ± 8.4; $F_2P—F$, 550.9 ± 1.9; $FP—F$, 530.6 ± 41.5; and $P—F$ 443.8 ± 41.5. In the studies of PF_3, P_2F_4 was also studied and it was shown that $D_0°(F_2P—PF_2)/(kJ\,mol^{-1}) = 172.7 \pm 20.0$, almost double that for N_2F_4, $D_0°(F_2N—NF_2)/(kJ\,mol^{-1}) = 90.4 \pm 20.0$.

From electron impact measurements of appearance potentials of the fragment ions from P_2H_4 and H_3SiPH_2, Saalfeld and Svec[31] derived $D_0°(PH_2—PH_2)/(kJ\,mol^{-1}) = 310.00 \pm 15.0$, a value consistent with $D_0°(H_2P—H)$ and $\Delta_f H°_0(P_2H_4, g)$, and $D_0°(H_3Si—PH_2)/(kJ\,mol^{-1}) = 369.0 \pm 15.0$, from which $\Delta_f H°(SiH_3PH_2, g)/(kJ\,mol^{-1}) = 8 \pm 30$ was derived. Sandaval *et al.*[32], from the appearance potentials of ions produced by electron bombardment of PCl_3 and P_2Cl_4, derived $D_0°(Cl_2P—PCl_2)/(kJ\,mol^{-1}) = 243 \pm 20$. By assuming that $D(Cl_2P—Cl) = E(P—Cl)$, the mean bond energy in PCl_3, they derived a value for $\Delta_f H°(P_2Cl_4, g)$ but, as a similar assumption fails badly in the case of PH_3 and PF_3, this subsidiary deduction should be discounted.

III. ENTHALPIES OF FORMATION OF PHOSPHORUS(III) COMPOUNDS

Table 1 lists enthalpies of formation of organophosphorus(III) compounds in the condensed and gaseous states as determined by the experimental methods described in

TABLE 1. Enthalpies of formation of organophosphorus(III) compounds at 298.15 K in kJ mol^{-1}

Compound	$\Delta_f H°$(c/l)	$\Delta H°$(sub/vap)	$\Delta_f H°$(g)
Me_3P(l)	−129.1 ± 4.8 {8}	28.0 ± 2.1 {33}	−101.1 ± 5.2
Et_3P(l)	−89.2 ± 12.6 {34}	39.7 ± 2.1 {35}	−49.9 ± 12.8
(n-Bu)$_3$P(l)	−123.9 ± 33.8 {14}	[70 ± 8]	−54 ± 35
9-Phenyl-9-phosphafluorene:			
$C_{18}H_{13}P$(c)	183.9 ± 17.0 {36}	[87.9 ± 6.3] {36}	271.8 ± 18.1
Ph_3P(c)	207.0 ± 3.5 {47}	113.2 ± 3.0 {47}	320.2 ± 4.6
Pentaphenylphosphole:			
$C_{34}H_{25}P$(c)	388.9 ± 28.8 {36}		
(t-BuO)P(n-Bu)$_2$(l)	−439.3 ± 35.0 {18}		
(MeO)$_3$P(l)	−742.4 ± 4.6 {18}	36.8 ± 4.2 {9}	−705.6 ± 6.2
(EtO)$_3$P(l)	−855.2 ± 3.2 {17, 9}	41.8 ± 4.2 {9}	−813.4 ± 5.3
(i-PrO)$_3$P(l)	−979.7 ± 8.4 {9}	46.0 ± 4.2 {9}	−933.7 ± 9.4
(Et_2N)$_3$P(l)	−286.3 ± 9.6 {38}	60.7 ± 4.2 {38}	−225.6 ± 10.5
$EtCl_2P$(l)	−311.3 ± 14.6 {16}	[35 ± 6]	−276 ± 16
(Et_2N)PCl_2(l)	−345.7 ± 3.7 {39}	[42 ± 6]	−388 ± 7
(Et_2N)$_2PCl$(l)	−332.7 ± 6.6 {39}	[51 ± 8]	−282 ± 10

TABLE 2. Enthalpies of formation of inorganic phosphorus(III) compounds at 298.15 K

Compound	$\Delta_f H°$/(kJ mol^{-1})	Ref.	Compound	$\Delta_f H°$/(kJ mol^{-1})	Ref.
P(g)	316.2 ± 0.3	40	PCl_3(g)	−286.2 ± 2.4	23
P_2(g)	143.4 ± 0.5	40	PBr_3(l)	−183.9 ± 3.2	23
P_4(g)	58.8 ± 0.9	41	PBr_3(g)	−138.7 ± 5.0	7
P_4O_6(c)	−1640.1 ± [8.4]	19	PI_3(c)	−59.3 ± 2.5	24
P_4O_6(g)	−1571.1 ± [9.5]	19	PI_3(g)	4.7 ± 10.0	24
H_3PO_3(c)	−958.4 ± 1.8	20	P_2I_4(c)	−113.1 ± 5.0	24
PH_3(g)	5.4 ± 1.7	25	P_2I_4(g)	−39.1 ± 11.2	24
P_2H_4(g)	20.9 ± 4.2	25	POF(g)	−404.4 ± 3.0	29
PF_3(g)	−957.3 ± 1.3	21	POCl(g)	−215.1 ± 5.0	28
PF_2I(g)(0 K)	−595.4 ± 4.2	30	PB(c)	−115.5 ± 4.6	43
P_2F_4(g)	−1134 ± 30	30	PN(g)	172.0 ± 14.8	44
PCl_3(l)	−318.9 ± 1.9	23, 42	H_3SiPH_2(g)	7.5 ± 12.0	31

Section II. Estimated values are placed in square brackets, [ ], and the references are given in braces, { }.

Table 2 lists the enthalpies of formation of inorganic phosphorus(III) compounds.

IV. BOND STRENGTHS IN PHOSPHORUS(III) COMPOUNDS

Several different quantities are commonly used as measures of bond strengths, viz. bond dissociation energy, bond dissociation enthalpy, mean bond dissociation energy, mean bond dissociation enthalpy, bond energy and bond enthalpy. It is important not to confuse these quantities and unfortunately the symbolism available does not match the number of different quantities. It is generally true, however, that data assigned to 0 K refer to energies whereas data at 298.15 K refer to enthalpies.

The bond dissociation energy as derived from spectroscopic or mass spectroscopic techniques, D_0° correspond to $\Delta U°$(0 K) for the process

$$X_nMX(g) \longrightarrow X_nM(g) + X(g) \qquad (8)$$

The thermochemist usually deals with data at 298.15 K and the enthalpy of the corresponding dissociation (reaction 9)

$$X_nMX(g, 298.15\,K) \longrightarrow X_nM(g, 298.15\,K) + X(g, 298.15\,K) \quad (9)$$

is the bond dissociation enthalpy, which will differ from D_0° and from the bond dissociation energy at 298.15 K, which may be defined as

$$D_{298}^\circ = \Delta U_{298}^\circ = \Delta H_{298}^\circ - 298.15\,R \quad (10)$$

It is the common convention that at 298.15 K, enthalpies are derived and used with the symbol D.

For a gaseous polyatomic molecule MX_n, where X is an atom, the enthalpy of atomization,

$$MX_n(g) \longrightarrow M(g) + nX(g) \quad (11)$$

is

$$\Delta H_{atom}^\circ = \Delta_f H^\circ(M, g) + n\Delta_f H^\circ(X, g) - \Delta_f H^\circ(MX_n, g) \quad (12)$$

where the normal thermochemical convention has been followed by not specifying temperature for processes at 298.15 K. If the M—X bonds in MX_n are regarded as equivalent, then $\Delta H_{atom}^\circ/n$ measures the mean bond dissociation enthalpy, and for this special case where X is an atom, $\bar{D}(M—X) = E(M—X)$, the bond enthalpy. For MR_n, where R is a radical, for the disruption of this molecule,

$$MR_n(g) \longrightarrow M(g) + nR(g) \quad (13)$$

$\Delta H_{disrupt.}^\circ/n$ is the mean bond dissociation enthalpy, $\bar{D}(M—R)$.

ΔH_{atom}° for any molecule can be calculated from $\Delta_f H^\circ(g)$ and it is possible to distribute this enthalpy of atomization amongst the constituent bonds of the molecule to derive bond enthalpies, symbolized by $E(M—X)$. The $E(M—X)$ values will depend on the distribution rules of the scheme adopted in apportioning ΔH_{atom}° amongst the various bonds. For organic compounds there are many data for compounds containing the same types of bond, hence the distribution schemes can be elaborate[2] and can be used confidently to predict unknown enthalpies of formation. For organophosphorus(III) compounds, it is apparent that the available thermochemical data are limited with respect to both quantity and quality so that derivation of a bond enthalpy scheme becomes problematic.

It is desirable to attempt some tests on the results for consistency, but because of the small number of data only a few internal examinations are possible. The enthalpies of the following gaseous redistribution reactions can be calculated:

	$\Delta_r H^\circ$/(kJ mol^{-1})
$1/3PCl_3 + 2/3P(NEt_2)_3 \rightleftharpoons (Et_2N)_2PCl$	-35.9 ± 12.2
$2/3PCl_3 + 1/3P(NEt_2)_3 \rightleftharpoons (Et_2N)PCl_2$	-121.5 ± 12.2
$2/3PCl_3 + 1/3PEt_3 \rightleftharpoons EtPCl_2$	-68.2 ± 16.6

If bond enthalpies were constant and transferable, then it would be expected that the enthalpies of these redistribution reactions would be zero. It is the general experience in organic thermochemistry, however, that the enthalpies of such redistribution reactions are not zero, hence the question arises as to whether the above values are reasonable. A comparison can be made with the following redistributions taken from organic thermochemistry[2]:

	$\Delta_r H^\circ$/(kJ mol^{-1})
$1/4CMe_4 + 3/4CCl_4 \rightleftharpoons MeCCl_3$	-23.4 ± 5.0
$1/2CMe_4 + 1/2CCl_4 \rightleftharpoons Me_2CCl_2$	-36.0 ± 13.3
$3/4CMe_4 + 1/4CCl_4 \rightleftharpoons Me_3CCl$	-30.1 ± 2.9

TABLE 3. Mean bond dissociation enthalpies in PR_3 molecules

Molecule	D(P—R)/(kJ mol^{-1})	$\Delta_f H°$(R, g)/(kJ mol^{-1})	Ref.
PH_3	323.4 ± 0.6	218.00 ± 0.01	45
PF_3	505.7 ± 0.5	79.39 ± 0.30	45
PCl_3	324.1 ± 0.6	121.30 ± 0.01	45
PBr_3	265.3 ± 1.7	111.86 ± 0.12	45
PI_3	210.6 ± 3.5	106.76 ± 0.04	45
PMe_3	285.4 ± 1.8	146.3 ± 0.6	46
PEt_3	230.1 ± 6.1	108.2 ± 4.3	46
P(*n*-Bu)$_3$	194.4 ± 14.1	71 ± 8	46
PPh_3	325.8 ± 6.2	325.1 ± 4.3	46
$P(OMe)_3$	358.6 ± 8.3	18 ± 8	46
$P(OEt)_3$	359.5 ± 8.2	−17 ± 8	46
P(O-*i*-Pr)$_3$	364.6 ± 8.6	−52 ± 8	46

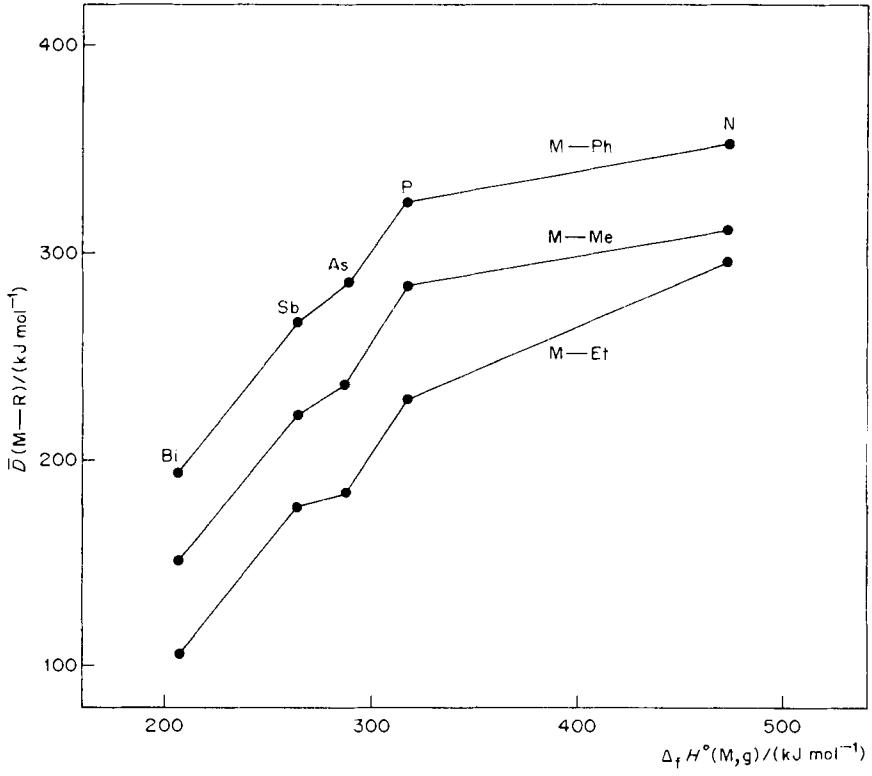

FIGURE 1.

This comparison suggests that the last two of the phosphorus(III) redistribution reactions have improbably high enthalpies, but more data are required before convincing tests of internal consistency can be made, and one is therefore directed towards external tests for consistency.

Table 3 lists the mean bond dissociation enthalpies, $\bar{D}$(P—R), that can be derived from the data given in Tables 1 and 2, together with the enthalpies of formation of R(g).

Pilcher and Skinner[4] showed that plots of $\bar{D}$(M—R) versus $\Delta_f H°$(M, g) for the elements in a particular group display a reasonably linear relationship. The $\bar{D}$(P—R) values for PMe_3, PEt_3 and PPh_3 are compared in this way with the corresponding values for the other Group V elements in Figure 1. It is apparent that the values fall into a sensible pattern, giving some confidence in the thermochemical data for these particular organophosphorus(III) compounds.

The phosphorus—phosphorus bond enthalpy, E(P—P), can be derived for several of these species. For P_4 it can be taken as one sixth of the enthalpy of atomization. For P_2X_4 it can be derived from the enthalpy of atomization:

$$P_2X_4(g) = 2P(g) + 4X(g) \tag{14}$$

$$\Delta H°_{atom} = 2\Delta_f H°(P, g) + 4\Delta_f H°(X, g) - \Delta_f H°(P_2X_4, g)$$

$$= 4E(P—X) + E(P—P) \tag{15}$$

To derive E(P—P), a value for E(P—X) must be chosen; this can be equated with $\bar{D}$(P—X) in PX_3. The values derived in this manner are listed in Table 4.

The data in Table 4 look surprising but, before considering the implications, it is useful to compare them with the corresponding data for nitrogen compounds, as was done by Berkowitz *et al.*[26] (Table 5). The D values are unambiguous quantities whereas the E values depend on the assumption that the transfer of E(M—X) in MX_3 to M_2X_4 is sensible.

TABLE 4. E(P—P)/(kJ mol^{-1})

Molecule	$\Delta H°_{atom}$	E(P—X)	E(P—P)
P_4	1206.0 ± 1.5		201.0 ± 0.3
P_2H_4	1483.5 ± 1.8	323.4 ± 0.6	189.9 ± 3.0
P_2F_4	2084.0 ± 30.0	507.5 ± 0.5	61.2 ± 30.0
P_2I_4	1098.5 ± 11.2	210.6 ± 3.5	256.1 ± 17.9
P_2			489.0 ± 0.8[a]

[a] E(P≡P)

TABLE 5. Comparison of thermochemical data for nitrogen and phosphorus compounds

Compound	$D°_0$(N—N)/(kJ mol^{-1})	E(N—N)/(kJ mol^{-1})
N_2H_4	273.2 ± 10.0	158.3 ± 4.2
N_2F_4	90.4 ± 20.0	156.0 ± 8.2
	$D°_0$(P—P/(kJ mol^{-1})	E(P—P)/(kJ mol^{-1})
P_2H_4	310.0 ± 15.0	189.9 ± 4.8
P_2F_4	172.2 ± 3.0	61.2 ± 30.0

The successive dissociation energies $D(X_2M—X)$, $D(XM—X)$ and $D(M—X)$ decrease in PF_3, PH_3 and in NH_3 whereas in NF_3 they increase. Moreover, for all the corresponding cases, $D(N—H) > D(P—H)$ but $D(N—F) < D(P—F)$. Clearly, P—F bonds have a higher ionicity than N—F bonds and the degree of ionic character will depend on the environment of the bond. Hence transfer of the bond energy $E(P—F)$ from PF_3 to P_2F_4 does not seem justified, and this may also be the case for NF_3 and N_2F_4, so that the agreement of $E(N—N)$ in N_2H_4 and N_2F_4 may be fortuitous.

V. CONCLUSIONS

It is apparent that there are insufficient thermochemical data of reliable quality for phosphorus(III) compounds to produce a table of bond energies that could be used for the prediction of unknown enthalpies of formation. If such a table were to be presented it would be misleading, especially because of the variation of $E(P—X)$ depending on the environment of the bond in the molecule. Such effects can be taken into account in modern bond-energy schemes for organic molecules[2], but to apply such schemes to organophosphorus compounds, the number of parameters required will exceed the number of primary thermochemical data at present available.

To advance this topic, most of the data presented in Table 1 should be remeasured using the most reliable techniques available; for the combustion measurements a gold-lined rotating-bomb method should be employed. Because such measurements are difficult and tedious, care should be taken in the selection of further compounds for study so that useful bond-energy schemes can be developed.

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The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

CHAPTER **6**

ESR spectra of free radicals derived from phosphines

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I. INTRODUCTION

Because of the multiple valencies available to phosphorus and the variety of groups that can be attached to it, the potential number of phosphorus-centred free radicals that may be envisaged is considerable. A number of reviews devoted primarily to the chemistry of these radicals with mention of their ESR features have appeared[1-12], in addition to two compilations of their ESR parameters covering the literature up to 1987[13,14].

Strictly, three classes of phosphorus-centred radicals can be considered to be derived directly from phosphines, Y_3P:

$Y_3P^{-\cdot}$ (1) $Y_3P^{+\cdot}$ (2) $Y_2P^{\cdot}$ (3)

Electron capture leads to the corresponding radical anion $Y_3P^{-\cdot}$ (**1**), while removal of an electron from the phosphorus lone pair leads to the corresponding radical cation $Y_3P^{+\cdot}$ (**2**). On the other hand, P—Y bond breaking either from Y_3P or the corresponding ion radicals can generate phosphinyl radicals, $Y_2P^{\cdot}$:

$$Y_3P \longrightarrow Y_2P^{\cdot} + Y^{\cdot} \quad (1)$$

$$Y_3P^{+\cdot} \longrightarrow Y_2P^{\cdot} + Y^{+} \quad (2)$$

$$Y_3P^{-\cdot} \longrightarrow Y_2P^{\cdot} + Y^{-} \quad (3)$$

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Information on both the geometry and the electronic structure of (**1**), (**2**) and (**3**) can be derived from their ESR spectra recorded either in solution or in the solid state. A selection of the most significant ESR studies devoted to these species are reviewed in the following pages. Only species having the odd electron centred primarily on phosphorus are considered. The coverage of the literature is up to 1988 and, because the coverage is not exhaustive, certain important contributions may have been omitted arbitrarily.

II. PHOSPHONIUMYL RADICALS, $Y_3P^{+\bullet}$, AND RELATED SPECIES

Formally cation radicals $Y_3P^{+\bullet}$ should be generated from the corresponding phosphonium ions Y_3PH^+ by hydrogen abstraction and thus 'phosphoniumyl' appears to be the most appropriate generic term for these cationic species.

A. Generation

A satisfactory general procedure for preparing matrix-isolated phosphoniumyl radicals involves exposure of dilute solutions of the parent phosphines in solvents such as dichloromethane, Freon ($CFCl_3$), sulphuric acid or sulphur hexafloride to ionizing radiation (^{60}Co γ-rays) at 77 K or lower[15–23]:

$$Y_3P \xrightarrow[^{60}Co\ \gamma\text{-rays}]{CFCl_3,\ 77\,K} Y_3P^{+\bullet} \qquad (4)$$

X-irradiation at room temperature of single crystals of triphenylphosphinetrichloroborane and triphenylphosphinetrifluoroborane was reported[24] to generate $Ph_3P^{+\bullet}$ radicals which, because of matrix effects, exhibit different phosphorus coupling (Table 1).

TABLE 1. ESR parameters (G) for matrix-isolated phosphoniumyl

Radical	$A_\parallel$	$A_\perp$	A_p^{iso}	B	g_{av}	p/s[a]	α^0
$H_3P^{+\bullet}$[19]	706	423	517	94	2.007	6.67	14.32
$Me_3P^{+\bullet}$[16]	584	285	385[b]	100	2.006	9.39	12.38
$nBu_3P^{+\bullet}$[16]	529	247	341	94	2.003	10.0	12.03
$Me_2(Ph)P^{+\bullet}$[20]	524	254	344	90	2.007	9.54	12.28
$Me(Ph)_2P^{+\bullet}$[20]	504	244	331	87	2.006	9.50	12.31
$Ph_3P^{+\bullet}$[20,c]	439	214	289	75	—	9.42	12.35
$Ph_3P^{+\bullet}$[20,d]	460	230	306	77	2.006	9.09	12.55
$Ph_3P^{+\bullet}$[24,e]	499	265	343	78	2.004	8.25	13.08
$Ph(Mes)_2P^{+\bullet}$[25]	432[i]	188	269	81	2.004	10.97	11.55
$Xyl_3P^{+\bullet}$[26,f]	411[j]	170	250	80	2.004	11.64	11.24
$Mes_3P^{+\bullet}$[26]	402[j]	171	248	77	2.005	11.26	11.41
$Mes_3P^{+\bullet}$[24,g]	405[i]	159	241	82	2.006	12.35	10.94
$Dur_3P^{+\bullet}$[26,h]	407[i]	150	236	86	2.004	13.17	10.62

[a]Spin densities in 3s and 3p orbitals of phosphorus calculated using $A_0 = 4748$ G and $B_0 = 131$ G, respectively[27], and taking the signs of the ^{31}P hfs tensor components as positive.
[b]11.5 G (9H).
[c]In H_2SO_4.
[d]In CCl_4.
[e]X-irradiation of single crystals of triphenylphosphinetrifluoroborane. X-irradiation of single crystals of triphenylphosphinetrichloroborane yielded $A^{iso} = 396$ G, $g_{av} = 2.004$.
[f]Xyl = xylyl
[g]Mes = mesityl.
[h]Dur = duryl.
[i]In $CFCl_3$.
[j]In *n*-PrCN.

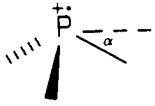

FIGURE 1. Deviation from planarity, α, for phosphoniumyl radicals.

The ESR parameters of a series of matrix isolated phosphoniumyl radicals are given in Table 1. Also given in Table 1 are the corresponding *p/s* ratio used to estimate deviations from planarity (α) for the radicals (Figure 1).

Attempts have also been made to record the liquid-phase ESR spectra of phosphoniumyl radicals generated within the cavity of an ESR spectrometer[28–31]. The radicals were produced by *in situ* electrochemical oxidation of a variety of phosphines in absence of nucleophilic counter ions. However, except for some very crowded triarylphosphines[28–30], only the corresponding dimeric cation radicals were observed[31] (equations 5 and 6)

$$Ar_3P \xrightarrow[AR = \text{mesityl, duryl, xylyl}]{-e} Ar_3P^{+\cdot} \tag{5}$$

$$2Ar_3P \xrightarrow[Ar = \text{phenyl}]{-e} Ar_3PPAr_3^{+\cdot} \tag{6}$$

Electrochemical oxidation of crowded tetraaryldiphosphines and cyclopolyphosphanes also provided a means of generating the ensuing cation radicals and to detect their ESR spectra[14,28,32]. The ESR parameters of different cation radicals obtained by electrochemical oxidation of phosphines, diphosphines and cyclopolyphosphanes are given in Table 2.

TABLE 2. Liquid-phase ESR parameters (G) for the cation radicals of different phosphines, diphosphines and cyclopolyphosphanes

Radical	A^{iso}(G)	*g*	*T*(K)
$Ph(Mes)_2P^{+\cdot}$[33]	279	2.0041	293
$Ph(Dur)_2P^{+\cdot}$[30]	264	2.0050	291
$Xyl_3P^{+\cdot}$[29,a]	244	2.0052	288
$pMeOXyl_3P^{+\cdot}$[26]	238	2.0052	253
$Mes_3P^{+\cdot}$[29,b]	240	2.0052	293
$Dur_3P^{+\cdot}$[30,c]	237	2.0052	293
$(Xyl_2P)_2^{+\cdot}$[29]	171(2P)	2.0060	291
$(p\text{-}MeOXyl_2P)_2^{+\cdot}$[26]	163(2P)	2.0060	291
$(Mes_2P)_2^{+\cdot}$[29]	170(2P)	2.0063	290
$(i\text{-}Dur_2P)_2^{+\cdot}$[26]	168(2P)	2.0060	282
$(2,4,6\text{-}triEtPh_2P)_2^{+\cdot}$[29]	175(2P)	2.0061	293
$(t\text{-}BuP)_4^{+\cdot}$[14]	63(4P)	2.014	220
$(i\text{-}Pr_2NP)_4^{+\cdot}$[32]	5(4P) 10(2N)	2.0095	283
$\{[(CH_3)_3Si]_2NP\}_4^{+\cdot}$[14]	75(4P)	2.0072	223
$\{[(CH_3)_3Si]_2CHP\}_4^{+\cdot}$	56(4P)	2.010	293

[a]Xyl = xylyl (2,6-diphenyl)
[b]Mes = mesityl.
[c]Dur = Duryl.

B. ESR Parameters, Structure

Matrix-isolated phosphoniumyl radicals or their glassy solutions exhibit ESR spectra which are characteristic of an axially symmetrical hyperfine tensor (Figure 2). The parallel ($A_\parallel$) and perpendicular ($A_\perp$) components are easily measured and give the magnitude of the isotropic A^{iso} and anisotropic B coupling constants (Table 1).

It is common practice[34] to convert isotropic A^{iso} and anisotropic B coupling constants into the approximate orbital populations, C_s^2 and C_p^2, by dividing these experimental parameters with the values calculated for unit population of the concerned atom. The hybridization ratios, $p/s = C_p^2/C_s^2$, are then incorporated into the classical Coulson equation to give the approximate pyramidalization angle values for the radicals (Figure 1). This approach gives the data shown in Table 3 (for all the radicals quoted in this chapter,

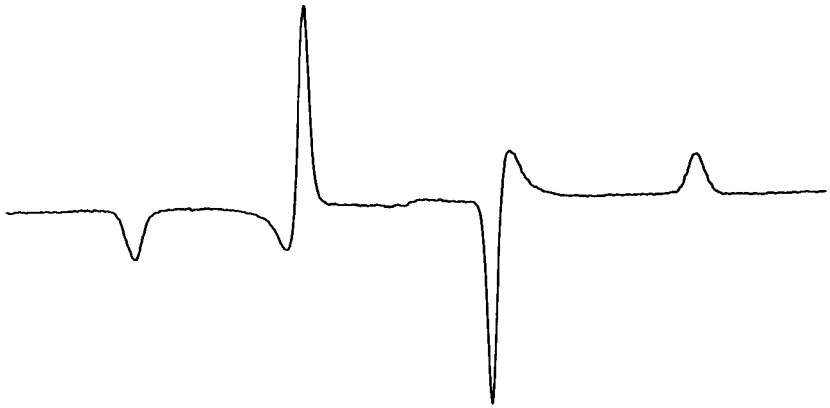

FIGURE 2. ESR spectrum of tridurylphosphoniumyl radical in glassy butyronitrile (145 K).

TABLE 3. Hybridization ratio (p/s) and pyramidalization (α^0) for matrix-isolated phosphoniumyl radicals

Radical	A_p^{iso}(G)	P/s[a]	α^0 (neutral) X-ray	α^0 (neutral) MM2[41]	α^0 (radical)
$H_3P^{+\cdot}$[19]	517	6.67	31.3[b]		14.32[c]
$Ph_3P^{+\cdot}$[20,d]	306	9.09	25[38]	26.9	12.55
$Ph(Mes)_2P^{+\cdot}$[25]	269	10.97	—	20.9	11.55
$Xyl_3P^{+\cdot}$[26,e]	250	11.64	19[39]	16.9	11.24
$Mes_3P^{+\cdot}$[26,f]	248	11.26	19[40]	17.3	11.41
$Dur_3P^{+\cdot}$[26,g]	236	13.17	—	14.9	10.62

[a]Spin densities in 3s and 3p orbitals of phosphorus calculated using $A_0 = 4748$ G and $B_0 = 131$ G, respectively[27], and taking the signs of the ^{31}P hfs tensor components as positive.
[b]*Ab initio* calculation[35]
[c]*Ab initio* calculation[36,37].
[d]In CCl_4.
[e]Xyl = xylyl.
[f]Mes = mesityl.
[g]Dur = duryl.

the orbital populations were estimated using the phosphorus atomic parameters proposed by Morton and Preston[27]).

The data in Table 3 and those in Table 1 indicate that ionization of a phosphine is accompanied by a drastic flattening of its pyramidal geometry. However in contrast to their nitrogen analogues, the corresponding phosphoniumyl radicals retain an equilibrium geometry which is still pyramidal. The phosphorus coupling decreases significantly when the steric hindrance around the phosphorus atom increases. This trend agrees with a pyramidal geometry which is expected to be substantially flattened by changing hydrogens for bulkier ligands such as phenyl, xylyl or duryl. This flattening is accompanied by a decrease in the s character of the SOMO and thus with a decrease in the phosphorus splitting. It is worth noting that phosphoniumyl radicals generated in glasses containing halide salts can react with halide ions, X^-, to form the σ^* radicals $Y_3P^{\cdot}\!-\!X$ which were identified by ESR[42].

Different *ab initio* calculations[36,37] have been carried out to investigate the electronic properties of $H_3P^{+\cdot}$. The geometry was optimized using different basis sets and the mean value of the pyramidilization angle (15°) matches very well the ESR finding. The inversion barrier was found[36] to be only 2.77 kcal mol^{-1} (close to 35 kcal mol^{-1} for PH_3), and this value is reduced to 1.66 kcal mol^{-1} when the zero point energy of the inversion vibration is considered.

The crowded triarylphosphines invert much more easily than H_3P and, according to the theoretical results on $H_3P^{+\cdot}$, the triarylphosphoniumyl radicals are expected to invert very easily. This prediction is in agreement with the total racemization observed when an optically active triarylphosphine is oxidized to the corresponding phosphine oxide via an electron-transfer process[43].

The *in situ* electrochemical oxidation of phosphines, at low temperatures in aliphatic nitrile solvents, within the cavity of an ESR spectrometer gives rise to the spectrum of the corresponding phosphine dimer cation radicals[31] (equation 6). These dimers were also detected on annealing systems containing $Y_3P^{+\cdot}$ radicals[44], or directly by γ-irradiation[16] at low temperature of rigid concentrated solutions of Y_3P.

The ESR parameters of different phosphines dimer cation radicals are given in Table 4. Because of the large phosphorus hyperfine splitting, the ESR spectra exhibit four lines resulting from coupling to two equivalent phosphorus nuclei. The $M_I = 0$ transition appears as a doublet corresponding to $I = 0$ or 1, that is, to the singlet or triplet states, respectively, of the two coupled phosphorus nuclei.

TABLE 4. ESR parameters (G) for phosphine dimer cation radicals

Radical	$A_\parallel$	$A_\perp$	A_p^{iso}	A_H	g_{av}	p/s[a]
$(Me_2PH)_2^{+\cdot}$[45]	581[b]	442	488	58(2H)	2.001	3.4
$(Me_3P)_2^{+\cdot}$[45,46]	569[b]	439	482	20(2H)	2.005	3.2
	592[c]	458	503	3.3[d]		
$(Et_3P)_2^{+\cdot}$[45]	549[b]	415	460	18(2H)	2.002	3.5
			469[31]	3.6(12H)[e]		
$(nBu_3P)_2^{+\cdot}$[47]	550	418	462		2.008	3.4

[a]Spin densities in 3s and 3p orbitals of phosphorus calculated using $A_0 = 4748$ G and $B_0 = 131$ G, respectively[27], and taking the signs of the ^{31}P hfs tensor components as positive.
[b]In CH_2Cl_2 at 77 K.
[c]In $CFCl_3$.
[d]18H.
[e]In butyronitrile–propionitrile (70:30, v/v) at 193 K; $g_{iso} = 2.0032$. At 140 K the coupling with only two protons is observed, $A_H = 18.6$ G.

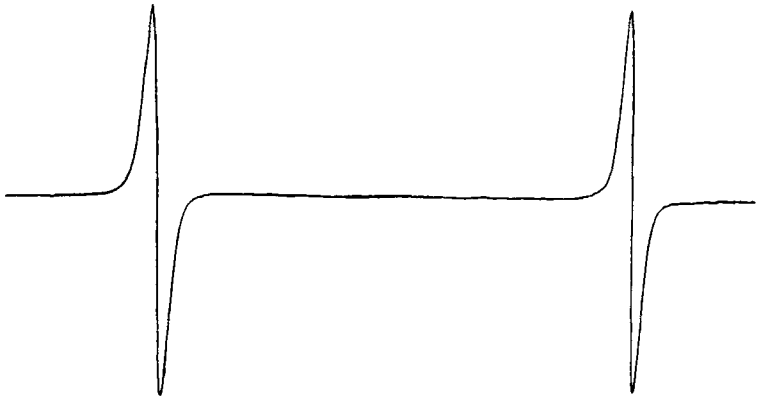

FIGURE 3. ESR spectrum of trixylylphosphoniumyl radical in butyronitrile (293 K).

According to their ESR parameters and MNDO[48] and *ab initio*[37] calculations, these dimeric cation radicals can be regarded as σ^* radicals in which the SOMO is an antibonding orbital concentrated primarily in the P—P bond. The p/s ratio (Table 4) decreases greatly relative to that for the corresponding phosphoniumyl radicals and inicates an sp^3 hybridization at the phosphorus centres. Also[45,46], for $(Me_3PPMe_3)^{+\cdot}$, the proton hyperfine coupling is drastically reduced relative to that for $(Me_3P)^{+\cdot}$ since[46] both an increased energy gap and a lower overlap disfavour the interaction between the SOMO and the $\sigma_{C\text{-}H}$ orbitals.

An important steric crowding around the phosphorus centre can prevent the formation of phosphine dimer cation radicals according to equation 6. Under these circumstances, the ESR spectra of the monomer cation radicals can be easily detected in thoroughly degassed solvents, over a wide temperature range[33,49] (Table 2). These spectra exhibit a doublet resulting from a relatively large phosphorus splitting (Figure 3), and apart from the phosphorus coupling no other coupling was resolved. However, the peak-to-peak line width was very large (ca 6 G), suggesting the existence of unresolved couplings with hydrogens, which was confirmed by deuteriation of the methyl groups in the case of the trimesitylphosphoniumyl radical[50].

Spin-trapping experiments[51] have been tentatively used to characterize short-lived phosphoniumyl radicals. However, phosphines react with nitrones[52] and nitroso[53] derivatives and therefore severe limitations exist in the use of these important classes of free-radical scavengers.

On the other hand, it has been shown[30,31] that in the presence of 1,1′-di-*tert*-butylethylene, in either nitrile or dichloromethane solution, phosphoniumyl radicals were trapped to give long-lived spin adducts with a β-phosphonium substituent (equation 7):

$$Y_3P^{+\cdot} + H_2C{=}C(t\text{-Bu})_2 \longrightarrow Y_3\overset{+}{P}CH_2\dot{C}(t\text{-Bu})_2 \qquad (7)$$

According to the magnitude of the β-proton and phosphorus splittings, these spin adducts were shown to exist predominantly in an eclipsed conformation for which overlap of the unpaired electron orbital with th β P—C bond is at a maximum. Then the phosphorus splitting depends on the electronegativity of the phosphorus substituents and can be used to identify the phosphorus environment.

A cyclic voltammetric study of a series of crowded tetraaryldiphosphines[29,33] showed a

single-electron reversible oxidation at room temperature (equation 8):

$$Ar_2PPAr_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} (Ar_2PPAr_2)^{+\cdot} \quad (8)$$

Ar = mesityl, xylyl, etc.

When the electrochemical oxidation of these diphosphines was performed within the cavity of an ESR spectrometer, in each case the four-line spectrum of the corresponding cation was observed over a large temperature range (-40 to $+50$ °C). The shape of these ESR spectra (Figure 4) is very similar to that of phosphine dimer cation radicals produced during the electrochemical oxidation of different phosphines. The line-width effect was interpreted in terms of nuclear spin relaxation induced by the time-dependent anisotropic dipolar phosphorus interaction[54].

The ESR features of diphosphine dimer cations are listed in Table 2. The large phosphorus splitting indicates that the phosphorus centres are strongly pyramidal. The mean P 3s orbital population is close to 7% whereas it is close to 5% for the corresponding triarylphosphoniumyl radicals, which are thus expected to be less bent at phosphorus. Owing to the long P—P bond (2.1–2.2 Å), a symmetric tetraaryldiphosphine bearing bulky aryl substituents is expected to be sterically less constrained and to be more pyramidal relative to the corresponding triarylphosphine. This difference is retained in the respective cation radicals. It is worth comparing the diphosphine cation radicals with their extensively studied nitrogen analogues[55]. Tetraaryl- and tetraalkyl-hydrazine cation radicals prefer planar, olefin-like geometries, with a delocalized or a localized strong three-

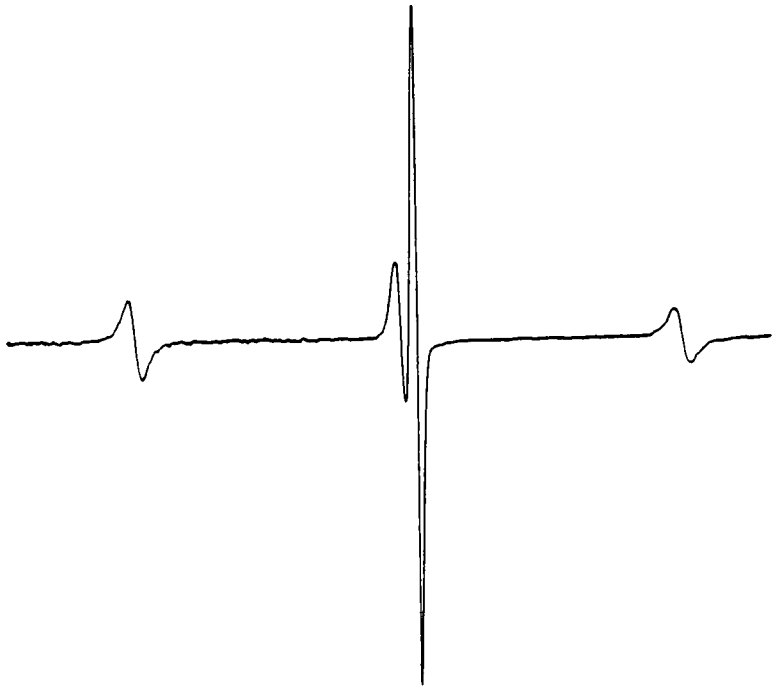

FIGURE 4. ESR spectrum of tetra(2,4,6-tri-ethylphenyl)diphosphine radical cation in butyronitrile (293 K).

electron bond. Since the nitrogen atoms are pyramidal in the preferred conformer of tetraalkylhydrazines, it is clear that in the corresponding cation radicals the energy required to make the nitrogen centers planar is largely compensated by three-electron π stabilization.

For the diphosphine cation radicals, as a result of the long P—P bond, there is a poor overlap between the P 3p orbitals and hence the three-electron stabilization is far too small to balance the energy required to make the two phosphorus centres planar. This conclusion agrees with theoretical calculations on $P_2H_4^{+\cdot}$[56,57], which is nevertheless stabilized relative to $PH_3^{+\cdot}$. This stabilization was attributed[56] to a strong mixing between the high-lying unsymmetrical lone-pair combination (n^-) and the phosphorus—phosphorus σ bonding orbital (σ_{PP}).

III. PHOSPHINYL RADICALS, $Y_2P^{\cdot}$

A. Generation

Phosphinyl radicals $Y_2P^{\cdot}$(Y = H, Cl or F) have been generated by γ-irradiation of Y_3P in rare-gas matrices[58]. The $^{\cdot}PH_2$ radical was clearly identified[59], but only the isotropic spectrum was observed in spite of the low temperature (4.2 K). Anchoring the radical by hydrogen bonding should prevent its rapid rotation and, although $H_3P^{+\cdot}$ was the major phosphorus-containing radical product, parallel features assignable to stationary $H_2P^{\cdot}$ radicals were clearly discerned during irradiation of H_3P in concentrated aqueous solutions of sulphuric acid[60].

The diphenylphosphinyl radical, $Ph_2P^{\cdot}$, has been observed in X-irradiated single crystals of triphenylphosphine oxide and in ultraviolet-irradiated polycrystalline diphenylphosphine at 77 K[61]. A strong matrix effect on A_P^{iso} has been detected for diphenylphosphinyl radicals occupying different sites in X-irradiated single crystals of Ph_3PBH_3[62].

The ESR parameters for a series of matrix-isolated phosphinyl radicals are given in Table 5.

Pioneering work by Lappert, Goldwhite and coworkers[65] established that phosphinyl radicals can be stabilized by means of sterically demanding substituents. Persistent phosphinyl radicals, $Y_2P^{\cdot}$ [Y = $CH(SiMe_3)_2$ (bisyl), $N(SiMe_3)_2$, etc.], were prepared by photolysis of degassed solutions of the corresponding three-coordinate chlorides, Y_2PCl, in the presence of an electron-rich olefin (ERO) (equation 9):

$$2Y_2PCl + (Me_2N)_2C{=}C(NMe_2)_2 \xrightarrow{h\nu} ERO^{2+}\ 2Cl^- + 2Y_2P^{\cdot} \qquad (9)$$

TABLE 5. ESR parameters (G) for matrix-isolated phosphinyl radicals

Radical	$A_{\parallel}$	$A_{\perp}$	A_P^{iso}	A(others)	g_{av}
$H_2P^{\cdot}$[59]	—	—	80	18(2H)	2.0087
$H_2P^{\cdot}$[60]	275[a]	−17.5[b]	—	—	—
$F_2P^{\cdot}$[63]	308.1	−27.2	84.6	32.8(2F)	2.0020
$Cl_2P^{\cdot}$[60]	272.5	−22.5	75.8	5.5(2Cl)	2.0109
$Ph_2P^{\cdot}$[60,61]	268[60]	−13	78.7	—	2.0047
$(Eto)_2P^{\cdot}$[64]	280	−12	85	—	2.002
$i\text{-}Pr_2P^{\cdot}$[60]	290	0	96.7	13(2H)[c]	—

[a]Experimental.
[b]Calculated assuming $A_P^{iso} = 80$ G.
[c]Only $A_{\parallel}$ assignable.

It is worth noting that in the absence of molecular oxygen, hydrocarbon solutions of $[(Me_3Si)_2CH]P^{\bullet}$ are stable indefinitely. The intensity of the corresponding ESR signal was found to depend reversibly on temperature and this was attributed to the phosphinyl radical being in equilibrium with its dimer (equation 10):

$$2[(Me_3Si)_2CH]P^{\bullet} \rightleftharpoons [(Me_3Si)_2CH]PP[CH(SiMe_3)_2] \quad (10)$$

Phosphinyl radicals can also be generated by free-radical addition to the phosphorus—phosphorus double bond of a diphosphene[66] (equation 11), or by reaction of *tert*-butoxyl radicals with diphosphines[14,67] (equation 12):

$$ArP=PAr + {}^tBuO^{\bullet} \longrightarrow Ar({}^tBuO)P\text{-}\dot{P}Ar + Ar\dot{P}OBu^t \quad (11)$$
(Ar = 2,4,6-*tert*-butylphenyl)

$$(Me_2N)_2PP(NMe_2)_2 + {}^tBuO^{\bullet} \longrightarrow {}^tBuOP(NMe_2)_2 + (Me_2N)_2P^{\bullet} \quad (12)$$

Photolysis of tetraphenyldiphosphine, triphenylphosphine and diphenylphosphine was shown to generate diphenylphosphinyl radicals[68]. However, the six-line ESR spectrum detected during irradiation of a degassed solution of tetraphenyldiphosphine in benzene at 77 K was misassigned to $Ph_2P^{\bullet}$[69].

Tert-butoxyl radicals abstract hydrogen from secondary phosphineboranes, $R_2PH \rightarrow BH_3$, to yield the phosphinylborane radical $R_2\dot{P} \rightarrow BH_3$ as the major product, although its ESR spectrum is difficult to detect. $R_2\dot{P} \rightarrow BH_3$ abstracts halogen from alkyl bromides and adds readily to alkenes and isocyanides. Spin trapping of $R_2\dot{P} \rightarrow BH_3$ with 2-methyl-2-nitrosopropane or phenyl-*N*-*tert*-butylnitrone affords the appropriate nitroxides[70].

The ESR parameters of selected phosphinyl radicals detected in the liquid phase are listed in Table 6.

TABLE 6. Liquid-phase ESR parameters (G) for different phosphinyl radicals

Radical	A_p^{iso}	A(others)	g	T(K)
$Me_2P^{\bullet}$ [71,a]	95.7	13.9(6H)	2.0084	245
$(Me_2N)_2P^{\bullet}$ [67]	70.2	4.2(2N) 2.1 (12H)	2.0032	253
$Bisyl_2P^{\bullet}$ [65,b]	96.3	6.4(2H)	2.009	300
$Ar_2P^{\bullet}$ [66,c]	103		2.007	298
$ArP(OBu^t)\dot{P}Ar$ [66,c]	102	44(1P)	2.008	298
$((Me_3Si)_2N)_2P^{\bullet}$ [72]	91.8		2.008	300
$Mes_2P^{\bullet}$ [30,d]	96.2		2.008	292

[a] In adamantane.
[b] Bisyl = $[(CH_3)_3Si]_2CH$.
[c] Ar = 2,4,6-tri-*tert*-butylphenyl.
[d] Mes = 2,4,6-tri-methylphenyl (mesityl).

B. ESR Parameters, Structure

The relative small magnitude of the phosphorus splittings (Tables 5 and 6) indicates that the orbital containing the unpaired electron has a very small P 3s character. On the other hand, the p/s ratios are very high (47.9 for $F_2P^{\bullet}$ and 43 for $Ph_2P^{\bullet}$), as expected for π radicals with the unpaired electron largely concentrated on phosphorus. The two ligands and the lone pair lie in a plane with the central phosphorus atom and the unpaired electron being contained in an almost pure p orbital perpendicular to this plane. The equilibrium

geometry (P—H = 1.407 Å, ∠ HPH = 93.40°) and the spin densities of $H_2P^{\bullet}$ have been determined by *ab initio*[73,74] and INDO calculations and agree with a π configuration. There is a clear increase in A_p^{iso} on going from $Ph_2P^{\bullet}$ (Table 5) to $Ar_2P^{\bullet}$(Ar = 2,4,6-tri-*tert*-butylphenyl, Table 6). As was suggestd for aminyl radicals[75], this trend could result[60] from an increase in the CMC angle (M = N or P).

For $Ph_2P^{\bullet}$, the high 3p spin density at the phosphorus atom and the absence of any detectable ring-proton hyperfine interaction indicate the absence of significant ring delocalization[63]. This contrasts with the extensive ring delocalization observed for the diphenylaminyl radical[76]. With phosphorus, 3p–2p(π) interaction is far less efficient than 2p–2p(π) interaction for nitrogen. However, for 3p–3p(π) orbitals the size and energy matching are greatly improved and significant spin delocalization could account for the low value of A_p^{iso} for the $(RS)_2P^{\bullet}$ radicals[60].

The proton splitting for $Me_2P^{\bullet}$ (Table 6) probably arises predominantly from a hyperconjugative mechanism and is smaller that that detected for $Me_2N^{\bullet}$ (27.4 G)[77], which again would be a consequence of a less efficient matching of the P 3p(π) orbital with the β C—H bond orbitals.

IV. ANION RADICALS DERIVED FROM PHOSPHINES

Electron fixation on phosphorus-containing molecules can be achieved by cathodic reduction, alkali metal reduction or irradiation (X-ray or γ-ray) and is well documented for tetra- and penta-coordinated species[11,13,15]. However, for a tricoordinated species there is usually no low-lying vacant orbital centred primarily on phosphorus to accommodate the extra electron. Electron capture is therefore highly energetic and yields transient anion radicals with a small unpaired electron density on phosphorus.

ESR spectra of the radical anion produced from dimethylphenylphosphine both by electrolysis and by reaction with alkali metals have been reported[78]. The ESR parameters (A_p = 8.5 G, A_H = 9.0 G (1H$_p$). A_H = 3.3 G (2H$_o$), A_H = 0.4 G (2H$_m$), A_H = 0.78 G (6H) in DMF at −50 °C) agree with those expected for the radical anion of benzene, substituted with an electron-withdrawing dimethylphosphinyl group. When the reduction was carried out with an alkali metal a secondary radical was observed which had been erroneously ascribed[79] to the primary radical anion.

Hanna[80] reported that the reaction of triphenylphosphine with alkali metals in THF produced the radical anion $Ph_3P^{-\bullet}\,M^+$, identified by its ESR spectrum. Considering the well known cleavage of phenyl groups from triphenylphosphine by alkali metals[81], Britt and Kaiser[82] re-investigated this reaction and found that the resultant radical has the formula $(Ph_2PM)^{-\bullet}$ [A_p = 8.4 G, A_H = 2 G (3H$_o$, SH$_o$), A_H = 0.8 G (4H$_m$)] and is formed according to the following sequence:

$$Ph_3P + 2M \longrightarrow Ph_2PM + PhM \tag{13}$$

$$Ph_2PM + M \longrightarrow (Ph_2PM)^{-\bullet}\,M^+ \tag{14}$$

Aryl cleavage has been observed for most triarylphosphine radical anions produced by alkali metal reduction[83–87].

When the phosphine contains only one aromatic group bonded to the phosphorus atom, however, the primary radical can be detected by ESR. Thus, Cowley and Hnoosh[85] observed the ESR spectrum from $[Me_2P(C_6H_4)PMe_2]^{-\bullet}\,M^+$ in THF at 193 K, whereas Gerson *et al.*[79] prepared $(Me_2PPh)^{-\bullet}$ by reduction with sodium or potassium in dimethoxyethane.

Santhanam and Bard[88] investigated the electrochemical reduction of triphenylphosphine and concluded that a single electron transfer generates $Ph_3P^{-\bullet}$, which readily decomposes to form diphenylphosphine and biphenyl. When the reduction was performed

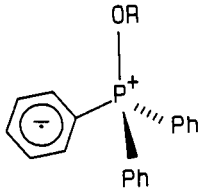

FIGURE 5. Electronic structure of 'phosphoranyl' radical resulting from addition of RO$^{\bullet}$ to PPH_3.

within the cavity of an ESR spectrometer, a weak signal, indicating an unstable radical, was obtained. By controlling the reduction potential within the limits corresponding to the one-electron process, Il'Yasov and coworkers[89,90] obtained satisfactory ESR spectra assignable to $Ph_3P^{-\bullet}$ [$A_p = 3.1$ G, $A_H = 2.2$ G ($6H_o$), $A_H = 1.1$ ($3H_p$), $g = 2.0031$[. Deuteriation of the phenyl groups confirmed that at the temperature of the study (210K) the unpaired electron is equally delocalized over all three benzene rings.

It is worth mentioning that addition of alkoxyl radicals to triphenylphosphine generates 'phosphoranyl' radicals with a small phoshorus coupling and with the unpaired electron contained in a π orbital centred on only one phenyl group at low temperature[91] (150 K) (Figure 5). However, at higher temperatures electron exchange renders the rings magnetically equivalent[92]. Exchange of the unpaired electron between the three phenyl groups could be an intramolecular analogue of the well known exchange reaction which occurs between arene radical anions and the neutral arenes.

The anion resulting from the addition of an electron has been trapped in an X-irradiated crystal of 1,2-phenylenephosphorochloridite[74]. According to the ESR tensors and the results of *ab initio* and INDO calculations, the unpaired electron was shown to be strongly localized in a P—Cl σ^* orbital. On the other hand, the radical anion thermally dissociated into a phosphinyl radical and a Cl^- ion.

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The Chemistry of Organophosphorus Compounds
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CHAPTER 7

Preparation of phosphines

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I. INTRODUCTION

Methods for the synthesis of phosphines were reviewed exhaustively in the treatise on organophosphorus chemistry by Maier[1], which was published in 1972 and is still useful. Since then there has been a comprehensive review by Elsner[2], a number of short papers or reviews covering restricted aspects of the subject[3–8] and a recent book on the formation of carbon—phosphorus bonds in general[9]. In addition, material since 1969 has been reviewed on a yearly basis in the Specialist Periodical Reports of the Royal Society of Chemistry entitled Organophosphorus Chemistry, Volumes 1–18[10]. Owing to the large numbers of phosphines which are reported each year, a treatment similar to that by Maier[1] is beyond the scope of this chapter, the objective of which is to give an overview of the subject. Readers who desire to prepare a particular phosphine are advised to check if it (or a related structure) was made prior to 1969 using the listing by Maier[1] and to search *Chemical Abstracts* after 1969. Those who require more detail on any of the following material, especially on general experimental procedures, should consult Elsner's work[2]. In addition to the reactions outlined here, there are a number of reported transformations of functionalized phosphines where reaction is at a position remote from phosphorus[2].

Although there have been useful improvements and extensions to some methods, it is probably fair to say that there has been no significant addition to the list of synthetic routes to phosphines given by Maier[1]. From that list there are three methods which are used for the formation of the majority of phosphorus—carbon and phosphorus—hydrogen bonds: via organometallic reagents and halogenophosphines, from metal phosphides or by hydride reduction. This is not surprising when one considers the possible disconnections of the P—C and the P—H bonds shown in equations 1–6 in conjunction with the available starting materials.

$$\text{P—C} \Rightarrow \text{P}^+ + \text{C}^-, \text{ equivalent to P—X + M—C} \quad (1)$$

$$\text{P—C} \Rightarrow \text{P}^- + \text{C}^+, \text{ equivalent to P—M + X—C} \quad (2)$$

$$\text{P—C} \Rightarrow \text{P}^\bullet + \text{C}^\bullet \quad (3)$$

$$\text{P—H} \Rightarrow \text{P}^+ + \text{H}^-, \text{ equivalent to P—X + H}^- \quad (4)$$

$$\text{P—H} \Rightarrow \text{P}^- + \text{H}^+ \quad (5)$$

$$\text{P—H} \Rightarrow \text{P}^\bullet + \text{H}^\bullet \quad (6)$$

Equation 1 represents the electrophilic phosphorus route via organometallic reagents and halogenophosphines (X = halogen or, less commonly, another leaving group—

discussed in Section II), which is often the method of first use. Undoubtedly this is because the required starting materials are readily available; in particular, the halogenophosphines are usually available in one or two steps from elemental phosphorus (see below) and often are commercially available.

Equation 2 represents the nucleophilic phosphorus route via metal phosphides and suitable carbon electrophiles, again often organohalogen compounds. This is also a popular and versatile route, although in some cases it may be slightly longer than the electrophilic route since the required phosphides may have to be derived from other phosphines. (see Section III)

Equation 3 represents a radical-based route to phosphine synthesis. This is much less common but nevertheless can be very useful in certain cases with multiple bonds as acceptors (see Section V.B).

Equation 4 represents the reduction of electrophilic phosphorus with the formation of a P—H bond. This is a very common way to prepare primary and secondary phosphines (see Section IV.B).

Equation 5 represents the quenching of a metal phosphide by acid, thus forming a primary or secondary phosphine. However, in most cases the metal phosphide will have been made from the same primary or secondary phosphine so that, although occasionally useful[11], at present this does not constitute a viable route to such phosphines. Industrially diphenylphosphine is made by the aqueous quenching of lithium diphenylphosphide[12].

Equation 6 is included for completeness and so far has not been the source of a useful route to phosphines.

In addition to the above methods which form the P—C and P—H bonds, there are a number of useful routes to phosphines via other organophosphorus compounds, in particular reduction of organophosphorus(V) compounds (treated in Section IV). Ironically, these other organophosphorus compounds will probably also have been made from phosphines. However, there are circumstances where such a roundabout route may be the most efficient one; for example, in the synthesis of optically active phosphines it is easier to resolve phosphonium salts or phosphine oxides than the parent phosphines (Section VII). Also, phosphine oxide can be used as a protecting group for phosphine since it is more inert towards electrophiles and oxidation than the parent phosphine and since quantitive regio- and stereo-specific interconversions in both directions are easily achieved.

In most cases, the ultimate source of the phosphorus atom in the synthesis of organophosphorus compounds is elemental phosphorus and therefore the lowest number of steps from it leads to the most efficient synthesis. However, there are only a few useful syntheses of phosphines directly from elemental phosphorus (see Section VI.A) and most syntheses make use of commercially available derivatives. Of these, by far the most common as starting materials are the halogenophosphines, prepared by reaction of either red or white phosphorus with the appropriate elemental halogen, e.g. equation 7[12]. Also, simple mono- and di-substituted alkyl and aryl halogenophosphines are available in bulk[12]. Other starting materials which are used include metal phosphides (see Section III) and phosphine itself, which is prepared from elemental phosphorus according to equation 8, purified by conversion to phosphonium iodide and regenerated with base according to equation 9[12].

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3 \tag{7}$$

$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_2 \tag{8}$$

$$PH_4I + KOH \longrightarrow PH_3 + H_2O + KI \tag{9}$$

While phosphines are classed as weak bases[13], their basicity increases regularly, and markedly, with the degree of substitution so that the order of basicity for the methyl derivatives is[14] $PH_3 < CH_3PH_2 < (CH_3)_2PH < (CH_3)_3P$. This effect can be useful in the

separation of primary, secondary and tertiary phosphines by judicious choice of acid extractant. Alternatively, if the phosphonium salts with hydrogen iodide are made, those formed from primary phosphines can be decomposed by water whereas those from secondary and tertiary phosphines require alkali[15].

Although many different methods are used for the synthesis of phosphines, there are certain precautions which are common to all methods. In particular, phosphines are usually oxygen sensitive and can react violently when exposed to air, so they must be stored and manipulated in a nitrogen or argon atmosphere. Note that this oxidation can be insidious; for example, triphenylphosphine is apparently air stable, but an open bottle will develop noticeable deposits of the oxide in a few weeks and solutions exposed to air have useful lifetimes as short as 1 day. Also, phosphines usually have a strong, unpleasant odour and must be assumed to be toxic; phosphine itself is a very toxic gas and great care should be exercised when handling it.

This chapter will discuss the synthesis of acyclic phosphines where the phosphorus is bonded to three carbons and/or hydrogens. Cyclic and polyphosphines are dealt with elsewhere. The words unsymmetric and asymmetric are used to denote phosphines of the forms R_2R^1P and RR^1R^2P, respectively. Also, this chapter is biased towards laboratory preparations of phosphines. Industrial preparations, although based on similar principles, tend to be specific for each individual case; for example, triphenylphosphine is made industrially by the reaction between chlorobenzene, molten sodium and phosphorus halogeno phosphines.

II. PREPARATION VIA ELECTROPHILIC PHOSPHORUS AND ORGANOMETALLIC REAGENTS

This route is most useful for the synthesis of tertiary phosphines according to equations 10–13, and has been used extensively for this purpose.

$$PCl_3 + 3R^- \longrightarrow R_3P + 3Cl^- \quad (10)$$

$$Cl_2PR^1 + 2R^- \longrightarrow R_2R^1P + 2Cl^- \quad (11)$$

$$ClPR^1{}_2 + R^- \longrightarrow R^1{}_2RP + Cl \quad (12)$$

$$R^1R^2PCl + R^- \longrightarrow RR^1R^2P + Cl^- \quad (13)$$

The method is less useful for primary and secondary phosphines because inaccessable halophosphines would be required as starting materials (equations 11–13; $R^1 = H$).

Below it is convenient to distinguish between different substituent patterns on phosphorus, and according to the type of organometallic reagent used. Note that the same variety of organometallic reagents is used as in the formation of carbon—carbon bonds[16], but the same cannot be said of the phosphorus acceptor species used, which are most often halogenophosphines.

A. Phosphines of the Form R_3P

1. Using Grignard reagents

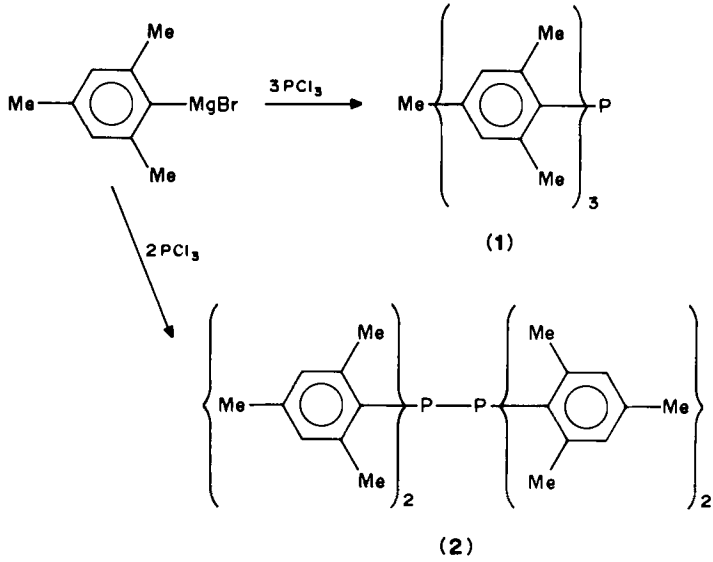
The reaction takes place according to equation 14. The original procedures, being straightforward, are still relevant; the phosphorus halide is added to the Grignard reagent and the reaction is completed after refluxing, usually in diethyl ether[17,18].

$$PCl_3 + 3RMgX \longrightarrow R_3P + 3MgXCl \quad (14)$$

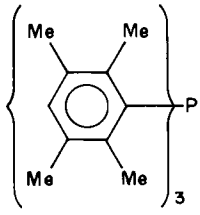
The products are usually separated by addition of ammonium chloride solution

followed by distillation of the ether. In some cases omission of this hydrolysis step and vacuum distillation lead to better yields[19]. For higher boiling products vacuum distillation may not be practicable and is not recommended[19].

Better yields are also said to be obtained when an excess of chloro-Grignard reagent is used and the two reactants are brought together at as low a temperature as possible[20-22], after which normal Grignard procedures follow. However, other workers have shown that excess of Grignard reagent has no effect on the yield[23]. One difficulty with the use of excess of Grignard reagent is that it can change the final product; for example, in the reaction of mesitylmagnesium bromide with phosphorus trichloride (Scheme 1), when excess of bromide is used the product is trimesitylphosphine (**1**), but when the bromide is limited the product is the diphosphine **2**[24]. In some cases, sterically hindered phosphines, e.g. **3**[25,26], can be made using excess of Grignard reagent instead of using the usual route via organolithium reagents[23] (se Section II.A.2).



SCHEME 1



Primary and aryl Grignard reagents usually give the best yields, whereas reagents derived from secondary[18] and tertiary halides give little or no tertiary phosphines[27-31]. Again, steric hindrance is said to be responsible since products are often isolated in which

full substitution has not occurred, as in, for example[32], equation 15.

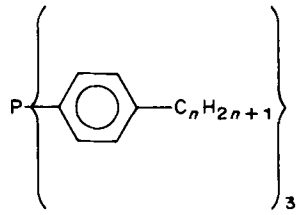
$$PCl_3 + \underset{\text{(excess)}}{Bu^tMgX} \longrightarrow Bu^t{}_2PCl \qquad (15)$$

The usual considerations of Grignard chemistry also apply. For example, trivinylphosphines are synthesized with thf as the solvent instead of diethyl ether[33] since vinyl Grignard reagents have to be synthesized in thf. Inclusion of the hydrolysis step in this synthesis lowers the yield[33].

Sometimes the halogen on the phosphorus makes a difference to the product. For example, the reaction of trifluorovinylmagnesium iodide and phosphorus trichloride does not give the expected tris(trifluorovinyl)phosphine (**4**)[34] but a polymeric material, whereas the use of phosphorus tribromide gives the required phosphine, the reaction being carried out in diethyl ether[35]. Note that the temperature stability of these perfluorovinylphosphines is not high and another disadvantage of this synthesis is that a number of polyfluorinated by-products are also isolated[36].

Within the above limitations, the Grignard procedure is very useful and some recent examples of its use are the syntheses of the following: (i) the series of arylphosphines (**5**, $n = 2$–9) with straight-chain alkyl substituents in the *para* position of the benzene ring[37] from the Grignard derived from *p*-bromo(alkyl)benzene; (ii) a range of long-chain (C_{10}–C_{19})trialkylphosphines[38]; (iii) triethylphosphines that are radio-labelled at the phosphorus and β-carbon[39]; (iv) phosphines bearing polyether substituents (**6**, R = Me or CH_2CH_2OMe) from Grignard reagents derived from the appropriate chloro ethers[40]; (v) an example in which a halide is not used as the electrophile is provided by the improved high-yield synthesis of trimethylphosphine from triphenylphosphate and methylmagnesium iodide[41].

$(CF_2{=}CF)_3P$ (**4**)



(**5**)

$(PCH_2CH_2CH_2OR)_3$ (**6**)

2. *Using organolithium compounds*

Organolithium compounds resemble Grignards in their reactions but are more reactive since the C—Li bond is more ionic in nature than the C—Mg bond[42]. For the synthesis of tertiary phosphines the procedure is again straightforward, an example being equation 16, and the yields are comparable[43] to those obtained using the Grignard method. The reactions are carried out using procedures similar to those used in Grignard reactions but in many cases the organolithium route may be used when Grignard method has failed. In particular, it is essential[23,44] to use the more reactive organolithium compounds when a sterically hindered phosphine is being synthesized, e.g. tri-*tert*-butylphosphine[23], and organolithium compounds are preferable in some cases involving the formation of aryl C—P bonds since aryllithium compounds are easier to prepare than the corresponding Grignards. For these reasons, and the fact that organolithiums are more available, this

route has gradually become the favoured one[2].

$$3RLi + PCl_3 \longrightarrow R_3P + 3LiCl \quad (16)$$

The organolithium compounds needed for these syntheses are prepared by the usual routes[16], the most common being metallation with base (equation 17), reductive metallation (equation 18) and halogen–metal exchange (equation 19)[45].

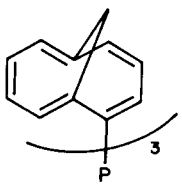
$$RH + R^1Li \longrightarrow RLi + R^1H \quad (17)$$

$$RX + 2Li \longrightarrow RLi + LiX \quad (18)$$

$$RLi + R^1X \longrightarrow R^1Li + RX \quad (19)$$

Again, considerations pertinent to normal organolithium chemistry apply. For example, the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) considerably enhances the thermal stability of *o*-lithiochlorobenzene, thus enabling tris(*o*-chlorophenyl)phosphine to be prepared in high yield[46].

A wide range of tertiary phosphines have been synthesized using the organolithium route[22,47–51] some recent examples being the following: (i) the 1,6-methano[10]annulenyl system[52] (**7**); (ii) a range of tris(2-imidazolyl)phosphines[53,54] (**8**) and tris(2-thiazoyl)phosphine (**9**)[48]; (iii) tris[*o*-(dimethylarsino)phenyl]phosphine (**10**) from the lithiation of *o*-bromophenyldimethylarsine with butyllithium and phosphorus trichloride[47]; (iv) the synthesis of tri(2-pyridyl)phosphine (**11**) from 2-bromopyridine, butyllithium and phosphorus trihalide[54a]; (v) pentadienylphosphines, e.g. **12**[55]; and (vi) again the leaving group on phosphorus does not have to be halide as, for example, in the improved synthesis of tris(2,4,6-trimethoxyphenyl)phosphine from 2,4,6-trimethoxyphenyllithium and triphenyl phosphite[57].



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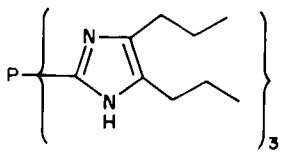
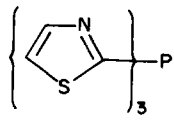
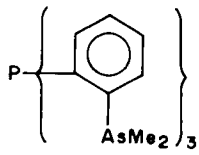


(8)



(9)



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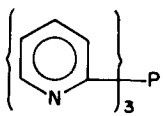


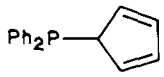
(11)

(12)

3. Using other organometallics

Reagents other than Grignards and organolithium have occasionally been used; e.g. trialkylaluminium compounds react with phosphorus trichloride to give range of tertiary phosphines[58–60], as do organo-copper[61], -mercury[62], -zinc[15,63], -silicon and -tin[2] compounds. Indeed, the earliest phosphine preparations used such reagents, e.g. involving

zinc[64]. Tris(trifluoromethyl)phosphine was prepared from the reaction of bis(trifluoromethyl)cadmium and triiodophosphine in dimethoxyethane, although the yield was low (20%)[65]. The phosphine **13** was prepared from chlorodiphenylphosphine and cyclopentadienylthallium and the tertiary arylethynylphosphines (**14**) were prepared from copper arylacetylides and the corresponding chlorophosphine in a polar aprotic medium containing dissolved lithium salts[66,67]. A useful recent example is the synthesis of 1,3-dienylphosphines by transfer of the dienyl group from zirconium[68].

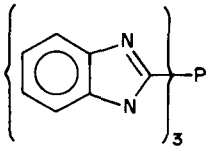


(**13**)

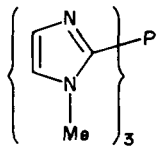
$(p\text{-}NO_2C_6H_4C{\equiv}C)_2PPh$

(**14**)

Phosphines **15** and **16** could not be synthesized using the lithiated heterocycles and trihalogenophosphines; instead, trichlorophosphine was reacted with trimethylsilyl-substituted heteroaromatics[69].



(**15**)

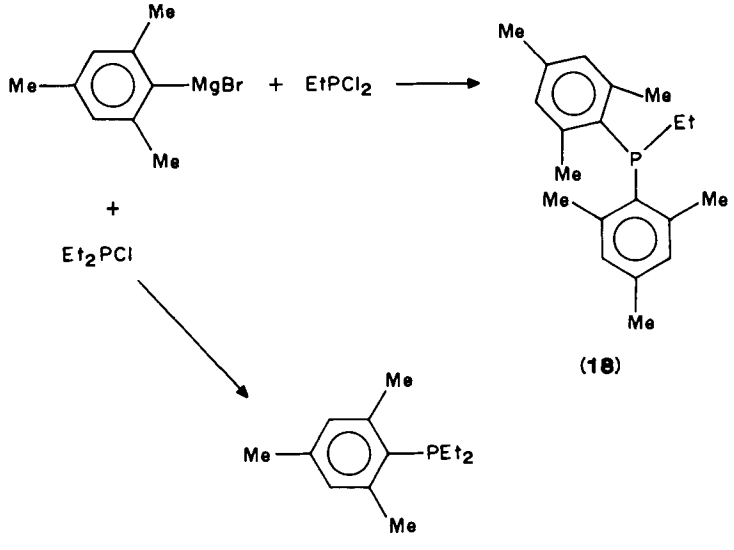


(**16**)

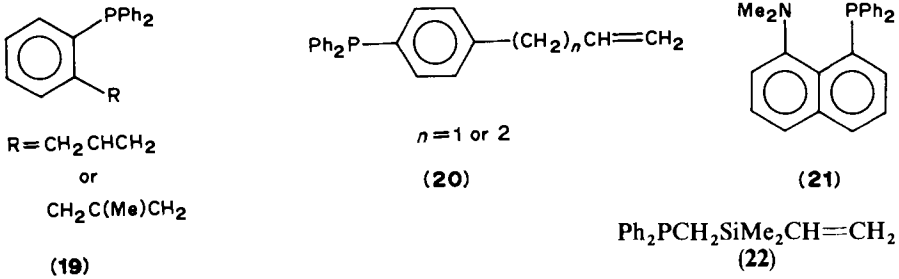
B. Phosphines of the Form R_2R^1P

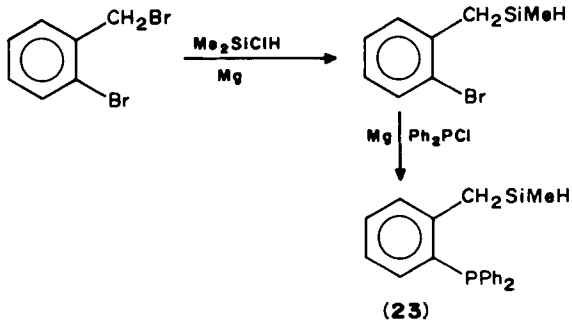
Unsymmetric tertiary phosphines may be synthesized using organometallic compounds according to equations 11 and 12[70–78]. Whether the phosphonous route (equation 11) or the phosphinous route (equation 12) is used depends on the availability of the starting materials, although the latter is more popular as it gives a wider range of phosphines. The reaction usually involves the addition of the appropriate halophosphine to the organometallic and is complete after refluxing. Again, keeping the initial reaction temperature as low as possible may increase the yield[22,79–81].

Some recent examples using the Grignard route are the following: (i) reaction of mesitylmagnesium bromide with chlorodiethylphosphine and dichloroethylphosphine at $-10\,°C$ in thf to yield mesityldiethylphosphine (**17**) and dimesitylethylphosphine (**18**), respectively[79] (Scheme 2); (ii) the preparation of the olefinic tertiary phosphines **19** and **20** from chlorodiphenylphosphine and the Grignards derived from *o*- and *p*-halogenoalkenylbenzenes[81–83]; (iii) the naphthylphosphine **21** from chlorodiphenylphosphine and the Grignard derived from 1-bromo-8-dimethylaminonaphthalene[84]; (iv) the silicon-substituted phosphine **22**, from chlorodiphenylphosphine and Grignard derived from the appropriate chloromethylsilane[85]; (v) the useful ligand **23** by the route shown in Scheme 3[86]; (vi) the bulky phosphines (**24**, R^1 = Bu^t, cyclohexyl; R^2 = H, Me) from chlorodi-*tert*-butylphosphine and chlorodicyclohexylphosphine[87a]; (vi) bis(trifluoromethyl)phenylphosphine (**25**) from bis(trifluoromethyl)chlorophosphine and phenylmagnesium bromide[87b]; (viii) the synthesis of norbornenylphosphines **26** and **27** from the isomeric norbornenyldichlorophosphines and methylmagnesium iodide, the similar norbornylphosphine **28** also being prepared using this method[88]; (ix) phosphine **29** from 2,4-dimethoxyphenyldichlorophosphine and methylmagnesium iodide[89]; (x) phos-



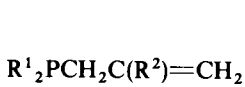
SCHEME 2



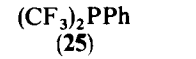


SCHEME 3

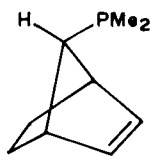
phines **30**[90] and **31**[91] using conventional aryl Grignard procedures; and (xi) the reactions of the unsaturated dichloroaminophosphine (**32**) with a range of alkyl Grignard reagents giving rise to a mixture of the rearranged phosphines **33** and **34**[92].



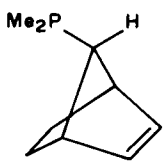
(**24**)



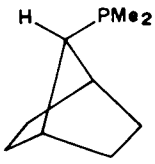
(**25**)



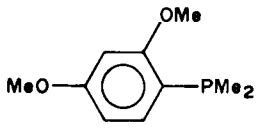
(**26**)



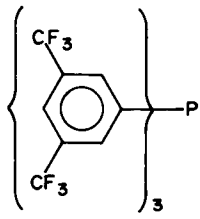
(**27**)



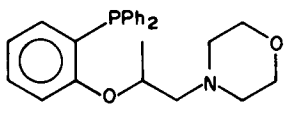
(**28**)



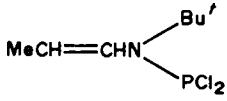
(**29**)



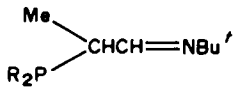
(**30**)



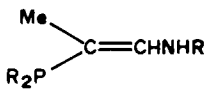
(**31**)



(**32**)



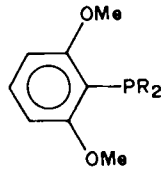
(**33**)



(**34**)

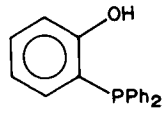
Some recent examples using the organolithium route are as follows: (i) the dimethoxyphenylphosphines **35**[93] and *o*-hydroxyphenylphosphine **36**[94], all from *ortho*-lithiation-based reactions; (ii) the development of an improved route to the polymeric phosphine (**37**) using the *n*-butyllithium–tmeda reagent followed by chlorodiphenylphosphine[95]; (iii) the synthesis of vinylphosphines and pentadienylphosphines[55,96]; and (iv) diphenylphenacylphosphine from chlorodiphenylphosphine and phenacyllithium, generated by treatment of acetophenone with lithium diisopropylamide[56].

Occasionally, it may prove necessary to protect some other functionality which is sensitive to organometallic reagents and this is exemplified by (i) the synthesis of the *o*-carboxarylphosphines **38**, where 2-oxazoline acted as a protecting group for the carboxy-group during the application of the Grignard route[97], and (ii) the synthesis of triarylphosphines with formyl or acetyl group as aromatic substituents, where the

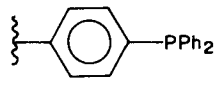


R=Ph or Bu^t

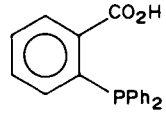
(35)



(36)

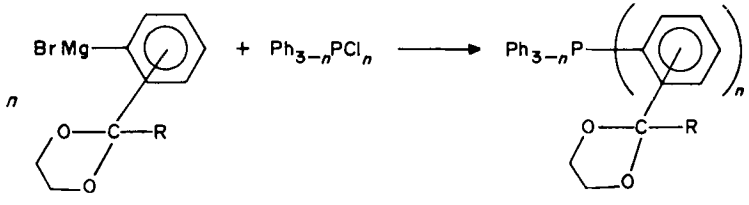


(37)



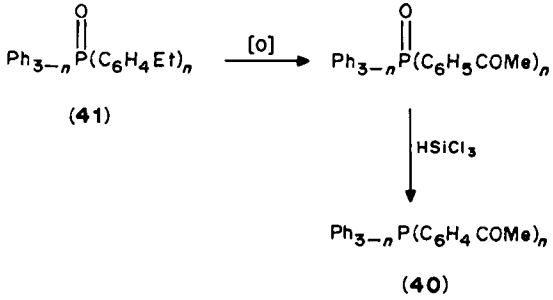
(38)

formation of the ethylene keto derivative serves as protection for the carbonyl group during the Grignard reaction, the resulting phosphines (**39**; Scheme 4, R = H, CH_3) being cleaved to the desired products by toluene-*p*-sulphonic acid[98]. Note that the acetyl derivatives (**40**) may also be prepared by oxidation of the ethyl derivatives (**41**) followed by reduction with trichlorosilane[99], according to Scheme 5.



(39)

SCHEME 4



(41)

(40)

SCHEME 5

Phosphorus(V) halides can also be used as electrophiles in these reactions[100–103]. For example alkyldiphenylphosphines have been prepared by the reaction of

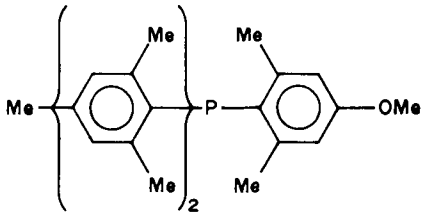
diphenyltrichlorophosphorane with alkyllithium reagents[100] and the reduction of tetrachlorophenylphosphorane with Grignard reagents gives a range of dialkylphenylphosphines[104,105]. Similarly synthesized were a range of dialkylstyrylphosphines[104,105], the neopentylphosphines **42** and **43**[106], the substituted vinylphosphines **44** (R = H, CH_3) and **45**[107] and the sterically hindered triarylphosphine **46**[108].

$Ph_2PCH_2CMe_3$ (42)

$PhP(CH_2CMe_3)_2$ (43)

$Ph_2PC(R)=CR_2$ (44)

$PhP(CH=CHMe)_2$ (45)



(46)

C. Phosphines of the Form RR^1R^2P

In principle, these much sought after asymmetric phosphines (see Section VII) can be synthesized by the electrophilic route either by the reaction of phosphinous halides (e.g. R^1R^2PCl) and an organometallic (RMgX, RLi) (equation 13) or by the reaction of phosphonous dihalides (e.g. $RPCl_2$) and a sequence of organometallics of different reactivity.[111] An alternative to the latter case is reaction of dihalide with a mixture of organometallics[109,110] (equation 20). Again, the choice is dictated by the availability of the starting materials, and also in the latter case by the consideration that the groups on the organometallics must be sufficiently different to allow separation of the desired asymmetric product from the unsymmetrical by-products. An example of the application of this idea is the synthesis of asymmetric arylphosphines[111] according to equation 21. However, the difficult nature of this approach is illustrated by the mixture of products that results from the use of Grignard reagents only, shown in equation 22. Recently, more progress has been made; for example, high yields of these tertiary phosphines are obtained (equation 23) when both the organolithium and the alkyl chloride are added simultaneously to a cyclopolyphosphane (**47**, R^1, R^2, R^3 = alkyl, R_3Si, R_3Ge or R_3Sn)[112].

$$R^1PCl_2 + R^2M + R^3M^1 \longrightarrow R^1R^2R^3P + R^1R^2{}_2P + R^1R^3{}_2P \quad (20)$$

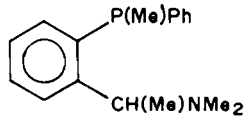
$$PhPCl_2 + Ar^1ZnCl + Ar^2Li \longrightarrow PhPAr^1Ar^2 \quad (21)$$

$$PhPCl_2 + EtMgBr + PhCH_2MgCl \longrightarrow PhEt_2P(24\%) + EtPh(PhCH_2)P(41\%) + Ph(PhCH_2)_2P(18\%) \quad (22)$$

$$(R^1P)_n + nLiR^2 + nR^3Cl \longrightarrow nR^1R^2R^3P + nLiCl \quad (23)$$

(47)

Some recent examples of the synthesis of asymmetric phosphines by the electrophilic route are the following: (i) a case in which both organolithium and Grignard reagents are used and the leaving group is other than a halide is seen in the synthesis of the phosphine **48** by reaction of the *o*-lithioaromatic with $Ph(Cl)PNEt_2$ and subsequent reaction with methylmagnesium bromide[113,114]; (ii) another case in which the leaving group is not a halide is the use of optically active phosphinites $RR^1P(OR^2)$ to generate enantiomeric phosphines by reaction with organometallics (see Section VII); and (iii) a combination of an organocadmium reagent with Grignard or organolithium can be used to replace sequentially (in one pot) the two chlorines of $PhPCl_2$ with different groups[115].



(48)

III. PREPARATION VIA NUCLEOPHILIC PHOSPHORUS FROM METAL PHOSPHIDES

This section is the obverse of Section II. In this case, phosphorus acts as the nucleophilic centre attacking an electrophilic carbon according to general equations 24–27. Once again we do not see the variety of nucleophilic species that are used in the formation of carbon—carbon bonds[116] and, although there are examples of all of the usual types of carbon electrophiles[116], organic halides are by far the most common. Unlike the electrophilic phosphorus route, the nucleophilic phosphorus route can be used for the synthesis of primary and secondary phosphines following equations 25–27 ($R^1 = H$).

$$P^{3-} + 3RX \longrightarrow R_3P + 3X^- \quad (24)$$

$$R^1P^{2-} + 2RX \longrightarrow R^1R_2P + 2X^- \quad (25)$$

$$R^1{}_2P^- + RX \longrightarrow R^1{}_2RP + X^- \quad (26)$$

$$R^1R^2P^- + RX \longrightarrow R^1R^2RP + X^- \quad (27)$$

The required phosphide and organophosphide anions can be made[2,112] in many ways which are very similar to the generation of carbanionic species[116]. Thus, although phosphine and primary and secondary phosphines are very weak acids (e.g. $PhPH_2$ has $pK_a = 24$[117]), they can be metallated by strong bases (e.g. sodium or potassium in liquid ammonia or *n*-butyllithium) to give the corresponding anions (equations 28–32). Other methods analogous to carbanion generation can also be used, such as reductive metallation (equation 33), halogen–metal exchange (equation 34) and metal–metal exchange (equation 35). In addition, the treatment of a tertiary phosphine with an alkali metal may result in the breakage of a P—C bond[118–120] (equation 36), and finally the binary metal phosphides are made by direct combination of phosphorus with a metal, usually sodium or potassium. Which of these routes is used will be dictated by availability of the starting materials, reactivity considerations and the experimental situation, e.g. the conditions to be used in the subsequent addition[2]. Recent innovations include the following: (i) the use of sonication to assist the metallation step, especially in P—C bond cleavage reactions with lithium[120–123] and sodium naphthalene[124]; (ii) the use of photostimulation in the reaction of sodium diarylphosphides in liquid ammonia[125–128]; (iii) the use of concentrated aqueous alkali in dmso as base[129]; and (iv) electroreduction of chlorophosphines with a sacrificial magnesium anode in the presence of alkyl halides, which probably involves organophosphides[130]. As in the case of organometallic reagents, organophosphides, especially lithium organophosphides, can display varying degrees of structural association[131,132].

$$PH_3 + KNH_2 \longrightarrow KPH_2 + NH_3 \quad (28)$$

$$RPH_2 + Na \longrightarrow RPHNa + 1/2H_2 \quad (29)$$

$$RPHNa + Na \longrightarrow RPNa_2 + 1/2H_2 \quad (30)$$

$$Ph_2PH + NaNH_2 \longrightarrow Ph_2Na + NH_3 \quad (31)$$

$$Me_2PH + LiBu \longrightarrow Me_2PLi + BuH \quad (32)$$

$$Ph_2PCl + 2Li \longrightarrow Ph_2PLi + LiCl \quad (33)$$

$$Ph_2PCl + BuLi \longrightarrow Ph_2PLi + BuH \quad (34)$$

$$MgBr_2 + 2Ph_2PK \longrightarrow Mg(Ph_2P)_2 + 2KBr \quad (35)$$

$$Ph_3P + 2Li \longrightarrow Ph_2PLi + PhLi \quad (36)$$

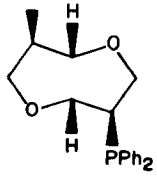
Although not strictly a synthetic method for phosphines, it is appropriate to note that recently there have been a number of cases in which metallation occurs at an atom or group adjacent to phosphorus in a phosphine[10] or a coordinated phosphine[7]. Reaction of the anion so produced with an electrophile then leads to a new phosphine. For example, the reaction of lithiomethyldiphenylphosphine with (i) hexafluoroacetone and di-*tert*-butyl ketone gives phosphines [$Ph_2PCH_2C(CF_3)_2OH$] and $Ph_2PCH_2C(OH)(t\text{-}Bu)_2$[133,134], respectively and (ii) various metal halides leads to phosphinomethyl derivatives of metals, e.g. [$(Cp)_2Ti(CH_2PPh_2)_2$]; other metals used include aluminium[135–137] and zirconium[138].

A. Tertiary Phosphines

The reactions of binary metal phosphides and organohalides follow equation 24 to give symmetric tertiary phosphines[1]. They are carried out in an inert solvent using stoichiometric amounts of the halide to avoid contamination with phosphonium salts[1]. Completion is effected by refluxing for up to 24 h, followed by removal of the metal halide by either filtration or washing, the phosphine being obtained from the residual organics by distillation. Both alkyl and aryl halides can be used and the yields are generally good[1]. However, the use of this route for these phosphines is not common compared with the alternative electrophilic phosphorus route (Section II, equation 10), because phosphorus trihalides are more readily available than metal phosphides.

Unsymmetric tertiary phosphines are also good candidates for synthesis using the nucleophilic phosphorus route, according to equations 25 and 26. The choice between the phosphonous (equation 25) and phosphinous (equation 26) routes is again based on the availability of starting materials. The procedures are similar to those for the symmetric phosphines given above and again the yields can be high. Also, again one will usually have the competing option of using an electrophilic phosphorus route (Section II, equations 11 and 12), but in this case the choice is not as clear since the starting materials may have similar availabilities and considerations of reactivity and the number of side-products may dictate the chosen route. Some recent examples based on equations 25 and 26 are as follows: (i) the synthesis of the phosphines **49** from lithioorganophosphides and α-chloromethyl sulphide[139]; (ii) the substituted diphenylphosphines **50**[140] and **51**[141] from potassium diphenylphosphide and suitable halide precursors; (iii) among many examples where the leaving group on carbon is tosylate or mesylate are the synthesis of the chiral diphosphines **52–54**[142,143]; (iv) vinyl and aryl halides can also be used as electrophiles but the reaction can be more complex and unpredictable with metal–halogen exchange commonly occuring[144–146]; (v) multiple bonds can also act as acceptors[2], a recent example being the use of pentamethylfulvene as the electrophile for lithium diphenylphosphide in the synthesis of **55**[147]; and (vi) the similar use of the stabilizing influence of the cyclopentadienyl system is seen in the use of the spiroheptadiene **56** as the electrophile in equation **37**[148,149].

Ph_2PCH_2SMe **(49)** $Ph_2P(CH_2)_nSPh$ **(50)** $RCH(NMe_2)CH_2PPh_2$ **(51)**



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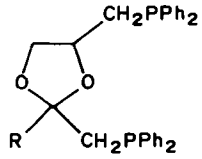

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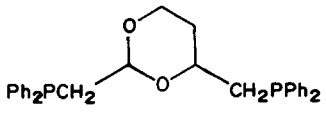

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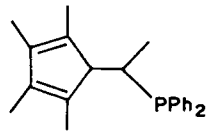

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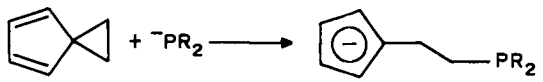
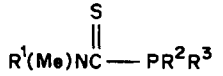


(56) (37)

Similar considerations apply to the synthesis of asymmetric phosphines using the nucleophilic phosphorus route following equation 27. However, in this case the choice between it and the alternative electrophilic route (Section II, equation 13) is much more finely balanced and the methods have been used to similar degrees. Some recent examples of the use of the nucleophilic phosphorus route to make asymmetric tertiary phosphines are the following: (i) the syntheses of the thiocarbamoylphosphines **57** from lithioorganophosphides and thiocarbamoyl chlorides[150,151]; (ii) the phosphines **58** from *o*-chlorophenyltrimethylstannane and simple phosphides[152]; (iii) the use of ethylene sulphide as an electrophile towards methyl phenyl phosphide to give (2-mercaptoethyl)methylphenylphosphine[153]; and (iv) the stereospecificity of phosphide additions is illustrated by, for example, the preparation of 1-menthylmethylphenylphosphine from methylphenylphosphide and 1-neomenthyl chloride and *vice versa*[154].

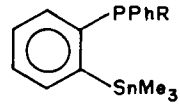


R^1 = Me or Ph

R^2 = Ph, alkyl or Me_3Si

R^3 = Ph or Me_3Si

(57)



R = Ph or Bu^t

(58)

Alkynes can be used as electrophiles for organophosphides, and the reaction can be made stereoselective to give either the *cis* or *trans* product. For example, in the reaction of diphenylphosphide and phenylacetylene in thf the *trans* product is predominant, whereas the *cis* product results when amines are included in the reaction[155].

B. Secondary Phosphines

Secondary phosphines may be made following equation 25 and 27 ($R^1 = H$). The latter is more common and the metal phosphide required for it is made by the action of a metal, usually sodium or potassium[156–161], on a primary phosphine, according to equation 29. Care has to be taken that a second substitution does not occur to give RPM_2 (equation 30). The reaction can be carried out in liquid ammonia[156,162,163], but a more convenient procedure is to reflux the finely divided metal with the phosphine in an inert solvent, keeping the temperature between 50 and 80 °C since above 90 °C the second substitution may occur. Treatment of the derived phosphine with an organohalide then generates a secondary phosphine and obviously the potential exists for this to be asymmetric (i.e. RR^1PH) if a halide is used which bears a group different from that on the original primary phosphine. A variety of electrophilic species have been used in this route to secondary phosphine, including alkyl halides[156,157,161–164], episulphides[165–167], sodium salts of halocarboxylic acids[168,169] and chloroalkylamines[170,171]. The reaction of organophosphide and 1,2-dichloroalkanes yields phosphiranes[172].

If, on metallating the primary phosphine, the dimetallated product is the only product obtained, then a remedy is to react it with another equivalent of the primary phosphine according to equation 38 (M = Na)[157]. Although it is more common to obtain secondary phosphines from the monometallated phosphide (equation 27, $R^1 = H$), it is possible to use equation 25. ($R^1 = H$) via a formally dimetallated phosphide. However, the yields are low. An example can be seen in the decomposition of calcium dihydrogenphosphide in a vacuum in the presence of methyl chloride according to equations 39 and 40[163]. Another example is the use of sodium phenylphosphide in the preparation of (2-pyrrolidinylmethyl)phenylphosphine, which was subsequently alkylated by treatment with sodium in liquid ammonia and butyl chloride[173].

$$RPM_2 + RPH_2 \longrightarrow 2RPHM \tag{38}$$

$$Ca(PH_2)_2 \cdot 6NH_3 \longrightarrow CaPH + PH_3 + 6NH_3 \tag{39}$$

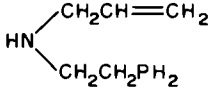
$$CaPH + CH_3Cl \longrightarrow Me_2PH \tag{40}$$

C. Primary Phosphines

The metal phosphide formed according to equation 28 can be reacted with an organohalide to give a primary phosphine (equation 41). The metal is usually sodium, calcium or lithium and the reaction is often carried out in the liquid ammonia used as the solvent for the generation of the phosphide, although this may lead to nitrogen-containing impurities. The alternative method of generating the phosphide using an alkyl- or aryllithium base leads to a cleaner reaction. Good yields of primary phosphines are also obtained from the alkylation of $NaPH_2$ in hexamethylphosphoramide[172].

$$MPH_2 + RX \longrightarrow RPH_2 + MX \tag{41}$$

Some examples of the synthesis of primary phosphines via nucleophilic phosphorus are as follows: (i) the phosphine **59** from potassium dihydrogenphosphide and allyl(2-chloroethyl)amine[174]; (ii) the reaction of 2-bromo-*p*-cymene with $NaPH_2$ or $LiPH_2$ to give a mixture of phosphines **60** and **61**[175]; (iii) the reaction of potassium phosphide (KPH_2) with benzoate esters, in the presence of a crown ether, leads initially to KPHCOPh which could be further alkylated to PhCOPHMe or protonated to benzoylphosphine[176]; and (iv) both monometallated phosphine and primary phosphines have been used in the phosphinylation of haloalkylpyridines to give phosphines **62** ($n = 1, 2$; R = alkyl).[177]



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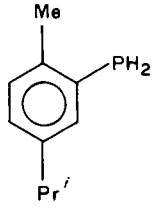

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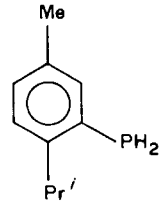

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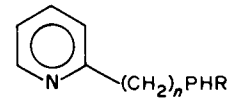


n = 1, 2
R = H, Pr', Bu', Ph

(62)

IV. PREPARATION BY REDUCTION OF OTHER PHOSPHORUS COMPOUNDS

Reduction is a very useful and popular route to phosphines. Within the very large range of reduction reactions giving phosphines as products, it is convenient to distinguish two categories. First, there are reductions which do not involve the formation of a new P—H bond; thus phosphine oxides, sulphides and phosphonium salts can all be reduced and the products are usually tertiary phosphines. Second, there are reductions which do form new P—H bonds; phosphinic and phosphinous acid derivatives are reduced to secondary phosphines and phosphonic and phosphonous acid derivatives are reduced to primary phosphines.

The stereochemistry of many of these reduction reactions has been investigated and a number of them are highly stereospecific. Thus they have great utility in the synthesis of chiral phosphines (see Section VII).

A. Tertiary Phosphines

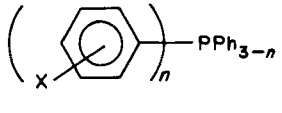
1. By reduction of phosphine oxides and sulphides

$$R_3P{=}X \xrightarrow{\text{reduction}} R_3P$$

$$X = O, S$$

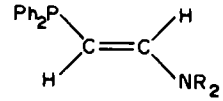
It is often the case that a phosphine can only be made via the phosphine oxide, which then has to be reduced. The reduction of phosphine oxides can be achieved using a number of reagents, the choice being dictated by the sensitivity of the oxide to reduction and the stereochemistry required in the product phosphine.

By far the most popular reductants are silanes, because they have broad scope, are easy to use and give clean stereochemistry and high yields[178–196]. Of the silanes, the most popular have been trichlorosilane[178,186,187,189–193], hexachlorodisilane[187,188,194] and phenylsilane[184,195]. Typical procedures for these reductions involve simply mixing the oxide and excess of silane, both in an inert solvent, in a flask under nitrogen. The reaction is often very vigorous and usually spontaneous but may have a slight induction period, so that, although some heat may be necessary to initiate the reaction, it is advisable to have a source of cooling available. A secondary or tertiary amine is often added in the case of the chlorosilanes to scavenge hydrogen chloride. The reaction is completed by refluxing (80–100 °C) and the phosphine is obtained by distillation or recrystallization. Another reason for the popularity of silanes is that often they can be used in the presence of other functional groups in the molecule[196], e.g. a carbonyl group as in the synthesis by trichlorosilane reduction of the phosphines **63**[196] and the phenylsilane route to dialkylaminovinylphosphines (**64**)[179].



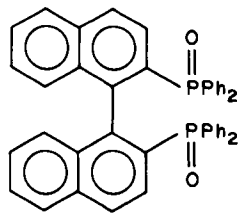
X = CN, CO_2H, CO_2Me

(63)



(64)

The stereochemistry of silane reductions depends on the silane used, the type and strength of base added, whether the substrate is cyclic or acylic and the harshness of the reaction conditions. However, it can be controlled fairly well. Thus, the action of trichlorosilane on acyclic substrates under mild conditions gives retention of configuration whereas the addition of triethylamine produces inversion[187,190,197]. If more forcing conditions have to be used racemic mixtures may result, whereas the use of weaker bases, e.g. pyridine or dimethylaniline[190], will give predominantly retention. The case of cyclic substrates is different and retention[193] is usually observed, although there are a few exceptions[198]. A recent example of stereospecific reduction using trichlorosilane is that of the resolved chiral phosphine oxides **65**[199]. Different reducing agents may give different results. For example, hexachlorodisilane nearly always gives inversion of configuration of acyclic substrates[186,187,200], cyclic substrates again giving retention[188], while phenylsilane usually gives retention[184,201,202].

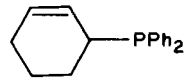


(65)

Lithium aluminium hydride has also been used extensively to reduce phosphine oxides[1,203,204]. However, its use has diminished with the development of the silane reagents. It may still need to be used for recalcitrant substrates or if cost is a major consideration. The usual procedures for $LiAlH_4$ reactions are used[203,204], but one variant is that addition slowly to a cold (temperatures as low as −78 °C) solution of substrate may give better yields[1]. The stereochemistry at phosphorus is usually retained in the reduction[203], although racemization can also occur[204]. Obviously, a disadvantage of the use of $LiAlH_4$ compared with silanes is that many more groups are sensitive to reduction by it. Lithium aluminium hydride can also be used in combination with other reagents, e.g. with cerium(III) chloride $LiAlH_4$ gives a reagent that is capable of reducing phosphine oxides in good yields under mild conditions, but the reaction is not stereospecific[205]. Another example of this combination possibility is that of lithium hydride and certain titanium complexes[206].

Some other reagents that have been used to reduce phosphine oxides are sodium borohydride[2], triphenyl phosphite[2], alanes[207], again in combination with a boron trihalide or ester[208,209], calcium aluminium hydride[210], calcium hydride[180], dialkylaluminium hydrides[211], magnesium and dicyclopentadienyltitanium, which reduces phosphine oxides with at least one phosphorus—aryl bond[212], a combination of sulphur (or selenium) and silicon tetrachloride catalyst which reduces triarylphosphine oxides[213], hydrogen itself via the dichlorophosphorane[2] and many others[2].

Phosphine sulphides are reduced by a similar range of reagents to those used in phosphine oxide reduction and, as before, the choice is made depending on the sulphide to be reduced and on the required product stereochemistry. Again silanes are the preferred reagents[168,185,186], although lithium aluminium hydride[214–216], calcium aluminium hydride[210], phenyllithium[217] and even tertiary phosphines[218,219] have been used. Sodium in toluene reduced the sulphide of the allylic phosphine **66** in good yield[220]. Some reagents selectively reduce P=S in the presence of P=O bonds or other easily reduced functional groups[221]. Studies show that the reduction of P=S can be made to proceed with full retention of configuration at phosphorus[223,224], in particular in Mathey's most recent reduction/complexation route involving iron pentacarbonyl[224b]. In the case of hexachlorodisilane, the stereochemistry of reduction is the opposite of that of the oxide[185].



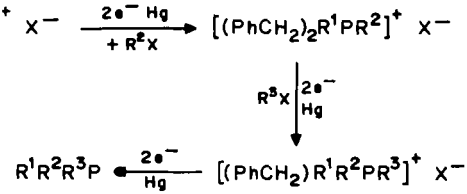
(66)

2. *Reduction of phosphonium salts*

The reduction of phosphonium salts to tertiary phospines must involve the cleavage of a phosphorus—carbon and there are a variety of ways to achieve this.

(a) Electrolytic reduction. This can be carried out using a number of different electrodes, the most popular and economical being lead and mercury cathodes, but carbon anodes surrounded by a clay diaphragm are also used. The procedure is reltively easy and does not require extreme conditions, e.g. temperatures of ca 70–90 °C and 24 V at 2–6 A. The phosphines are obtained, after extraction with diethylether, in good yields (80–90%)[2,225,226].

The product of the reduction depends on the groups present on phosphorus in the phosphonium salt. Some groups are better leaving groups than others, e.g. benzyl groups are cleaved particularly easily, which was taken advantage of in one of the early syntheses of asymmetric tertiary phosphines by sequential cleavage of benzyl groups from tribenzylphosphonium salts as outlined in Scheme 6[227–230].



SCHEME 6

Another advantage of this electrolytic reduction route is that it proceeds stereospecifically with retention of configuration at phosphorus[227,230], so that inclusion of a resolution step in Scheme 6 leads to optically active phosphines (see also Section VII).

The nature of the electrode can have a substantial effect on the product of an electrolytic reduction. For example, in the reduction of $[Ph_3PMe]^+Br^-$, the use of a mercury cathode gives 83% Ph_2MeP and 5.5% Ph_3P whereas a lead cathode gives 40% Ph_2MeP and 53% Ph_3P[172,173]. Unexpected products may also arise[227,228]. Other electrodes which have been used are platinum, tin and copper[226]. Quasiphosphonium salts can also be reduced electrochemically to phosphines[2].

(b) Base-induced cleavage. Quaternary phosphonium salts give tertiary phosphine oxides and hydrocarbons when hydrolysed by an alkali metal hydroxide and, of course, the phosphine oxides may then be reduced to phosphines using the methods outlined in Section IV.A.1. The useful feature of this route is that the hydrolysis step often proceeds with inversion of configuration at phosphorus, the opposite of the result in the electrolytic route (Section IV.A.2a).

However, it is possible, via a β-elimination route, to go directly from a phosphonium salt to a tertiary phosphine, as outlined in equation 42. This route works particularly well if the group X is capable of stabilizing the developing double bond by conjugation. Thus, 2-cyanoethylphosphonium salts are decomposed by ethoxide[231,232], which forms the basis of one of the classic syntheses of optically active phosphines using sequential cleavage from tris- and bis-(2-cyanoethyl)phosphonium salts in a manner similar to that in Scheme 6[232,233]. Hydroxymethylphosphonium salts also undergo β-elimination to give formaldehyde and a phosphine[2,234–245], another source of a similar useful route to optically active phosphines[245]. Note that there is retention of configuration at phosphorus in these routes to optically active phosphines, since the reaction occurs at a position remote from phosphorus.

$$[R_3PCH_2CH_2X]^+ + \text{Base} \longrightarrow R_3P + CH_2{=}CHX + \text{Base} - H^+ \qquad (42)$$

Potassium cyanide in water or dimethyl sulphoxide also induces cleavage of phosphonium salts to phosphines[246–248], again useful in the synthesis of optically active phosphines[249] and both cyanide and alkali metal hydroxide can cleave certain bisphosphonium salts to tertiary phosphines[233,250–253] (equation 43). Tertiary phosphines with chloromethyl groups are obtained from the action of aqueous alkali on chloromethylphosphonium salts[1].

$$[Ph_3PCH_2CH_2PPh_3]^{2+} \xrightarrow{2CN^-} 2Ph_3P + NCCH_2CH_2CN + 2KBr \qquad (43)$$

Some cleavage reagents not only cleave a group but may also react with some of the other groups remaining on the phosphine. For example, tris(dialkylaminomethyl)-phosphines are obtained from the reaction of hydroxymethylphosphonium chlorides and amines[254]. The product acrylonitrile interferes in the decomposition of tetrakis(hydroxymethyl)phosphonium chloride, replacing all the hydroxymethyl groups[255–257].

Acetyl, benzoyl and carboxylethyltrialkylphosphonium salts are decomposed by alkali metal hydroxide to give a tertiary phosphine and the corresponding acid[258,259] (equation 44, $R^1 = CH_3$, C_6H_5, OEt)

$$[R^1COPR_3]^+X^- \xrightarrow{NaOH} R_3P + R^1COOH + NaX \qquad (44)$$

(c) Thermal decomposition. It has long been known that high temperatures (> 300 °C) cause quaternary phosphonium salts to decompose with the loss of one organic group to give tertiary phosphines[260–264]. Good yields of a single product are usually obtained if ethyl is one group on the phosphonium centre due to the reaction shown in equation 45. The tertiary phosphine is then isolated by base treatment of the hydrochloride[260–265].

$$(R_3PC_2H_5)^+Cl^- \longrightarrow CH_2{=}CH_2 + R_3P{\cdot}HCl \qquad (45)$$

The reaction of tris(trifluoromethyl)phosphine with methyl iodide at 240 °C gives perfluoroalkyl tertiary phosphines[266] and the same products are obtained from the reaction of trialkyl- or triaryl-phosphines with perfluoroalkyl iodides as in equation 46[267–269]. Bisphosphonium salts can also be decomposed thermally to give

tertiary phosphines[163].

$$2R_3P + CF_3I \longrightarrow R_2PCF_3 + R_4PI \quad (46)$$

(d) Hydride reduction. Lithium aluminium hydride reduces phosphonium salts with cleavage of one group to the corresponding tertiary phosphines in yields of 50–80%[270,271]. As with alkali metal hydroxide-induced cleavage (Section VI.A.2.b), there is preferential cleavage of a benzyl group and, since only one group is removed at a time, this may also form the basis of a synthesis of asymmetric phosphines via sequential cleavage from tribenzylphosphonium salts similarly to Scheme 6 above. Reduction of alkyltriphenylphosphonium salts with $LiAlH_4$ affords alkyldiphenylphosphines if the alkyl group is primary[272]. A recent example is the cleavage of a furfuryl group from a range of furfurylphosphonium salts[273].

B. Secondary and Primary Phosphines

Primary and secondary phosphines are oxidized very easily, e.g. when exposed to the air. Although it is possible to isolate some secondary phosphine oxides[274–276], the products of these oxidations are almost invariably the phosphonic and phosphinic acids, respectively, produced by tautomerization and further oxidation[15]. The corollary of this is that it should be possible to reduce phosphonic and phosphinic acids and their derivatives to the corresponding primary and secondary phosphines. In practice, a wide range of phosphonic and phosphinic derivatives have been so reduced (equations 47 and 49), as have the corresponding phosphonous and phosphinous derivatives where these are isolable compounds (equations 48 and 50). X in these equations is usually halide (sometimes OR[277], occasionally SR[278] or NR_2[279] and less commonly OH) and in fact the reduction of the appropriate phosphonous and phosphinous halides is the most widely used method for the synthesis of primary and secondary phosphines.

$$RP(O)X_2 \longrightarrow RPH_2 \quad (47)$$

$$RPX_2 \longrightarrow RPH_2 \quad (48)$$

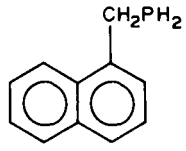
$$R_2P(O)X \longrightarrow RPH_2 \quad (49)$$

$$R_2PX \longrightarrow R_2PH \quad (50)$$

The reagent of choice for these reductions is lithium aluminium hydride[137,156,216,280–301], usually in excess to avoid by-products[289]. Often the reaction is refluxed and followed with an aqueous work-up. However, it has been found more recently that if the $LiAlH_4$ added very slowly to a solution of the phosphorus compound at a temperature as low as $-78\,^{\circ}C$, the yields can be greatly enhanced[290,291]. An illustration of this is the reduction of phenylphosphonous dichloride (dichlorophenylphosphine); the normal $LiAlH_4$ procedures give a yield of 25%[292], which can be increased to 50% with care[292,293], whereas the low-temperature addition procedure gives a yield of 90%[290]. As before, combination reagents may prove effective. Thus, for example, $LiAlH_4$ has been used in combination with trimethylsilyl chloride[277], e.g. in the synthesis of **67**[294].

Ortho-substituted phenylphosphonic acid esters have been reduced selectively by $LiAlH_4$ to form primary phosphines that bear reactive functional groups in the *ortho* position[295], as have the analogous phosphinate esters, e.g. in the synthesis of the phosphine **68**[296]. A recent illustration of the use of $LiAlH_4$ is the reduction of the Diels–Alder adduct of diethyl vinylphosphonate and 1,3-diphenylisobenzofuran with $LiAlH_4$ to give the phosphine **69**, a precursor of vinylphosphine[301].

Alkyl- and aryl-phosphonic dichlorides are also reduced by $LiBH_4$ to the corresponding phosphines[297], as are alkylenebis(phosphonic dichlorides)[299]. Phenylsilane and tri-



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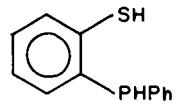

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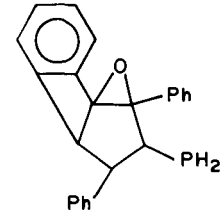
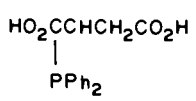


(69)

chlorosilane have also been used to reduce phenylphosphonous dichloride to phenylphosphine in high yield (80%)[1], as has hydrogen sulphide[302].

V. PREPARATION BY CATALYSED ADDITION OF P—H-CONTAINING COMPOUNDS TO MULTIPLE BONDS

Phosphine and primary and secondary phosphines can be added to multiple bonds to yield primary, secondary and tertiary phosphines, respectively. This is usually done catalytically, although in some cases, e.g. if the multiple bond is activated by electron-withdrawing substituents, a catalyst may not be necessary[1,303]; for example, the addition of diphenylphosphine to maleic anhydride leads, after hydrolysis, to **70**[304], and the addition of secondary phosphines to alkyl isothiocyanates gives phosphines, e.g. the chiral phosphine **71**[305]. These reactions have proved particularly useful for the synthesis of cyclic phosphines and polyphosphines[10]. Thus, although there are a large number in the literature[10], only a restricted selection of examples is given to show the applicability of the method. In addition, the addition reactions of P—H compounds with C=O and C=N systems have been reviewed[306]. It is convenient to distinguish between those additions which are ionic and those which are radical in nature.



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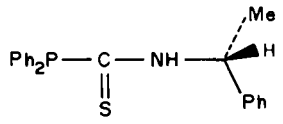


(71)

A. Ionic Addition

The acid-catalysed addition of phosphines to alkenes probably proceeds by a carbocation mechanism, since alkenes which form the most stable carbocations give high yields in the reaction (equation 51)[1]. Typical catalysts which have been used are hydrogen chloride[2], carboxylic acids[2], sulphonic acids and boron trifluoride[1,2]. The reaction is particularly successful for the addition of phosphine to tertiary alkenes, giving high yields of primary phosphines (equation 51)[1]. A recent example is the formation of tertiary phosphines from secondary phosphines and methyl vinyl ethers[307]. However, a general difficulty with the acid-catalysed route is that a nearly stoichiometric amount of catalyst may be required because the phosphine formed may be a strong enough base to neutralise the catalyst[1].

$$R_2C{=}CH_2 + H^+ \longrightarrow R_2C^+CH_3 \xrightarrow{+PH_3} H_3P^+CR_2CH_3 \longrightarrow H_2PCR_2CH_3 + H^+ \quad (51)$$

The base-catalysed addition process has also been known for a long time[1]. Indeed, the 2-cyanoethylphosphonium salts required for the alkali metal hydroxide cleavage route to asymmetric phosphines (see Sections IV.A.2.b and VII) can also be made by this process according to equations 52–54. The catalyst in that case was a two-phase acetonitrile–aqueous potassium hydroxide system and the degree of substitution could be controlled by the ratio of phosphine to acrylonitrile[1]. However, more typically a stronger base is used, such as organometallic compounds, *tert* butoxides and phosphides[2]. Recently, a slightly modified procedure for the base-catalysed addition of diphenylphosphine to acrylonitrile and methacrylonitrile has been reported[308].

$$PH_3 + OH^- \longrightarrow PH_2^- + H_2O \tag{52}$$

$$PH_2^- + CH_2{=}CHCN \longrightarrow H_2PCH_2C^-HCN \tag{53}$$

$$H_2PCH_2C^-HCN + H_2O \longrightarrow H_2PCH_2CH_2CN + OH^- \tag{54}$$

Base-catalysed addition of diphenylphosphine to acetylene in the presence of a phase-transfer catalyst gives high yields of $Ph_2PCH_2CH_2PPh_2$[309]. The base-catalysed route has been developed into a useful synthesis of poly(tertiary phosphine) by the *tert*-butoxide-catalysed addition of a phosphorus—hydrogen bond to the carbon—carbon double bond of various vinylphosphines[310,311] or vinylphosphine derivatives[312], e.g. as in equation 55. In some cases this route to polydentate legands may be improved by coordinating the phosphines initially, i.e. a metal-template-assisted addition[313,314].

$$R_2PH + CH_2{=}CHP(S)(CH_3)_2 \longrightarrow R_2PCH_2CH_2P(S)(CH_3)_2 \tag{55}$$

The reaction of diphenylphosphine catalysed by sodium with a range of vinyl- and styrene-sulphonamides gives the corresponding [(2-aminosulphonyl)ethyl]-diphenylphosphines and their 1-phenyl-substituted derivatives[315].

B. Radical Addition

The free-radical addition of phosphines to alkenes has been much more widely studied and used than ionic additions[1,10]. The reaction follows a chain mechanism as outlined in equation 56[316], and can be initiated by all the usual radical initiators, including ultraviolet light, peroxides and α,α'-azobisisobutyronitrile (aibn)[1].

$$\begin{aligned} &R_2PH + \text{initiator} \longrightarrow R_2P^{\bullet} \\ &R_2P^{\bullet} + RCH{=}CH_2 \longrightarrow R_2PCH_2C^{\bullet}HR \\ &R_2PCH_2C^{\bullet}HR + R_2PH \longrightarrow R_2PCH_2CH_2R + R_2P^{\bullet} \end{aligned} \tag{56}$$

Phosphine and many different primary and secondary phosphines have been used successfully with both activated and unactivated alkenes and alkynes and high yields of single products can often be obtained[1]. Where more than one product can be formed, the distributions can be controlled to a certain extent by varying the molar ratio of phosphine to alkene, e.g. in the addition of phosphine to oct-1-ene[317] the use of a relatively low concentration of phosphine leads to good yields of tertiary phosphines whereas higher concentrations give the primary phosphine. Also, bulky alkenes shift the product ratio in favour of the less substituted phosphine[317,318].

Some recent examples of the use of this method are as follows: (i) the synthesis in quantitative yields of alkylbis(trifluoromethyl)phosphines from the addition at 40 °C with ultraviolet light of bis(trifluoromethyl)phosphine to simple alkenes[319]; (ii) the sequential addition of silanes and secondary phosphines to $\alpha\omega$-dienes under UV light gives silylalkylphosphines (**72**)[320]; (iii) aibn-initiated addition of trimethylsilylphosphine to various alkenes and dienes gives a range of both acylic and cyclic phosphines, from which the trimethylsilyl group is easily removed by hydrolysis, thus leading to primary and

secondary phosphines[321].

$$R_2P(CH_2)_2(CH_2)_n(CH_2)_2SiR_2 \ (n = 1\text{–}4)$$
(72)

As in the case of the base catalysis, the radical-catalysed process has been developed into a useful, and somewhat more general route to poly(tertiary phosphines). Even in those cases where reagents are available for the base-catalysed method, the radical method appears to give higher yields and purer products, especially if ultraviolet irradiation is used. The reactions are fast, give high yields and are efficient not only for the vinyl compounds[322] but also for selected allylic derivatives[322,323] and ω-alkenylphosphines[324].

VI. OTHER METHODS FOR PHOSPHINE SYNTHESIS

There are a considerable number of other methods for the synthesis of phosphines[1,10]. The selection below is intended to indicate those which have been the subject of detailed study, or that have some generality or are particularly useful for certain phosphines.

A. From Elemental Phosphorus

Ultimately all phosphines are synthesized indirectly from elemental phosphorus, usually via trihalides which are made by direct combination[12]. However, under certain circumstances, phosphines can be synthesized directly from white or red phosphorus[1,2,325]. The reagents used are usually either organohalides (with some sort of catalyst or promoter) and/or organometallic reagents and the reactions are usually carried out at high temperatures and/or pressures, often in sealed containers. The yields usually are not very high, although this may be less of a problem if the starting materials are cheap and product isolation is easy[1,325].

Some examples of the synthesis of tertiary phosphines are as follows: (i) the reaction of white phosphorus with an organolithium or phenylsodium and alkyl halides gives unsymmetric tertiary phosphines in 40–50% yields[326,327]; (ii) tertiary phosphines are obtained in high yields (70–80%) when red phosphorus is refluxed with certain alkyl iodides and a catalytic amount iodine[328], and (iii) tris(pentafluorophenyl)phosphine can be made by heating red phosphorus and bis(pentafluorophenyl)thallium(III) bromide[329].

Examples of primary and secondary phosphines made from elemental phosphorus are the following: (i) the interaction of phenyllithium and phenylmagnesium bromide with elemental phosphorus gives a low yield (15–35%) of diphenylphosphine; dibutylphosphine and butylnaphthylphosphine may be similarly prepared[327,330]; (ii) a very early example is the reaction of white phosphorus and aliphatic alcohols in a sealed flask which gives low yields of primary phosphines[331]; and (iii) white phosphorus, aqueous sodium hydroxide and alkyl halides react to give primary phosphines according to equation 57, with yields in the range 20–30%[15].

$$P_4 + 6NaOH + 2RI \longrightarrow 2RPH_2 + 2NaI + 2Na_2HPO_3 \qquad (57)$$

The electrolysis of white phosphorus leads to both primary and secondary phosphines but the yields are very low (10%)[2,332].

B. From Other Phosphines

1. By combined alkylation and dehydrohalogenation

Alkylation of phosphine, primary phosphines or secondary phosphines, followed by removal of the elements of hydrogen halide from the resulting phosphonium salt, leads to

the synthesis of primary, secondary or tertiary phosphines, respectively, according to Scheme 7. (R,R^1 = alkyl, H; R^2 = alkyl; X = halide, often iodide). This was one of the original methods of phosphine synthesis[333] and in many cases the yields can be very high[2,15,63,318,334].

$$RR^1PH + R^2X \longrightarrow RR^1R^2PH^+X^-$$

$$RR^1R^2PH^+X^- + NaOH \longrightarrow RR^1R^2P + NaX + H_2O$$

SCHEME 7

A number of different reaction conditions have been used to expedite this sequence; the alkylation can be carried out at room temperature in methanol or by heating the neat reactants with subsequent treatment by base[15,63,318,334]; the $AlCl_3$ complex of the phosphine can be used[318], alkylation may be done in the presence of the base in dmso[335] or phosphonium iodide itself may be alkylated in the presence of zinc oxide at 100–180 °C[12,63,335–337].

Although it is possible to obtain secondary and tertiary phosphines from the reaction of phosphine with alkyl halides, the reaction usually gives more than one product and it is more advantageous to use primary and secondary phosphines, respectively[15,63,318]. Alkylacylphosphines can be synthesized in good yields by this route using acyl halides[2,336]. Recent examples of the application of this method are the synthesis of di(*tert*-butyl)(cyclopropylmethyl)phosphine from the quaternization of di(*tert*-butylphosphine with cyclopropylmethyl bromide[338] and of (1-adamantyl)dimethylphosphine via methylation of 1-adamantylphosphine[339].

2. *By condensation/elimination reactions*

Phosphines bearing a hydrogen react with, for example, amines and alcohols by replacement of the hydrogen and the elimination of a small molecule as shown in equations 58 and 59[2].

$$R_2PH + NR^1{}_3 \longrightarrow R_2PR^1 + HNR^1{}_2 \quad (58)$$

$$R_2PH + R^1OH \longrightarrow R_2PR^1 + H_2O \quad (59)$$

Related to this is the phosphorus-modified Mannich reaction[340,341], represented overall by equation 60, which has recently been reviewed[342]. Also related to the above and to the nucleophilic phosphorus route, but of more recent application, are the reactions of trimethylsilyl- and similarly substituted phosphines with organic chlorides, according to equation 61, which are proving to be of fairly general use. Thus vinyl chlorides[343,344], acyl chlorides[345,346a] and, with a catalyst, aryl halides,[346b] among others[2], can be used.

$$R_2PH + CH_2O + HNR^1{}_2 \longrightarrow R_2PCH_2NR^1{}_2 + H_2O \quad (60)$$

$$Me_3SiPR_2 + R^1Cl \longrightarrow R^1PR_2 + Me_3SiCl \quad (61)$$

3. *From phosphine*

Tertiary phosphines containing hydroxymethyl groups are formed when PH_3, RPH_2 or R_2PH compounds are reacted with aldehydes[1,2]. In particular, tris(hydroxymethyl)phosphine is made from formaldehyde and phosphine (equation 62)[2,347,348]. A recent example is the formation of (1-adamantyl)bis(hydroxymethyl)- phosphine from 1-adamantylphosphine and formaldehyde with acid catalysis[339].

$$PH_3 + CH_2O \longrightarrow P(CH_2OH)_3 \quad (62)$$

Finally, good yields (75%) of primary and secondary phosphines are obtained from PH_3 with alcohols over dehydrated aluminosilicate[306].

C. From Polyphosphines

Much of the chemistry of diphosphines and polyphosphines involves cleavage of the phosphorus—phosphorus bond and phosphines may be obtained from the products by methods discussed earlier in this chapter. For example, alkali metals and organometallics react with diphosphines to give phosphide anions (together with phosphines in the latter case) (equations 63 and 64)[1,2,117], strong acid cleavage leads to phosphonium salts of secondary phosphines (equation 65)[12] and hydrolysis, usually assisted by alkali, gives secondary phosphines (equation 66)[117].

$$R_2PPR_2 + 2M \longrightarrow 2R_2PM \tag{63}$$

$$R_2PPR_2 + LiR^1 \longrightarrow R_2PLi + R_2PR^1 \tag{64}$$

$$R_2PPR_2 + 2HCl \longrightarrow R_2P^+H_2Cl^- + R_2PCl \tag{65}$$

$$(CF_3)_2PP(CF_3)_2 + H_2O \longrightarrow (CF_3)_2PH + (CF_3)_2POH \tag{66}$$

It is possible to form a phosphonium salt from a biphosphine by treatment of tetraalkylbiphosphines with alkyl iodides. Either the diphosphine is monoquaternized (equation 67) or cleaved (equation 68). Which occurs depends on the attached groups; electronegative and bulky substituents usually leading to cleavage (e.g. R = CF_3, Ph, *t*-Bu, *c*-C_6H_{11})[1,117]. The direct route (equation 68) requires excess of halide and elevated temperatures[349,350].

$$R_2PPR_2 + MeI \longrightarrow R_2PP^+(Me)R_2I^- \tag{67}$$

$$R_2PPR_2 + MeI \longrightarrow R_2PI + R_2PMe \tag{68}$$

Secondary phosphines are obtained directly from the reduction of diphosphines and diphosphine disulphides, and this is a useful route since the starting material is often readily available. As in Section IV.B, the usual reductant is lithium aluminium hydride in various ether solvents[1,2], although high yields (90%) can also be achieved with hydrogen and Raney copper[280,351,352].

Thermal decomposition of diphosphines can also be used to generate phosphines[353,354].

D. By Disproportionation of Secondary Phosphine Oxides

Dialkylphosphine oxides undergo a thermal disproportionation according to equation 69, usually at high temperatures[355]. Recently, an improvement resulting in milder conditions for the reaction has been reported using a catalyst system generated by the addition of carbon tetrachloride[356].

$$2R_2P(O)H \longrightarrow R_2PH + R_2P(O)OH \tag{69}$$

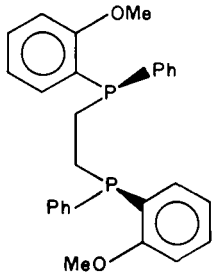
E. By Rearrangement of Phosphorus Ylides

The phosphorus analogue of the Stevens rearrangement[357] should provide access to phosphines, as shown in equation 70. However, as yet there are only a few examples of such reaction, both catalysed[358] and uncatalysed[359].

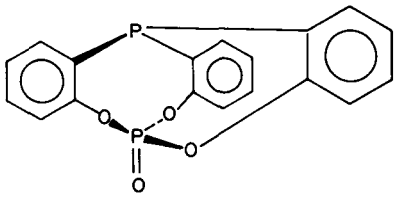
$$R_3P{=}CH_2 \longrightarrow R_2PCHR \tag{70}$$

VII. SYNTHESIS OF CHIRAL PHOSPHINES

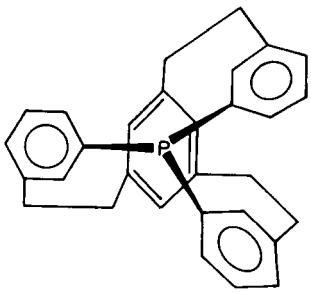
Optically active phosphines are of great interest, particularly by for their use as ligands in catalysts for various asymmetric syntheses[360,361]. Chiral phosphines may derive their chirality by virtue of having either a chiral centre at phosphorus or at another atom, usually carbon. The latter have been much more widely synthesized and used than the former; for example, in the field of asymmetric hydrogenations, of all the chiral phosphines giving a high enantiomeric excess only one, albeit one of the best (**73**), is chiral at phosphorus[362–364]. An additional possibility is that both phosphorus and its substituents may have chiral centres, but these are even rarer than the first category (for examples see refs 365 and 366). Note also that, as in other areas of stereochemistry, a chiral phosphine does not necessarily have to be asymmetric, as has been demonstrated recently by Sharpless and coworkers[367,368] in their syntheses of the dissymmetric phosphines **74** and **75**.



(**73**)



(**74**)



(**75**)

We shall not be concerned here with phosphines that are not chiral at phosphorus, which are made by application of the methods described in previous sections using fragments chiral at carbon. Further, the subject has been reviewed[365,366] and so we present here an overview only.

To make useful quantities of optically active phosphines, two issues have to be addressed: first, how to place efficiently three different groups on phosphorus, and second, how to achieve this with a high degree of stereocontrol. It can be seen from the previous sections that great progress has been made recently with the first objective. Unfortunately, however, those methods most efficient at placing groups on phosphorus (Sections II and III) have not yet been made amenable to facile stereocontrol (with one exception—see Section VII.D.1). Therefore, various strategems have been developed to meet the second

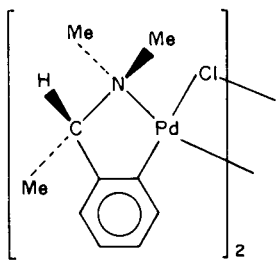
requirement. These strategems make use of known stereospecific reactions in phosphorus chemistry, some of which have been mentioned earlier, and it is appropriate to enumerate these as far as they are relevent to the following discussion.

(a) The reduction of phosphine oxides can be done with retention or inversion with a high degree of stereocontrol (see Section IV.A.1). However, although there are examples which fail to give good stereocontrol in both cases, those methods giving inversion appear to be more reliable[365].
(b) Oxidation of phosphines to the more optically stable phosphine oxides with, for example, hydrogen peroxide proceeds reliably with retention of stereochemistry[369]. Note that it is often more convenient to separate diastereomeric phosphines by chromatography of the corresponding phosphine oxides[154], and enantiomeric phosphine oxides can be separated by liquid chromatography on a chiral stationary phase[370]. Also note that in some cases it may be necessary to synthesize a particular enantiomer of a phosphine by first making the mirror image, then oxidizing it with retention and reduction with inversion[365].
(c) Quaternization of phosphines to give phosphonium salts proceeds with retention[2,371].
(d) Electrolytic reduction of phosphonium salts proceeds with retention (Section IV.A.2.a).
(e) β-Elimination from phosphonium salts also proceeds with retention (Section IV.A.2.b).
(f) Alkali metal hydroxide hydrolysis of phosphonium salts leads to phosphine oxides with inversion of configuration in favourable cases[372], but there are many exceptions[365].
(g) Phosphinate esters, $R^1R^2(OR)P{=}O$, give phosphine oxides, $R^1R^2R^3P{=}O$, on treatment with an organometallic reagent MR^3, the reaction proceeding with inversion of configuration in favourable cases[373]. Phosphonate esters react similarly.

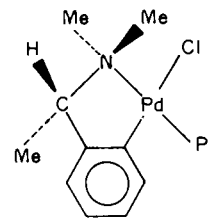
The reactions have been combined into the various schemes for the synthesis of chiral phosphines discussed below. Finally, it should be noted that the optical stability of phosphines may also be a matter of concern, in that racemization will occur in many cases on heating to 80–100 °C[373,374].

A. The Complexation Method

In principle, the most direct route to optically active phosphines is to resolve the racemic phosphine by making diastereomeric transition metal complexes, and in fact this has been done in some cases. For example, complex **76** reacts with racemic triarylphosphines to give the diastereomeric complexes **77**. These could be separated by fractional crystallization



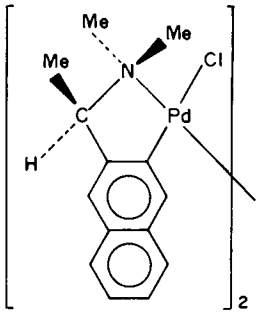
(**76**)



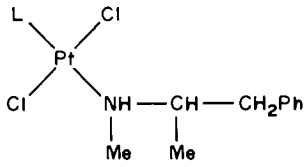
P = PPh (α-Naph)(*o*-MeC_6H_4)
P = PPh (α-Naph)(*p*-$EtOC_6H_4$)
P = PPh (*t*-Bu) Me.

(**77**)

and the enantiomeric phosphines liberated by decomplexation with 1,2-bis(diphenylphosphino)ethane[375]. Similarly, aryldialkylphosphines were resolved by the use of complex **78**[376], the 1,2-naphthyl analogue of which having also found use in resolution[377,378]. Another example is the use of the complex **79**[379]. Surprisingly however, the method has not come into general use, possibly because fractional crystallization has to be used, which may not be successful in all cases[367,368], the other optically active ligands may have to be made and perhaps because the expensive metals have to be recycled.



(**78**)



(**79**)

B. The Phosphonium Salt Method

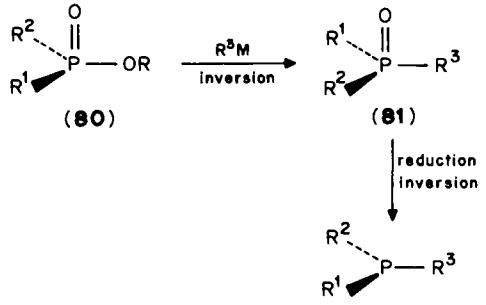
Phosphonium salts offer the possibility of a more classical approach to the resolution of phosphorus compounds since diastereomers can easily be formed by the use of a chiral counter ion. Indeed, the first practical route to chiral phosphines was that of Horner[371] using the dibenzoyltartrate salts, which remain the salts of choice[365,380].

Once the salts are separated (again usually by fractional crystallization), they can be converted to phosphines by (i) electrolytic cleavage (retention)[371], (ii) β-elimination when applicable (retention)[381,382] or (iii) hydrolysis to the phosphine oxide (inversion) followed by reduction (inversion or retention)[365]. A recent example of the use of this route is the synthesis of menthylmethylphenylphosphines and their neomenthyl isomers[383]. Although useful, this route has some limitations, especially in cleavage reactions where the stereochemical outcome cannot be fully guaranteed[365].

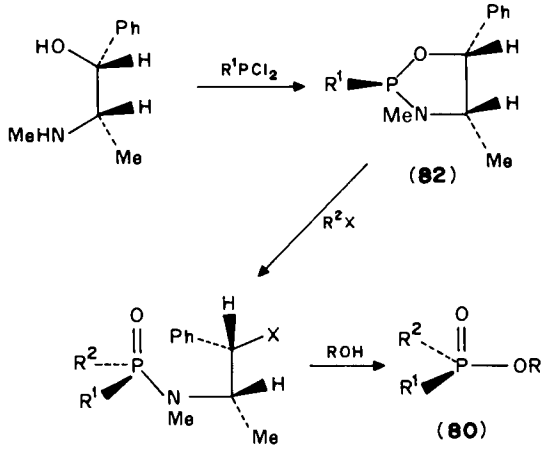
C. The Phosphinate Ester Method

To date this is the most widely used method for the generation of chiral phosphines[365] and its application is illustrated by Scheme 8. The success of the method depends on the availability of chiral phosphinate esters (**80**). In the original version, introduced by Mislow[373], diastereomeric menthyl phosphinate esters (**80**, R = Menthyl) are separated by fractional crystallization and both can be subjected to the sequence leading to both enantiomers of the phosphine. Alternatively, the phosphine oxide **81** could be reduced by a method giving retention leading to the other enantiomer of the phosphine.

Much effort and ingenuity has been expended in the search for methods to generate the chiral phosphinate esters **80**[10,365] so as to make the method more flexible and to avoid the tedious separation of diastereomers. An example of this is shown in Scheme 9 where (−)-ephedrine is used to prepare the oxazaphospholidines **82** by reaction with either R^1PCl_2 or $R^1P(NR_2)_2$[384–387]. These are then subjected[386,387] to Arbusov reaction with R^2X and alcoholysis to give the phosphinate esters **80**. Since only one diastereomer of the



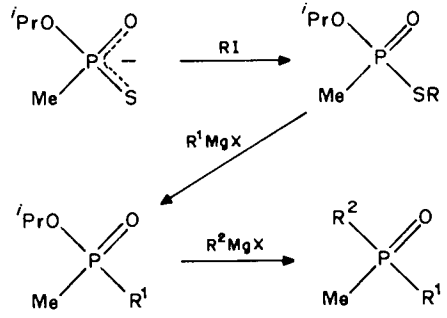
SCHEME 8



SCHEME 9

oxazaphospholidine **82** is produced, the resulting phosphinates have high enantiomeric excess. The other enantiomers are available by initial use of R^2PCl_2 followed by R^1X.

Instead of using a phosphinate, an alternative is to use a chiral phosphonate, $R^1(OR^4)(OR^5)P{=}O$, and react it sequentially with two organometallic reagents, MR^2



SCHEME 10

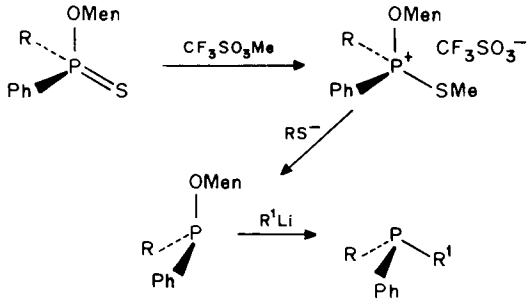
and MR^3, to lead to the phosphine oxide **81**. This works well, for example, when a cyclic phosphonate derived from a carbohydrate precursor is used[365]. Another route, shown in Scheme 10, which has potential generality starts from readily available optically active *O*-isopropylmethylphosphonothioic acid salts[388], members of the very restricted chiral phosphorus pool[365]. The success of the method is due partly to the preferential initial displacement of the alkylthio group and also to the high degree of stereospecificity in the addition reactions[388].

D. Other Methods

1. Phosphinites

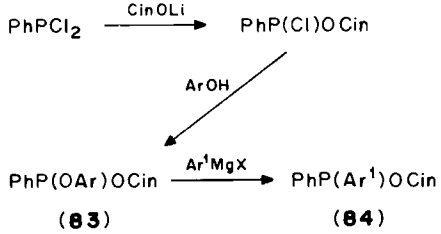
One of the most direct syntheses of chiral phosphines would be to use the electrophilic phosphorus route (Section II) with a chiral electrophile. This has been achieved[365] using chiral phosphinites as shown in equation 71. Again, a good deal of ingenuity has had to be used to make the requisite phosphinites. One approach via menthyl phosphinites[389] is outlined in Scheme 11. These then yield phosphines, with inversion, on treatment with organolithium compounds[389].

$$R^1R^2P(OR) + R^3M \longrightarrow R^1R^2R^3P \qquad (71)$$



SCHEME 11

Again, instead of using a phosphinite, a phosphonite approach can be used as shown in Scheme 12 using the phosphonous chloro esters of cinchonine or cinchonidine. The phosphonites **83** are obtained with high diastereomeric purity (if OAr is bulky), as are the resultant phosphinites **84**. Treatment of **84** with methyllithium then leads to arylmethylphenylphosphines of high enantiomeric purity[390]. A similar example is the sequential reaction of two different bulky organolithium compounds with menthyl or bornyl phosphonites, which also proceed with high diastereoselectivity[391].

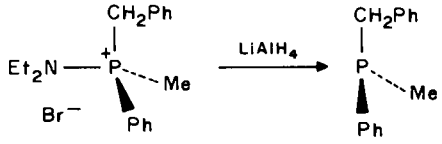


SCHEME 12

One difficulty with these routes is that the phosphinites have low optical stabilities compared with phosphines[365].

2. Amidophosphonium salts

Among the many useful transformations of optically active amidophosphonium salts (**85**) is reduction with lithium aluminium hydride to phosphines with retention of configuration (equation 72)[392].



(**85**)

3. Asymmetric reduction of phosphine oxides

As already mentioned, phosphine oxides have great utility in the synthesis of chiral phosphines because of their easy, stereospecific interconversion. Thus they are used as intermediate points in synthetic schemes and as surrogates for the fractional crystallization and chromatography of phosphines. An additional possibility is the reduction of racemic phosphine oxides using an optically active reducing agent, which has great appeal as a very direct route to enantiomeric phosphines. However, in one of the few studies of this possibility, modification of lithium aluminium hydride with an optically active diamine led to poor enantiomeric excesses in the phosphine products[393].

4. Asymmetric alkylation/dehydrohalogenation

In a reaction based on those noted in Section VI.B.1, Crisp *et al.*[394] reported that the alkylation of phenylphosphine with methyl iodide in the presence of triethylamine within the coordination sphere of a chiral iron complex leads to a 4:1 mixture of the diastereomers of the coordinated chiral secondary phosphines and to the phosphines themselves if a suitable displacement reaction can be found.

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The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

CHAPTER 8

The preparation and reactivity of bi- and poly-dentate phosphines with P—C_n—P bonding

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I. INTRODUCTION

Phosphines containing two or more phosphorus atoms linked together by chains of carbon atoms are of increasing interest as multifunctional ligands. Since the early reports on simple bi- or tridentate tertiary phosphines such as $Ph_2PCH_2CH_2PPh_2$ and $PhP(CH_2CH_2PPh_2)_2$, a considerable number of new and 'tailor-made' phosphine ligands have been synthesized. They produced an extremely rich coordination chemistry, the most striking example being the selectivity in homogeneous hydrogenation by use of chiral phosphines as co-catalysts.

It is the scope of this chapter to review the most important developments covering the literature up to the end of 1987 and part of 1988. We had to be selective and perhaps subjective in order to keep the size of the review within bounds. We feel, however, that we have covered what is essential in this area since 1972. The earlier literature has been collected in monographs and series[1–4]. We shall therefore refer to prior work only if it is required for a full description of a particular topic. Recent reviews[5–7] dealing *inter alia* with bi- and poly-dentate phosphines have appeared. They survey only selected features of the extended chemistry of these compounds. A few scattered reports are devoted to special aspects and these will be cited in the introductory remarks of the appropriate sections.

II. PREPARATION OF BI- AND POLY-DENTATE PHOSPHINE LIGANDS WITH P—C_n—P BONDING

In spite of the large number of publications on the coordination chemistry of bi- and poly-dentate phosphines, it cannot be said that, with a very few exceptions, novel synthetic routes for the syntheses of these ligands have been reported in the period under review. Using well established synthetic procedures, phosphine ligands with novel structural features and unusual coordination behaviour were obtained, however. Mainly four types of reactions have been employed for the syntheses of bi- and poly-dentate phosphines with P—C_n—P bonding:

i. reaction of halogenophosphines with organometallic reagents (RLi, RMgX);
ii. reaction of metallated phosphines R_2PM (M = Li, Na, K) with organic halides;
iii. reduction of phosphine oxides and sulphides or derivatives of phosphinous, phosphonous, phosphinic or phosphonic acids;
iv. addition of PH_3, primary or secondary phosphines to unsaturated phosphorus compounds or olefins and acetylenes.

For the purpose of clarity and readability, the syntheses of phosphine ligands with P—C_n—P bonding are presented in four sections (A–D) according to the different topologies (number of P atoms and nature of 'C_n bridging') met with the ligands to be discussed.

A. Bidentate Phosphine Ligands

The ligand properties of bidentate phosphines are strongly dependent on the nature of the C_n bridging units[8-10]. A great variety of phosphine ligands with different backbones 'C_n' have therefore been synthesized using the preparative methods mentioned above.

1. Bidentate phosphines with methylene bridging, P—CH_2—P

The ability of these ligands to form bridged complexes and to bind reactive transition metal centres in close proximity has led to increasing interest in these and related donor systems (Table 1)[11]. Their synthesis is therefore discussed in detail.

The diprimary phosphine **1.1** has been synthesized by reaction of $Cl_2PCH_2PCl_2$[12] or $[(i\text{-PrO})_2P(O)]_2CH_2$[13] with $LiAlH_4$ or Ph_2SiH_2, respectively, in moderate yields. In a similar way, $LiAlH_4$ reduction of the phosphonates obtained by C—Sn cleavage reactions in phosphonomethyltriorganostannanes with phenylchlorophosphines produces primary secondary and tertiary primary phosphines **2.1** and **3.4**[23].

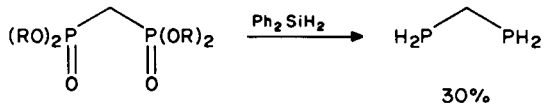
Grignard or organolithium reagents (RMgX, RLi) have been employed for the introduction of organic substituents into $Cl_2PCH_2PCl_2$[18]. For bulky substituents such

TABLE 1. Methylenebisphosphines

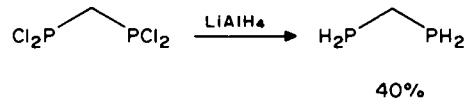
$R_2PCH_2PR_2$ (1)		$R_2PCH_2PRR^1$ (3)		
No.	R	No.	R	R^1
1.1[12,13]	H	**3.1**[12]	H	Me
1.2[12,14-17]	Me	**3.2**[12]	H	*i*-Pr
1.3[17]	Et	**3.3**[12]	H	CH_2Ph
1.4[12,17,18]	*i*-Pr	**3.4**[23]	H	Ph
1.5[17]	*s*-Bu	**3.5**[22]	Ph	Me
1.6[15]	*t*-Bu	**3.6**[12,26]	Me	H
1.7[12]	CH_2Ph	**3.7**[12]	*i*-Pr	H
1.8[19]	*o*-Tol	**3.8**[26]	*t*-Bu	H
1.9[20-22]	Ph	**3.9**[26]	Ph	H
		3.10[12]	CH_2Ph	H

$R_2PCH_2PR^1_2$ (2)			$R^1RPCH_2PRR^1$ (4)		
No.	R	R^1	No.	R	R^1
2.1[23]	H	Ph	**4.1**[12,26]	H	Me
2.2[16,24]	Ph	Me	**4.2**[12,27]	H	*i*-Pr
2.3[24]	Ph	*i*-Pr	**4.3**[12]	H	*t*-Bu
2.4[25]	Ph	*t*-Bu	**4.4**[12]	H	CH_2Ph
2.5[16]	Me	*t*-Bu	**4.5**[26]	H	Ar'[a]
			4.6[26]	H	Ar''[b]
			4.7[28,29]	H	Ph
			4.8[17]	*i*-Pr	Me
			4.9[17]	*i*-Pr	Ph
			4.10[22]	Ph	Me
			4.11[29]	Ph	$2R^1 = (CH_2)_n$ ($n = 2$–4)

[a]Ar' = 2,4,6-$Me_3C_6H_2$
[b]Ar'' = 2,4,6-*t*-$Bu_3C_6H_2$



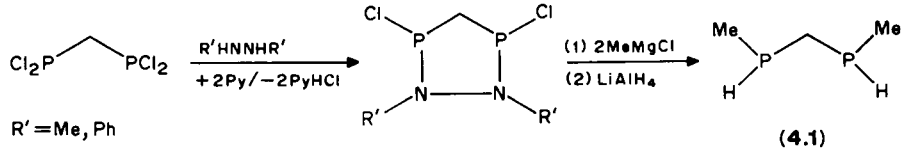
(1)



(2)

as *i*-Pr, *t*-Bu and CH_2SiMe_3 the degree of substitution can be controlled by the stoichiometric ratios. By reduction of the partially substituted derivatives of $Cl_2PCH_2PCl_2$ with $LiAlH_4$ the PH-functional methylenebisphosphines **3.1**–**3.3**, **3.7** and **3.10**[12] and **3.8** and **4.1**–**4.7**[12,26,27,29] may be obtained. With Grignard reagents RMgX (R = Me[12,15,17], Et[17], *i*-Pr[12,17,18], CH_2Ph[12], *s*-Bu[17]) or organolithium compounds RLi (R = *t*-Bu[15]), all four Cl atoms in $Cl_2PCH_2PCl_2$ may be substituted even by bulky groups (e.g. *t*-Bu).

For a partial replacement of the chlorine atoms in $Cl_2PCH_2PCl_2$ by less bulkier substituents (e.g. Me, Ph), protecting groups, e.g. NMe_2[12] or *i*-PrO[29], —NR′—NR′— (R′ = Me, Ph)[26] or —NMe—CO—NMe—[26] have to be introduced in order to prevent complete substitution on reaction with Grignard reagents (equations 3 and 4).



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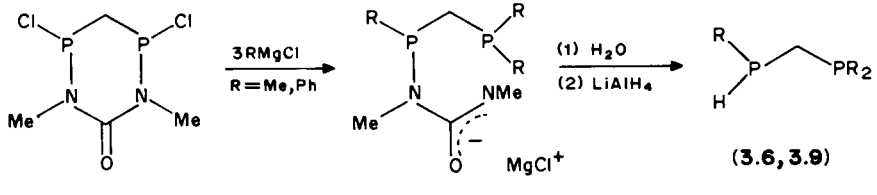


(4)

The formation of the PCP skeleton by reaction of *C*-lithiated methylphosphines, $LiCH_2PR_2$, or the sulphides $LiCH_2P(S)R_2$ with chlorophosphines R^1_2PCl or R^1R^2PCl represents an interesting synthetic approach to unsymmetrical ($R_2PCH_2PR^1_2$ and $R_2PCH_2PR^1R^2$)[16,24,25] and symmetrical methylenebisphosphines ($Me_2PCH_2PMe_2$)[16] (equation 5). As will be shown later, this procedure has also been used in the synthesis of polydentate phosphines with PCP bonding (Section B.1).

$$R_2PCH_3 \xrightarrow[\text{pentane}]{t\text{-BuLi}} R_2PCH_2Li \xrightarrow{R_2^1PCl} R_2P\overset{\frown}{}PR_2^1 \quad (5)$$

(**2.2**–**2.5**)

R = Ph; R^1 = Me, *i*-Pr, *t*-Bu; R = Me, R^1 = *t*-Bu

Methylenebisphosphines may alternatively be obtained by alkylation of organolithium phosphides, R_2PLi, with chloromethyl phosphines, e.g. $ClCH_2PMe_2$[14], or dihalomethanes, CH_2X_2 (e.g. **1.2**). The well known $Ph_2PCH_2PPh_2$ (**1.9**) has been synthesized by reaction of Ph_2PNa with CH_2Cl_2 using either liquid ammonia, thf or dioxane as solvents[21]. The same type of reaction was used for the synthesis of the ditertiary ligand **1.8**[19] (equations 6 and 7).

$$Me_2PCH_2Cl + PMe_2Li \xrightarrow[Et_2O]{-LiCl} Me_2P\overset{\frown}{}PMe_2 \qquad (6)$$

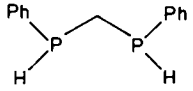
(1.2)

$$2\ Ph_2PH + ClCH_2Cl \xrightarrow[45\text{–}50\ ^\circ C]{H_2O,\ KOH,\ dmso} Ph_2P\overset{\frown}{}PPh_2 \qquad (7)$$

(1.9)

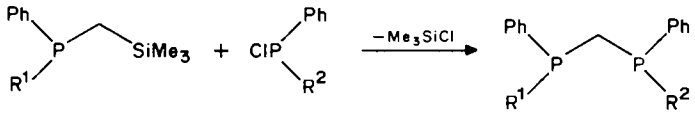
In the two-phase systems dmso/H_2O/KOH and dmf/H_2O/KOH the acidity of primary and secondary phosphines with Ph substituents is several pK units higher than that of water. The phosphines may therefore be deprotonated by OH^- to give the anions $PhPH^-$ on $PhPR^-$, respectively, in equilibrium. This was used by Tsvetkov *et al.*[20] for an elegant high-yield synthesis of $Ph_2PCH_2PPh_2$ according to equation 7. Surprisingly, the disecondary methylenebisphosphine HPhP CH_2PPhH could be obtained in an analogous way in high yield using $PhPH_2$ as starting material[28] (equation 8). The side-products (e.g. PhPHMe) observed in this reaction have been explained by intermediate formation of the reactive phosphaalkene $PhP{=}CH_2$.

$$2PhPH_2 + ClCH_2Cl \xrightarrow{H_2O,\ KOH,\ dmf} \qquad (8)$$



(4.7)

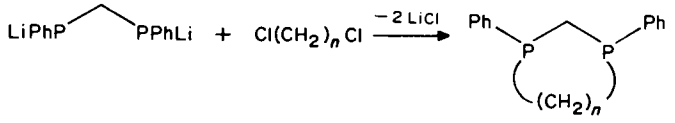
Another novel synthetic route to methylenebisphosphines makes use of a C—Si—cleavage reaction between diorgano[(trimethylsilyl)methyl]phosphines and chlorophosphines $ClPR_2$ (equation 9)[22].



(9)

(1.9, 3.5, 4.10)

Five-, six- and seven-membered 1,3,-diphosphacycles (**4.11**) can readily be synthesized by cyclization reactions of lithiated methylenebisphosphine HPhPCH$_2$PPhH with the appropriate α,ω-dihaloalkanes (equation 10)[29]. The diastereoisomers of the 1,3-diphenyl-1, 3-diphosphorinane (n = 3) were separated by complexation at platinum(II) centres.



(10)

(4.11)

2. Bidentate methylenebisphosphines with substituents in the P—CH_2—P bridging units

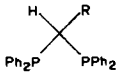
As shown in the preceding section, the synthetic approach to methylenebisphosphines containing the P—CH_2—P skeleton is well established. In contrast only a comparatively small number of bridge-substituted derivatives are known, although one might expect interesting changes of the ligand properties by introduction of appropriate groups R at the central carbon atom. Alkyl- and aryl-substituted derivatives (Table 2) are obtainable in some cases simply by reaction of the corresponding geminal dihalides, e.g. $RHCX_2$, with organolithium phosphides[30] (equation 11).

$$2\ Ph_2PLi + Cl_2CHMe \xrightarrow[-2LiCl]{C_6H_6} Ph_2PCHMePPh_2 \quad (11)$$

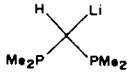
80%
(5.1)

By analogy with arylmethanes $ArCH_2Ar$, the CH_2 groups of methylenebis-

TABLE 2. Methylenebisphosphines with substituted bridging units

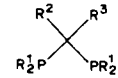


No.	R
5.1[30,31]	Me
5.2[31]	Et
5.3[31]	CH_2Ph
5.4[32]	CH_2OMe
5.5[33]	CHMe(OMe)
5.6[34]	COAr
5.7[35]	p-$C_6H_4NMe_2$
5.8[22,36,37]	Li
5.9[22]	Me_3Si



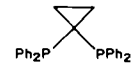
5.10[38]	

No.	R
6.1[39,40]	Me
6.2[39,40]	Et
6.3[39,40]	n-Bu
6.4[39]	Ph

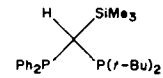


No.	R^1	R^2	R^3
7.1[42]	Ph	Me	Me
7.2[43]	i-Pr	CF_3	OH
7.3[43]	n-Bu	CF_3	OH
7.4[43]	Et	CF_3	OH

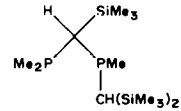
8[41]



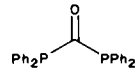
9[44]



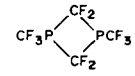
10[45]



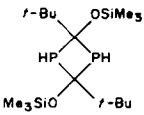
11[46]



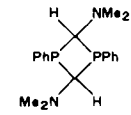
12[47]



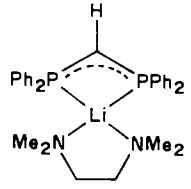
13[48]



14[49]



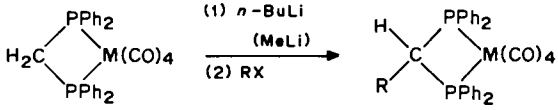
(diphenylphosphine) may be lithiated by methyl- or butyl-lithium to give $Ph_2PCHLiPPh_2$ (**5.8**). Interestingly, lithium does not bind to the bridging carbon in the solid state of the tmeda adduct, but instead contains a CP_2Li four-membered ring system with two Li—P bonds[36]. The anion $[Ph_2PCHPPh_2]^-$ is ambidentate and its reactions with electrophiles have been studied in detail[37]. Charge distribution in this ambidentate anion may be represented by the mesomeric structures I and II.



(**5.8**·tmeda)

$$R_2\bar{P}—\bar{C}H \longleftrightarrow R_2\bar{P}=CH$$
I II

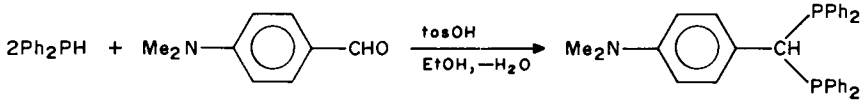
In order to direct the attack of electrophiles to the bridging carbon atom the two phosphorus atoms in **5.8** have to be protected by coordination to transition metal centres. Using this strategy, a range of *C*-alkylated derivatives of $Ph_2PCH_2PPh_2$ have been obtained (equation 12)[31–34,42].



(12)

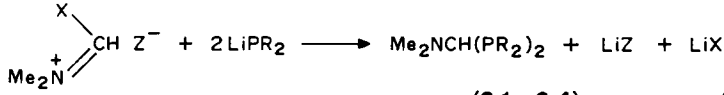
(**5.2—5.6, 7.1**)

Reactions of secondary phosphines or their alkali metal derivatives with aromatic aldehydes[35,50] or immonium salts $Me_2N{=}CHX^+Z^-$ (X = Cl, OMe; Z = Cl)[39] represent another interesting synthetic approach to *C*-substituted methylenebisphosphines. The use of these Mannich-type reactions in synthetic phosphorus chemistry has been discussed by Kellner and Tzschach[40] (equations 13 and 13a).



(**5.7**)

(13)



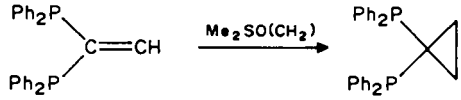
(**6.1—6.4**) (13a)

X=Cl, OMe; Z=Cl, SO_4Me

Perfluorocarbonic acid chlorides in presence of triethylamine react with secondary phosphines to give acylphosphines. The hydroxy-substituted derivatives **7.2–7.4** are formed as side-products[43].

In $Ph_2P\,CH_2PPh_2$, both H atoms of the CH_2 bridge may be replaced by one oxygen atom, leading to carbonylbis(diphenylphosphine) (**11**) which is stable at room temperature. It has been synthesized by a P—Si cleavage reaction between $COCl_2$ and Ph_2PSiMe_3 in about 40% yield[46].

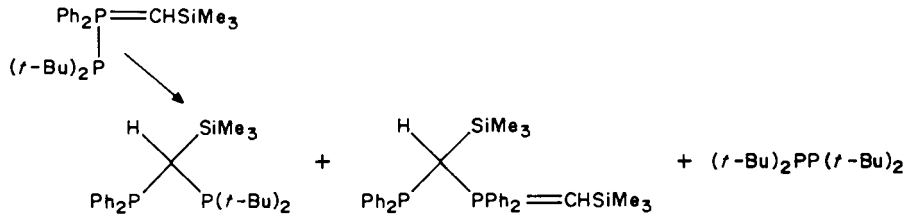
The first geminal bisphosphinocyclopropane (**8**) in which the bridging C atom is part of a strained ring system was reported by Schmidbaur and Pollock[41]. Dimethylsulphonium methylide was used as a CH_2 transfer reagent for the cyclopropanation of the vinylidene phosphine $CH_2{=}C(PPh_2)_2$ (equation 14).



(14)

(**8**)

Methylenebisphosphines containing Me_3Si substituents at the bridging C atoms have also been reported[22,44,45]. The derivative **5.9** is obtained by silylation of $(Ph_2P)_2CHLi$ with Me_3SiCl[22]. On thermolysis of the ylid $(t\text{-}Bu)_2PPh_2P{=}CHSiMe_3$ the *C*-silylated methylenebisphosphine **9** is formed in about 43% yield[44] (equation 15).



(**9**) (15)

The methylenebisphosphine **10** has been obtained by reaction of $(Me_3Si)_2NP{=}CHSiMe_3$ with MeLi and trapping the intermediate product with MeSiCl[45].

Four-membered cyclic methylenebisphosphines, 1,3-diphosphetanes, with functional groups or substituents at the ring carbon atoms have been obtained as dimerization products of methylenephosphines, e.g. **12**[47], **13**[48] and **14**[49]. These reactions will, however, not be discussed in further detail since this subject is covered in chapter 10.

3. Bidentate phosphines with P—C_n—P backbones (n ≥ 2)

During the past few years, there has been a surge of interest in the synthesis of new bidentate phosphine ligands with backbones of different lengths and flexibilities and optically active centres (P or C). These characteristics will be used in this section to systematize the discussion of the different types of bidentate phosphines and their syntheses in a logical way.

a. Bidentate phosphines with P–$(CH_2)_n$–P backbones (n = 2, 3). The reduction of phosphine oxides, sulphides or phosphonates and phosphinates, obtained by addition of primary and secondary phosphines to vinyl or allyl compounds or Arbusov-type reactions, continues to be an important route to bidentate $(CH_2)_n$-bridged phosphines (Table 3).

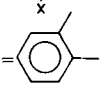
TABLE 3. Bidentate phosphines with P—C_n—P bonding ($n = 2, 3$)

$R_2P(CH_2)_nPR_2$			$Ph_2P(CH_2)_nPR_2$		
No.	n	R	No.	n	R
15.1[51]	2	H	**19.1**[70,71]	2	H
15.2[52–54]	2	Me	**19.2**[72,73]	2	Me
15.3[52,55]	2	Et	**19.3**[74]	2	*n*-Bu
15.4[57]	2	*i*-Pr	**19.4**[75]	2	CF_3
15.5[56]	2	*neo*-Pen	**19.5**[76]	2	4-MeC_6H_4
15.6[52,55]	2	*c*-Hex	**19.6**[77]	2	3,4-FC_6H_4
15.7[1,55,58–62]	2	Ph	**19.7**[77]	2	3-$CF_3C_6H_4$
15.8[55,63]	2	Ar[a,b]	**19.8**[78]	2	C_6F_5
15.9[19,55]	2	*o*-Tol	**20.1**[79–81]	3	Me
15.10[55,65]	2	C_6F_5	**20.2**[80,81]	3	Et
16.1[64]	3	H			
16.2[67,67a]	3	Me			
16.3[64a]	3	*i*-Pr			
16.4[66]	3	Ph			
16.5[19]	3	*o*-Tol			

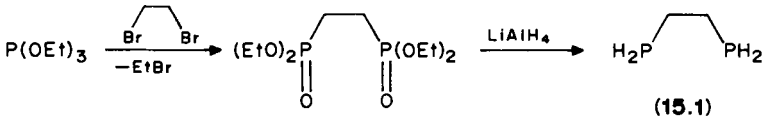
$R_2P(CH_2)_nPR^1H$				$R^1R^2P(CH_2)_nPR^1R^2$			
No.	n	R	R^1	No.	n	R^1	R^2
17.1[68]	2	*n*-Pr	Ph	**21.1**[82,82a]	2	H	Me
17.2[68]	2	Ph	*n*-Hex	**21.2**[83]	2	H	Et
17.3[68]	2	*n*-Bu	*n*-Hex	**21.3**[84]	2	H	*t*-Bu
17.4[56]	2	*neo-Pen*	Ph	**21.4**[85]	2	H	Ph
18.1[69]	3	*i*-Pr	Me	**21.5**[63]	2	Ar[b]	Ph
18.2[69,69a]	3	Ph	Me	**22.1**[64,82]	3	H	Me
				22.2[64]	3	H	*n*-Bu
				22.3[86]	3	H	All
				22.4[2,85]	3	H	Ph
				22.5[64]	3	Me	*n*-Bu
				22.6[64]	3	CH_2	*n*-Bu

$Ph(n\text{-}Bu)P(CH_2)_3PPhR$		$R_2P(CH_2)_2PRR^1$			$R_2P(CH_2)_3PRR^1$		
No.	R	No.	R	R^1	No.	R	R^1
23.1[87]	Et	**24.1**[88,89]	H	Ph	**25.1**[92]	H	All
23.2[87]	*n*-Pr	**24.2**[88]	H	*n*-Hex	**25.2**[69]	Me	H
23.3[87]	*i*-Pr	**24.3**[89,90]	Ph	H	**25.3**[69a,90]	Ph	H
23.4[87]	*n*-Pen	**24.4**[74,90]	Ph	Me	**25.4**[81]	Ph	Me
23.5[87]	*n*-Hex	**24.5**[74,91]	Ph	Et	**25.5**[81,87]	Ph	Et
		24.6[74,91]	Ph	*i*-Pr	**25.6**[87,95]	Ph	*n*-Bu
		24.7[74,91]	Ph	*n*-Pr	**25.7**[81]	Ph	*c*-Hex
		24.8[74,91]	Ph	*s*-Bu	**25.8**[95]	*n*-Bu	*n*-Hex
					26[96] $Me_2P(CF_2)_2PMe_2$		

[a] Ar =  ; X = 4-OMe, 4-Me, 2,4,6-Me_3, 4-Cl, 4-NMe_2, 4-CF_3[55].

[b] Ar =  —OR; R, Me, Et, *t*-Bu[63].

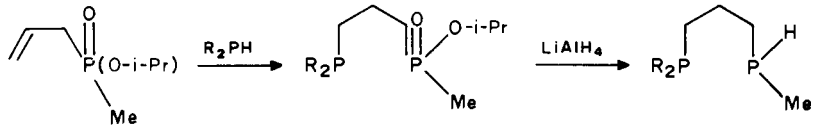
Sodium metal[56], iron powder[54], $HSiCl_3$[63] or $LiAlH_4$[51,69–73,82,83,88,89] have been used as reducing agents (equations 16–17).



(15.1) (16)

$$MeP(O\text{-}i\text{-}Pr)_2 \xrightarrow[(2)\ LiAlH_4]{(1)\ Br(CH_2)_nBr} MeHP(CH_2)_nPMeH \quad (16a)$$

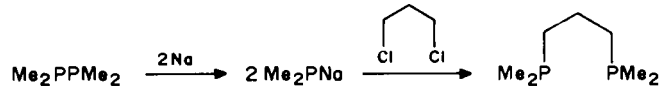
(21.1, 22.1)



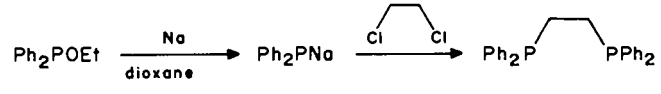
(18.1, 18.2, 25.2) (17)

Coupling of organophosphides with bifunctional organic halides is the method of greatest applicability for the synthesis of bidentate phosphine ligands. The ultility of the anions $RR'P^-$ arises from their ready availability, the high yields in which these coupling reactions proceed and the variability of phosphide and substrate.

For the preparation of the organophosphides RR'PM (M = Li, Na, K), diphosphines R_2PPR_2[67a,87,95], phosphinites R_2POR[62], chlorophosphines R_2PCl[19], primary[64,69a,86,93] or secondary phosphines[53,64,64a,93] were employed as starting materials (equation 18–22).



(15.2) (18)



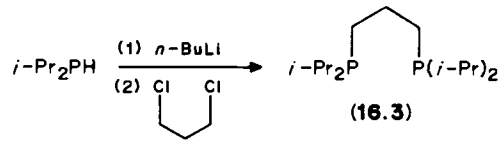
(15.7) (19)

$$2(o\text{-}Tol)_2PCl \xrightarrow[(2)\ X(CH_2)_nX]{(1)\ Li} (o\text{-}Tol)_2P(CH_2)_nP(o\text{-}Tol)_2 \quad (19a)$$

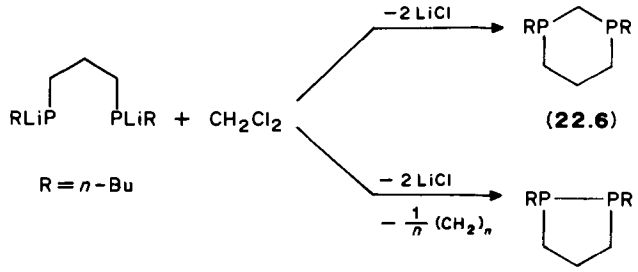
(15.9, 16.4)

$$H_2P(CH_2)_nPH_2 \xrightarrow[liq.NH_3]{2M} HMP(CH_2)_nPMH \xrightarrow{2RX} RHP(CH_2)_nPRH \quad (20)$$

(15.1, 16.1) (22.2, 22.3)



(21)



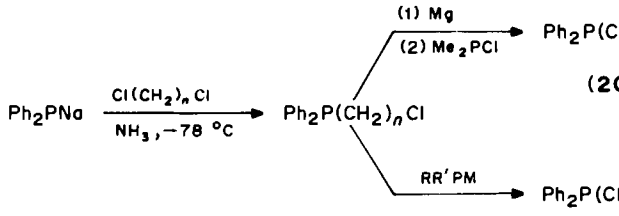
(22)

(22a)

Attempts to obtain the six-membered ring system **22.6**[64] through cyclization of $RLiP(CH_2)_3PRLi$ (equation 22) have been hampered by halogen–metal exchange reactions[97] with CH_2Cl_2. As a result the 1,2-diphospholane is formed through P—P coupling (equation 22a) in addition to **22.6**. The formation of P—P coupling products in reactions of type 22, however, is not a convincing evidence for halogen–metal exchange between organic halides and organophosphides. As shown by a series of ^{31}P CIDNP experiments, these products may be radical-derived in some cases[98].

Unsymmetrical ligands $R^1{}_2P(CH_2)_nPR^2{}_2$ (**19**, **20**) or $R_2P(CH_2)_nPRR^1$ (**24**, **25**) have been prepared by a procedure which involves P—C (aromatic) cleavage of Ph_3P[79,91] or alkyldiphenylphosphines Ph_2PR[79,91] with lithium or sodium using thf or liquid ammonia as solvents. Reaction of the alkali metal phosphides obtained with diphenylvinylphosphine followed by hydrolysis gives the required ligand as shown in equation 23. Alternatively, the phosphides may be reacted with equimolar amounts of $Cl(CH_2)_nCl$ to give the ω-chloroalkylphosphines. These are useful intermediates for the syntheses of the unsymmetrical substituted ligands **18.2**, **20.1** and **25.3**[69a,79,93] according to equations 24–26.

(23)



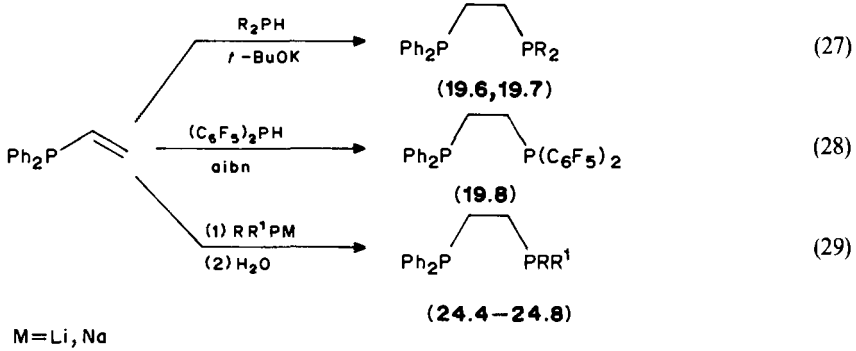
(24)

(25)

(26)

The addition of primary and secondary phosphines to olefinic systems under free-radical or base-catalysed conditions is a well established synthetic method for the design of bidentate phosphine ligands with $-(CH_2)_2-$ and $-(CH_2)_3-$ backbones and different patterns of substitution at the P atoms.

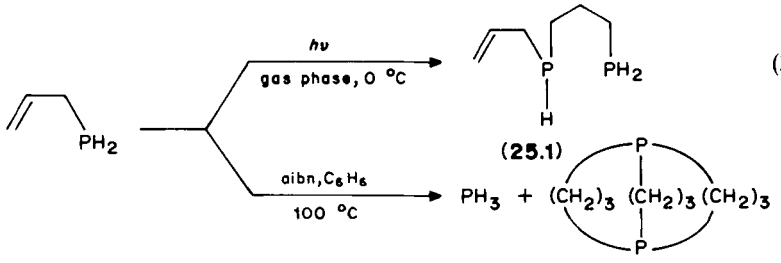
Bidentate phosphines that contain the $-PCH_2CH_2P-$ unit have been synthesized by base-catalysed[56,74–77,91,99,100] (**15.5, 17.4, 19.3–19.7, 24.4–24.8**) or free-radical initiated[68,78] (**17.1–17.3, 19.8**) or photo-induced addition of primary or secondary phosphines to vinylphosphines (equations 27–29). Allylphosphines in an analogous way give phosphines with $-P(CH_2)_3P-$ bridging[92]. The photo-induced head-to-tail addition of allylphosphine produces a primary secondary phosphine(**25.1**) whereas under free-radical conditions the bicyclic phosphine **27** is obtained (equations 30 and 31).



(27)

(28)

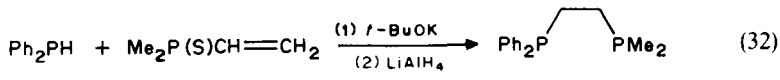
(29)



(30)

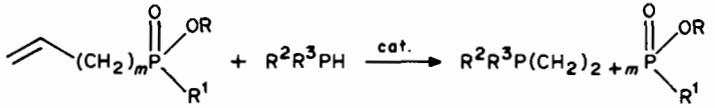
(31)

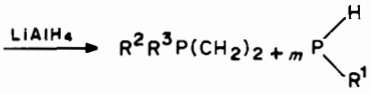
In order to overcome problems in handling volatile and air-sensitive vinylphosphines in these reactions, King's group[56,72,73] use the sulphides of these ligands. Desulphurization of the reaction products obtained after the addition reactions (e.g. equation 32) was achieved with $LiAlH_4$ in boiling dioxane or with sodium metal.



(32)

Allyl and vinyl phosphinates and phosphonates have been employed as building blocks for the synthetic design of various PH-functional bidentate phosphine ligands in consecutive 'addition–reduction' synthetic procedures[69–71,88,89] as indicated in equation 33.

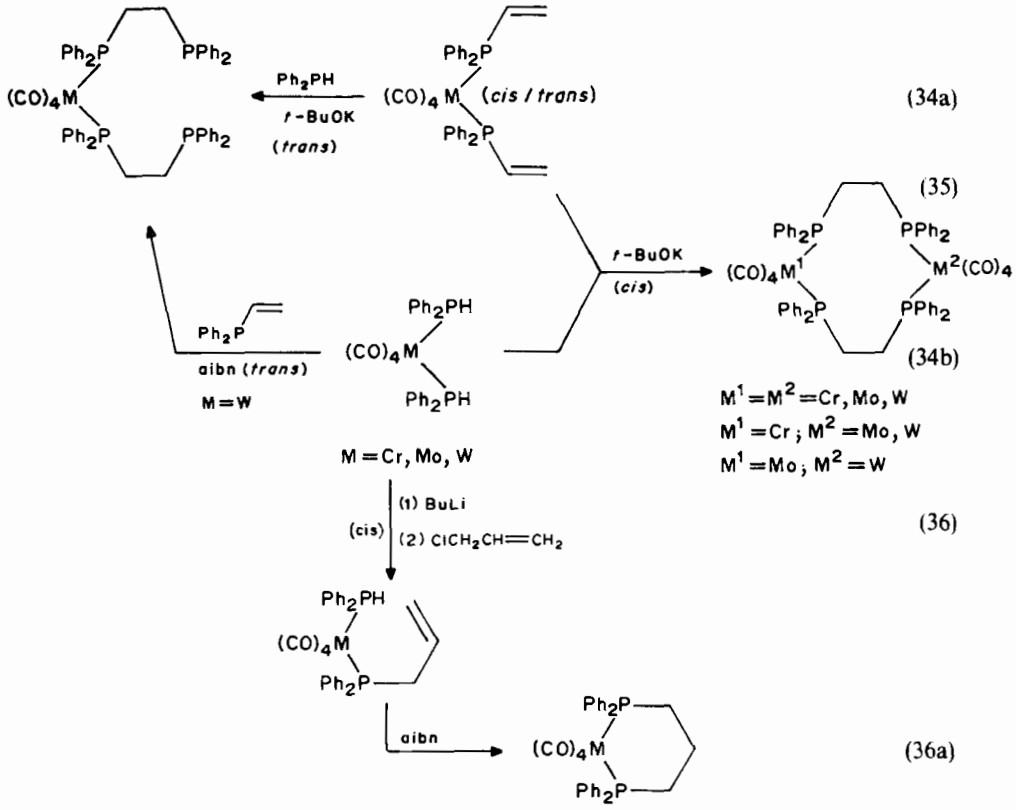




(33)

Cat. = *t*-BuOK, aibn; $m = 0, 1$ (**18.1, 18.2, 19.1, 24.1–24.3**)

Addition of coordinatively bound vinylphosphines to secondary phosphines (or vice versa) provides a potentially useful route to transition metal complexes of bidentate phosphines (equations 34a, 34b and 35). The number of metal sites to which the phosphine legand coordinates may be controlled by suitable choice of the reactants[58–60,101,102]. A stepwise formation of $Ph_2P(CH_2)_3PPh_2$ (**16.4**) within the coordination sphere of *cis*-disubstituted complexes is also possible[66] (equations 36 and 36a). This procedure is reminiscent to the template synthesis of bidentate phosphine ligands $Me_2P(CH_2)_nPMe_2$ ($n = 2$–6) (e.g. **16.2**) or $HPhP(CH_2)_3PPhH$ (**22.4**) through alkylation of *cis*-$[Mo(CO)_4(PMeLi)_2]$ or $[M(CO)_x(PPhHLi)_2]$ ($M = Mo$, $x = 4$; $M = Ni$, $x = 2$) with



(34a)

(35)

(34b)

$M^1 = M^2 = Cr, Mo, W$

$M^1 = Cr$; $M^2 = Mo, W$

$M^1 = Mo$; $M^2 = W$

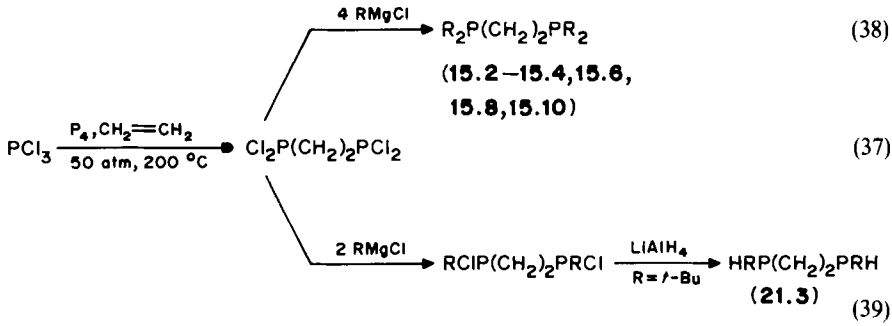
(36)

(36a)

$X(CH_2)_nX$ ($X = Cl, Br$)[67,103]. Base-induced addition of coordinated Ph_2PH to activated acetylenes $RC{\equiv}CR^1$ ($R^1 = R = CO_2Me$; $R = H$, CO_2Et, $R^1 = Ph$) gave metal complexes of chelating bidentate phosphine ligands in moderate yields. These reactions occur within *cis*-$[M(CO)_4(Ph_2PH)(Ph_2PLi)]$ ($M = Cr$, Mo) and *fac*-$[Mn(CO)_3(Ph_2PH)(Ph_2PLi)Br]$. They are assumed to be a type of Michael addition proceeding via carbanion intermediates. *Trans* stereochemistry at the CHRCHR bridge ($R = COOMe$) was determined in one case from NMR data[104].

Later it was found that the reaction of $[Cr(CO)_4(PPh_2H)_2]$ with $CF_3C{\equiv}CCF_3$ gave a binuclear complex of 1,2,3,4-tetrakis(diphenylphosphino)-1,4-difluorobutadiene, *cis*-$[Cr(CO)_4]_2[C_4F_2(PPh_2)_4]$. The mechanism suggested for this unusual reaction involves sequential deprotonation of the phosphine ligands, nucleophilic attack at the fluorocarbon and fluoride ion elimination[105].

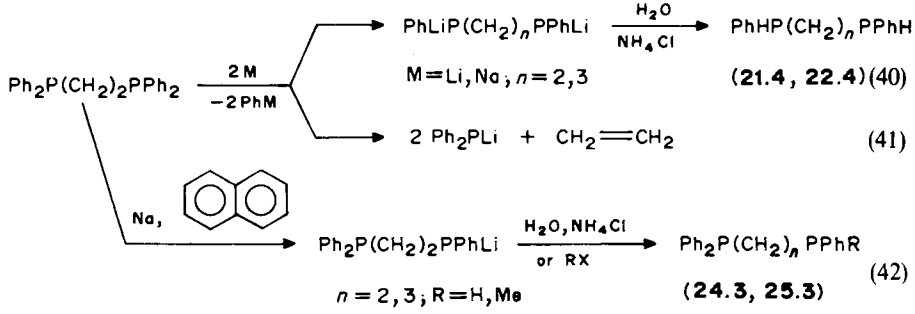
Reaction of chlorophosphines with organolithium or Grignard reagents is a well established synthetic route to tertiary phosphines PR_3. It has been applied for the synthesis of ditertiary and disecondary phosphines $R_2P(CH_2)_2PR_2$[52,55,57a,65] and (*t*-Bu)$HP(CH_2)_2P$(*t*-Bu)H[84], respectively, using $Cl_2P(CH_2)_2PCl_2$ as starting material (equations 38 and 39). The latter was obtained by a high-pressure reaction between PCl_3, ethylene and elemental phosphorus (equation 37).



Bifunctional chlorophosphines of the type $RXP(CH_2)_nPRX$ ($n = 2, 3$; $R = i$-Pr; $X = Cl$, Br) have been reported by Diemert *et al.*[106].

As discussed earlier in this section, reductive cleavage of phosphorus—aryl bonds in monodentate arylphosphines RR'ArP by alkali metals leads to phosphide ions RR'PM[79,85]. Using the air-stable, easily accessible $Ph_2P(CH_2)_2PPh_2$ in this type of reaction, the well known phosphides $PhMP(CH_2)_2PPhM$ ($M = Li$, Na)[107] are obtained[85,94,108]. A reinvestigation[94,108] of the cleavage reaction of the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) with lithium in thf revealed the exceptional behaviour of $Ph_2PCH_2PPh_2$ since it reacts exclusively with cleavage of the alkyl—phosphorus bond, whereas the others preferably form the phosphides $PhLiP(CH_2)_nPPhLi$ ($n = 2,3$). The ethane–phosphine, however, gave variable amounts (0–30%) of Ph_2PLi together with C_2H_4 as side-products (equations 40 and 41). $PhLiP(CH_2)_2PPhLi$, first reported by Issleib and Böttcher[109], is of importance in synthesis as a 1,2-ethylenebis(phenylphosphido) transfer reagent. The crystal structure of its thf adduct has been determined recently by two groups[108] independently.

Sodium–naphthalene was found to be a homogeneous and selective reducing agent for the cleavage of only one P—Ar bond in $Ph_2P(CH_2)_2PPh_2$ according to equation 42[90]. Treatment of $Ph_2P(CH_2)_nPPh_2$ with lithium under ultrasound irradiation affords $PhLiP(CH_2)_nPPhLi$[94]. By protonation or alkylation of these phosphides $PhLiP(CH_2)_2PPhLi$ or $Ph_2P(CH_2)_2PPhLi$ the corresponding bidentate phosphines with



symmetrical or unsymmetrical substitution at the phosphorus atoms may be obtained[85,90,94].

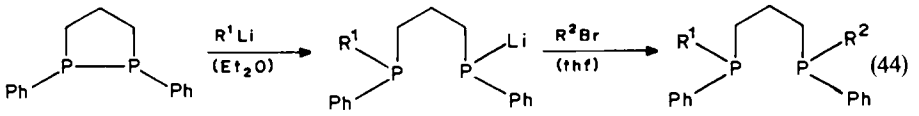
Briggs and Dyer[81] reported a facile synthesis of the bidentate phosphines $RPhP(CH_2)_nPPh_2$ ($n = 3$–6) (e.g. **25.4**, **25.5**, **25.7**) based on P—Ar bond cleavage in phosphonium salts during hydrolysis. This preparation procedure has been extended to synthesize ligands of the type $R_2P(CH_2)_3PPh_2$[80] (equation 43).

$$Br(CH_2)_nBr \xrightarrow{Ph_3P} [Br(CH_2)_nPPh_3]Br \xrightarrow{PhR_2P}$$

$$[PhR_2P(CH_2)_nPPh_3]^{2+}\,2Br^- \xrightarrow[H_2O]{NaOH} R_2P(CH_2)_nP(O)Ph_2 \xrightarrow[NEt_3]{SiHCl_3} R_2P(CH_2)_nPPh_2 \quad (43)$$

(20.1, 20.2)

Cyclic diphosphines $Ph_2P_2(CH_2)_n$ have been employed recently for syntheses of unsymmetrically substituted phosphines of the type $PhR^1(CH_2)_nPPhR^2$ ($n = 3,4$). Nucleophilic ring opening of 1,2-diphenyl-1,2-diphospholane or 1,2-diphenyl-1,2-diphosphorinane was the key step in these syntheses. Reaction of the phosphides obtained with electrophiles gave the phosphines (equation 44)[87,95].

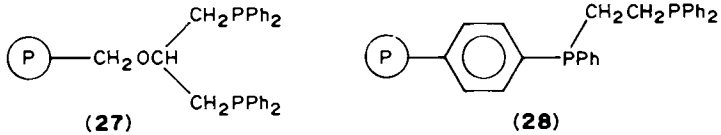


(23.1—23.5, 25.5, 25.6, 25.8)

Thermal addition of tetrafluoroacetylene to tetramethyldiphosphine afforded the bidentate phosphine ligand **26** with a CF_2CF_2 backbone in a radical process[96].

A novel synthetic approach to the well known ditertiary phenyl substituted phosphine $Ph_2PCH_2)_2PPh_2$ (**15.7**) uses the electrochemical coupling of Ph_2PCl with α,ω-dihalides $X(CH_2)_nX$ (X = Cl, Br; $n = 2,4$)[61].

Bidentate phosphine ligands have been anchored to chloromethylated or bromosubstituted polystyrene, Ⓟ, via functional groups in the C_n backbone (**27**)[110] or anionic phosphorus atoms (**28**)[111].



b. Bidentate phosphines with flexible long alkylene chain backbones $(CH_2)_n$ *(*$n \geq 4$*).* The ability of bidentate phosphine ligands P-C_n-P to form *cis*-chelate ring system is widely used in coordination chemistry to control the stability of transition metal complexes. It reaches a maximum for ethylene bridging, propylene-bridged bidentate phosphine ligands being comparable in their tendency to form *cis*-chelate ring systems. Hence most bidentate ligands employed in coordination chemistry contain $-(CH_2)_2-$ or $-(CH_2)_3-$ backbones.

Recently, however, there has been renewed interest in the synthesis of bidentate ligands $R_2P(CH_2)_nPR_2$ ($n \geq 4$) with longer and flexible C_n bonding units capable of spanning *trans* positions in square-planar or octahedral complexes and forming large chelate rings (larger than eight-membered) in which non-bonded interactions favour cyclometallation reactions.

The ligands to be presented in this section (Table 4) were synthesized either by modifying the substituents at the terminal phosphorus atoms of easily accessible bidentate phosphines $R_2P(CH_2)_nPR_2$ (e.g. **29.1**[64], **29.3**[106], **30.3**, **30.4**[90], **30.5**[95], **30.6**[64]) (equations 45–47) or by interconnection of two R_2P groups by long alkylene chains using suitable reactions.

$$H_2P(CH_2)_nPH_2 \xrightarrow[(2)\ RX]{(1)\ K,\ liq.\ NH_3} HRP(CH_2)_nPRH \quad \textbf{(30.6)} \tag{45}$$

$$Br_2P(CH_2)_5PBr_2 \xrightarrow{4\ EtMgX} Et_2P(CH_2)_5PEt_2 \quad \textbf{(29.3)} \tag{46}$$

$$Ph_2P(CH_2)_nPPh_2 \xrightarrow[(2)\ NH_4Cl]{(1)\ Na,\ \langle\bigcirc\bigcirc\rangle} Ph_2P(CH_2)_nPPhH \quad \textbf{(30.3)} \tag{47}$$

TABLE 4. Bidentate phosphines with flexible long alkyl chain backbones, $(CH_2)_n$ ($n \geq 4$)

$R_2P(CH_2)_nPR_2$			$RR^1P(CH_2)_nPRR^2$				
No.	n	R	No.	n	R	R^1	R^2
29.1[64]	4	H	**30.1**[85]	4	Ph	H	H
29.2[67]	4–6	Me	**30.2**[117]	6	Ph	Et	Et
29.3[106]	5	Et	**30.3**[90]	4–6	Ph	Ph	H
29.4[112]	5–8	*t*-Bu	**30.4**[90]	4–6	Ph	Ph	Me
29.5[113]	9, 10	*t*-Bu	**30.5**[95, 117]	4, 6	Ph	Ph	Et
29.6[61,114]	4	Ph	**30.6**[64]	4	H	*n*-Bu	H
29.7[112]	5	Ph					
29.8[115,116]	6, 8, 10, 12	Ph	**31.1**[118]	*t*-$Bu_2P(CH_2)_2CHMe(CH_2)_2P$(*t*-Bu)			
29.9[19]	4, 6, 8	*o*-Tol	**31.2**[119]	*t*-$Bu_2PCH_2CHMe(CH_2)_3P$(*t*-Bu)			

$R^1_2P(CH_2)_nPR^2_2$			
No.	n	R^1	R^2
32.1[80]	4	Me	Ph
32.2[80]	4	Et	Ph

Alkylation of alkali metal phosphides R_2PM (M = Li, Na) by α,ω-dichloroalkanes $X(CH_2)_nX$ (**29.8**[115,116], **29.9**[19], **30.1**[85]) or nucleophilic replacement of halogen in R_2PX by bifunctional organolithium compounds (**29.4**[112], **29.7**[112], **31.1**[118], **31.2**[119]) (equations 48 and 49) have been used in addition to deprotonation of tertiary phosphonium salts $[R_2PH(CH_2)_nPHR_2]^{2+}$ $2X^-$ (**29.4**[112], **29.5**[113]) obtained by alkylation of secondary phosphines with α,ω-dihalides $X(CH_2)_nX$ (equation 50).

$$BrCH_2CHMe(CH_2)_3Br \xrightarrow{Li} LiCH_2CHMe(CH_2)_3Li \xrightarrow{2\ (t\text{-}Bu)_2PCl} (t\text{-}Bu)_2PCH_2CHMe(CH_2)_3P(t\text{-}Bu)_2 \quad (48)$$

(31.2)

$$Li(CH_2)_5Li \xrightarrow{2\ Ph_2PCl} Ph_2P(CH_2)_5PPh_2 \quad (49)$$

(29.7)

$$Br(CH_2)_nBr \quad n = 5\text{–}8 \xrightarrow[(2)\ NaOH]{(1)\ (t\text{-}Bu)_2PH} (t\text{-}Bu)_2P(CH_2)_nP(t\text{-}Bu)_2 \quad (50)$$

(29.4)

Cleavage of P—Ar bonds on hydrolysis of bifunctional phosphonium salts $[R_2R^1P(CH_2)_nPR_2R^2]^{2+}$ $2X^-$ affords the oxides $RR^1P(O)(CH_2)_nP(O)RR^2$, which may be reduced with $HSiCl_3/NEt_3$ or $(MeHSiO)_n$ to the corresponding phosphines (**30.2**, **30.5**[117], **32.1**, **32.2**[80]) (equation 51).

$$Br(CH_2)_6Br \xrightarrow[C_6H_6,\ \Delta]{Ph_3P} [Br(CH_2)_6PPh_3]^+\ Br^- \xrightarrow[dmf,\ \Delta]{Ph_2EtP}$$

$$[Ph_2EtP(CH_2)_6PPh_3]^{2+}2Br^- \xrightarrow{NaOH} PhEtP(=O)(CH_2)_6P(=O)Ph_2$$

$$\xrightarrow{(MeHSiO)_n} PhEtP(CH_2)_6PPh_2 \quad (51)$$

(30.5)

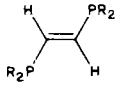
Sixteen membered cyclic tetraphosphonium salts are accessible by macrocyclization of $Ph_2P(CH_2)_2PPh_2$ with 1,4-dichlorobutene-2 (*cis* and *trans*). After hydrogenation with H_2/Raney nickel and PPh cleavage with NaOH, **29.6** and its dioxide were obtained[114].

The electrochemical coupling of Ph_2PCl and $X(CH_2)_nX$ has been shown to be an attractive synthetic route to $Ph_2PCH_2)_4PPh_2$ (**29.6**)[61]. In a template reaction, the methylated bidentate phosphines **29.2** could be synthesized as molybdenum (0) complexes by alkylation of *cis*-$[Mo(CO)_4(PMe_2Li)_2]$ with $Br(CH_2)_nBr$ ($n = 4\text{–}6$)[67].

c. Bidentate phosphine ligands with unsaturated backbones. The bonding modes in which bidentate ligands can bind to transition metals are governed by the length and the nature of the P-C_n-P backbones. The greater stability of mononuclear complexes of *cis*-$Ph_2PCH{=}CHPPh_2$, for example, is attributed mainly to the rigid olefinic backbone. The presence of antibonding π-orbitals in the C=C bond and the more electronegative sp^2 carbon atoms favour metal–ligand back-donation, thus enforcing the M—P bonds. The π^* antibonding ligand orbitals may be involved in an M → ligand electron transfer leading to complexes of radical anions **[34.2]**$^{\cdot}$ in the extreme[127] (see page 244).

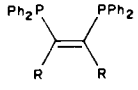
Cis- and *trans*-olefinic bidentate phosphines **33.1**–**33.4**[120–122], **34.1**[125,126] and **44**[140] (Table 5) have been obtained by stereospecific nucleophilic displacement reactions of chlorine in *cis*- or *trans*-1,2-dichloroethene, dimethyl-2,3-dichloromaleate or, 1,6-

TABLE 5. Phosphines with olefinic and acetylenic backbones

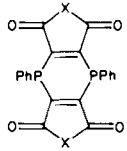


(33.1)[120] R = Me
(33.2)[121,125] R = Ph
(33.3)[122] R = 4-MeC$_6$H$_4$

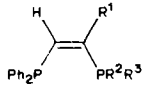
COOMe(PPh$_2$)HC=CH(PPh$_2$)COOMe
33.4[123,124]



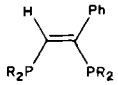
(34.1)[121,125,126] R = H
(34.2)[127,128] 2R = (CO)$_2$X[a]



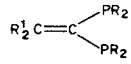
(35)[129] X = O, S



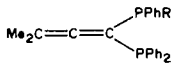
R^1 = CF$_3$,*t*-Bu,Ph
R^2 = Ph, (CH$_2$)$_2$CN
R^3 = Et, Ph, (CH$_2$)$_2$CN
(36.1)[130]



R = Me, Et, Ph
(36.2)[131]

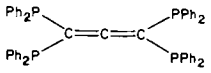


(37.1)[132,133] R = Ph, R^1 = H
(37.2)[43] R = *n*-Bu, R^1 = CF$_3$

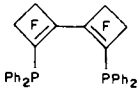


(38.1)[134] R = Ph
(38.2)[134] R = *t*-Bu

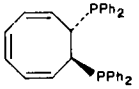
(Ph$_2$P)$_2$C=C=CHPPh$_2$
(39)[135]



(40)[135,136]

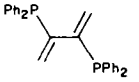


(41)[137]

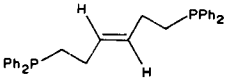


(42)[138]

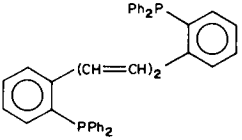
Ph$_2$P(CH=CH)$_4$PPh$_2$
(43.1)[138]



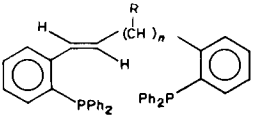
(43.2)[139]



(44)[140]



(45)[141]



(46.1)[142-144] R = H, Me; *n* = 1
(46.2)[145] *n* = 0

[R$_2$P(CH$_2$)$_n$]$_2$(C≡C)
(47.1)[146,147] *n* = 1, R = Ph
(47.2)[148] *n* = 4, R = *t*-Bu

[*t*-Bu$_2$PC≡C]$_2$(CH$_2$)$_n$
(48)[149] *n* = 4, 5

[a]X = O, S, NMe. CH$_2$, NPh, N(CH$_2$)$_3$Si(OEt)$_3$.

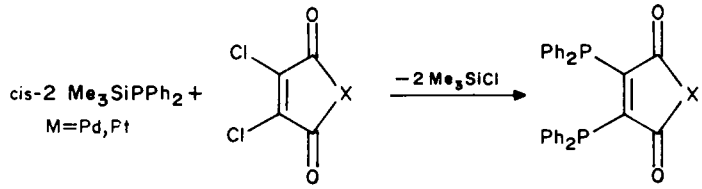
dichloro-*trans*-hex-3-ene, respectively, by lithium phosphides R_2PLi (R = Me, Ph, 4-MeC_6H_4) (equation 52). Surprisingly, the reaction of Ph_2PLi with a 30-fold excess of *cis*-1,2-dichloroethene yields only the *cis*-diphosphine **34.1**[125], no *cis*-$Ph_2PCH{=}CHCl$ being formed. If 1,2-dibromoalkenes are employed instead of the chloro analogues in these reactions, nucleophilic attack of the organophosphide anion Ph_2P^- on halogen gives an acetylene and Ph_2PPPh_2 (equation 53)[150].

$$2\ R_2PLi + ClRC{=}CRCl \xrightarrow[-\ LiCl]{} R_2PCR{=}CRPR_2\ (\mathbf{33}, \mathbf{34}) \qquad (52)$$

$$2\ Ph_2P^-Li^+ + Br{-}C{=}C{-}Br \xrightarrow[-\ 2\ LiBr]{} RC{\equiv}CR + Ph_2PPPh_2 \qquad (53)$$

(R R)

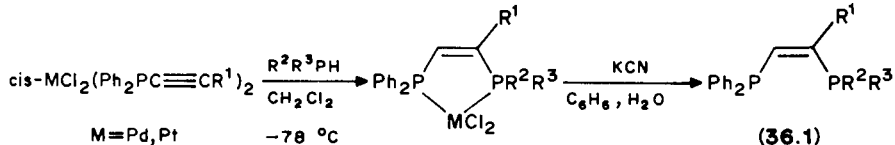
The diphenyltrimethylsilane Ph_2PSiMe_3 may be employed instead of Ph_2PLi for the nucleophilic displacements of Cl atoms in activated 1,2-dichloroolefins under mild conditions, as shown by the synthesis of **33.4**[123,124] and 2,3-bis(diphenylphosphino)maleic anhydride **34.2**[127,128] (equation 54). Derivatives of 1,4-dihydro-*p*-diphosphorine system **35**[129] have been obtained in a similar way using $PhP(SiMe_3)_2$ instead of Ph_2PSiMe_3.



(54)

(34.2)

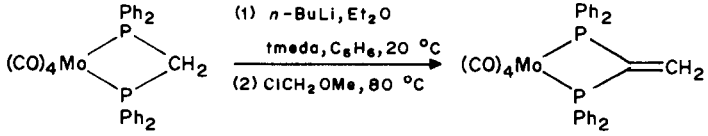
Unsymmetrically substituted 1,2-diphosphinoethenes are accessible by addition of secondary phosphines R^1R^2PH to acetylenic phosphines in a transition metal template[130] (equation 55).



(36.1) (55)

Addition of diphosphines R_2PPR_2 to acetylenes, e.g. HC≡CPh, provides another synthetic route to olefinic diphosphines (**36.2**) with substituted backbones[131].

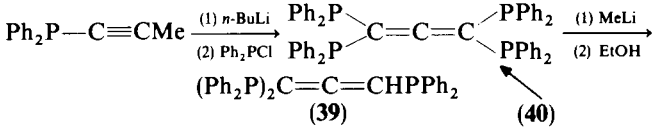
The geminal ditertiary phosphine **37.1**[132,133] has been obtained by nucleophilic displacement reactions of the Cl atoms in 1,1-dichloroethylene with Ph_2PLi[132]. The activation of the methylene group in $(Ph_2P)_2CH_2$ through coordination to transition metals has been used to synthesize the 1,1-diphosphinoethenes in suitable templates (equation 56)[32–34].



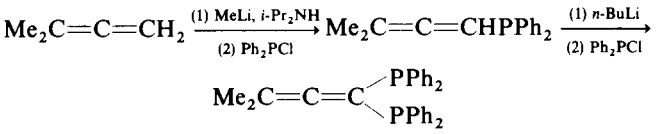
(56)

In a condensation-type reaction between bis(trifluoromethyl)ketene and dibutylphosphine, the 1,1-diphosphinoethene **37.2**[43] is formed as a side-product in addition to $(CF_3)_2CHCOP(n\text{-}Bu)_2$.

1,1-Bis, 1,1,3-tris- and 1,1,3,3-tetrakis-(diphenylphosphino) allenes have been reported by Schmidbaur and coworkers[134–136]. These interesting compounds were synthesized using 1,1-dimethylallene or the phosphinoacetylene $Ph_2PC{\equiv}CMe$ as starting materials according to equations 57 and 58.



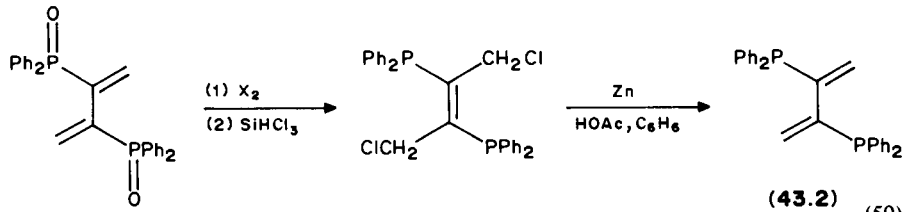
(57)



(58)

Bidentate phosphine ligands with conjugated olefinic backbones have been obtained by reaction of the corresponding dichlorides $ClC{=}\frown{=}CC{-}C{=}\frown{=}CCl$ [$\frown = (CF_2)_2$] and secondary phosphines (**41**[137]) or by spontaneous conrotatoric ring opening of **42**[138] yielding **43.1**.

2,3-Bis(diphenylphosphino)buta-1,3-diene (**43.2**)[139] was prepared in a multi-stage synthesis using $Ph_2P(O)C(=CH_2)C(=CH_2)P(O)Ph_2$ as starting material (equation 59).

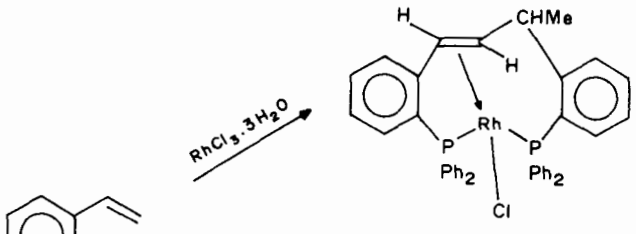


(59)

Chelating diphosphines **46.1** and **46.2** with olefinic and *o*-phenylene units in their backbones are accessible by template-mediated vinyl coupling reactions or dehydrogenation of $o\text{-}Ph_2PC_6H_4CH{=}CH_2$ or $\{o\text{-}Ph_2PC_6H_4\}_2(CH_2)_n$ ($n = 2, 3$), respectively. Thus diphenyl(*o*-vinylphenyl)phosphine is dimerized on heating with $RhCl_3$ in 2-methoxyethanol to form the diphosphine **46.1**[142,143] (equation 60), whereas with $[Ru_3(CO)_{12}]$ *cis–trans* **45** is formed by dehydrogenation and vinyl coupling[141] (equation 61). Metal-induced hydrogen abstraction from $(Ph_2PC_6H_4)_2(CH_2)_n$ ($n = 2,3$) affords **46.1**[144] or **46.2**[145], respectively.

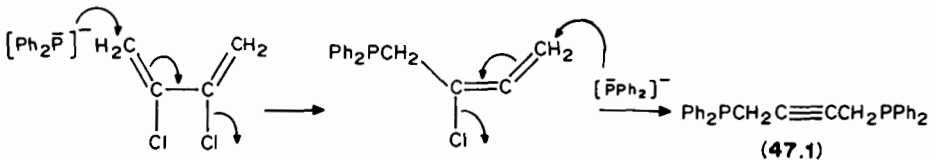
Introduction of acetylenic or aromatic units into the C_n bridges renders bidentate ligands $R_2PC_nPR_2$ conformational less flexible than their polymethylene analogues. Acetylenic phosphines, e.g. **48**, were synthesized by reaction of α,ω-dialkynyllithium reagents with chlorophosphines[149] or by conjugate addition of phosphides R_2PLi to chlorobutadienes[146,147] (equation 62). Quaternization of secondary phosphines ($t\text{-}Bu_2PH$) by 1,10-dichlorodec-5-yne followed by deprotonation of the phosphonium salt formed yields **47.2**[148].

Internal entropy and conformational effects favour chelate formation of ligands with the



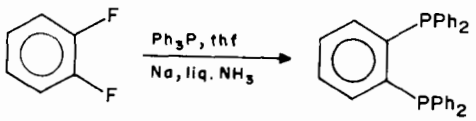
(60)

(61)



(62)

rigid *o*-phenylene backbone. New synthetic procedures for these ligands have been developed. The nucleophilic displacement of halogen in *o*-xylylene dihalides by organophosphides $R_2PM(M = Li, Na)$ seems to be the method of choice (**49.2**[151], **49.3**[152], **49.9**[153]) (equation 63) (Table 6).

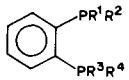


(49.3)

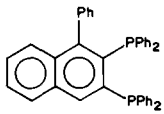
(63)

Kyba *et al.*[154] reported an improved procedure for the syntheses of the bifunctional phosphonates[154,155] (equation 64), which on reduction with $LiAlH_4/Me_3SiH$ afford the 1,2-bisphosphinobenzene **49.1** (equation 65)[155]. An alternative route[157] to these esters involves a Diels–Alder reaction with a cyclic diene according to equation 68. The diprimary phosphine **49.1** has also been obtained by $LiAlH_4$ reduction of the chlorophosphine $1,2\text{-}(PCl_2)_2C_6H_4$ (equation 67)[156]. The *para* derivative **55** ($n = 1$) and its 4,4'-biphenyl analogue **55** ($n = 2$) were synthesized by a related method[166].

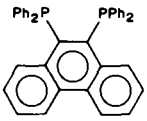
TABLE 6. Phosphines with aromatic backbones



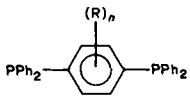
(49.1)[154–156] R^1–R^4 = H
(49.2)[151,154] R^1–R^4 = Me
(49.3)[152,154,157] R^1–R^4 = Ph
(49.4)[154,158] R^1,R^3 = H; R^2,R^4 = Me
(49.5)[158] R^1,R^3 = H; R^2, R^4 = Et
(49.6)[154,158] R^1,R^3 = H; R^2,R^4 = *i*-Pr
(49.7)[154] R^1,R^3 = H; R^2,R^4 = *t*-Bu
(49.8)[154,159] R^1,R^3 = H; R^2,R^4 = Ph
(49.9)[153,154] R^1,R^3 = Me; R^2,R^4 = Ph



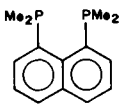
(50)[160]



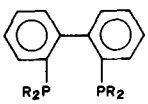
(51)[161]



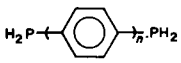
(52.1)[162] R = OEt
(52.2)[162] R = O-*t*-Bu
n = 2



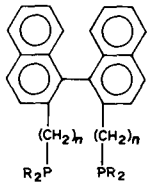
(53)[163]



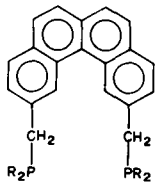
(54.1)[164] R = Me
(54.2)[165] R = Ph



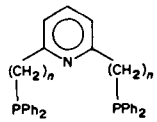
(55)[166] *n* = 1, 2



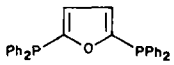
(56.1)[167–169] *n* = 0; R = Ph
(56.2)[167] *n* = 0; R = *p*-Tol
(56.3)[167] *n* = 0; R = *p*-(*t*-Bu)C_6H_4
(56.4)[170] *n* = 1; R = Ph



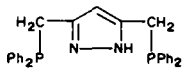
(57.1)[171] R = Me, Et, *t*-Bu, *c*-Hex, Ph
(57.2)[171] R = C_6H_4X, X = *m*-CF_3, *m*-Me, *p*-OMe



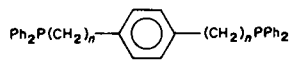
(58.1)[172] *n* = 0
(58.2)[173] *n* = 1
(58.3)[174] *n* = 2



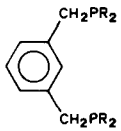
(59)[175]



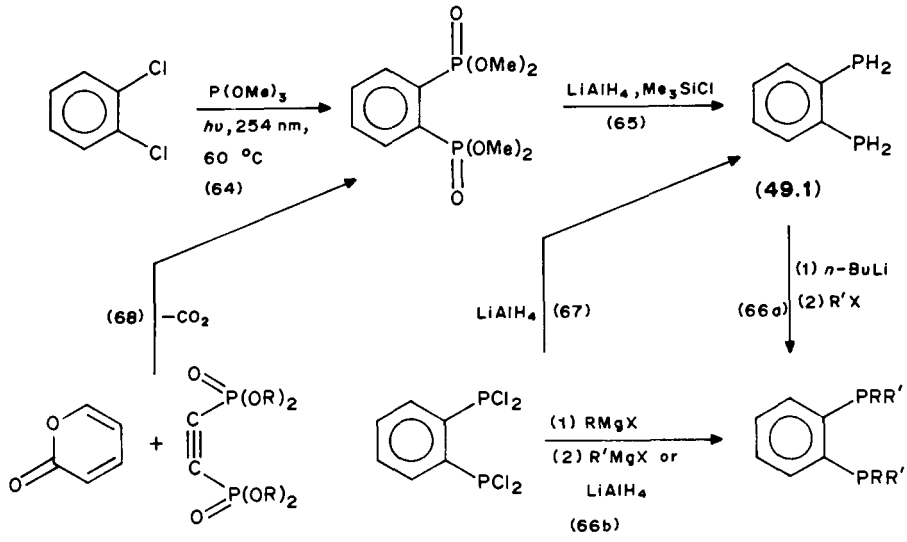
(60)[176]



(61.1)[177] *n* = 1
(61.2)[177] *n* = 2



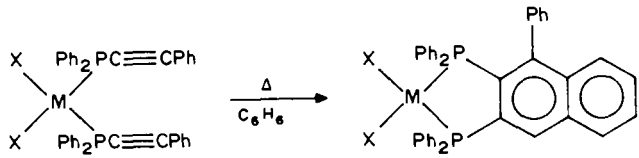
(62.1)[178] R = Me
(62.2)[179] R = *t*-Bu
(62.3)[180] R = Ph



(64–68)

The diprimary phosphine **49.1** and the chloro analogue, 1,2-$(PCl_2)_2C_6H_4$ have been employed as starting materials for the syntheses of various derivatives (**49.2**–**49.9**)[154,155,158,159] (equations 66a and b).

In an unusual template reaction, the 2,3-diphosphino-1-phenylnaphthalene **50** is formed on heating the *cis*-platinium or palladium complexes of phenylethynyldiphenylphosphine in benzene (equation 69)[160].



(69)

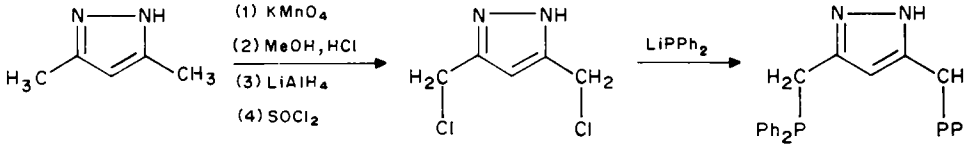
Reaction of 9,10-dichlorophenanthrene with $LiPPh_2$ afforded the 9,10-phenanthrene bridged ditertiary phosphine **51**[161].

Horner and Simons[162] reported a convenient synthesis for a *p*-phenylene bridged bidentate phosphine (**52**) based on the reaction of chlorophosphines with organolithium reagents formed by two fold lithiation of hydroquinone ethers.

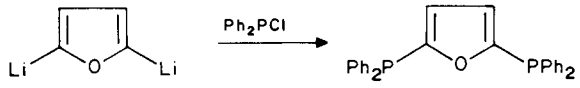
1,8-Naphthalene, 4,4'- or 2,2'-biphenyl and 1,1'-binaphthyl bridged ditertiary phosphines have been obtained by reaction of the corresponding organolithium derivatives with chlorophosphines R_2PCl (**53**[163], **54**, **55**[164–166], **56.1**[168,169]). The bidentate ligands **56.3** and **56.4** were synthesized by reduction of their oxides with $HSiCl_3/NEt_3$[167,170]. By virtue of the C_2 chirality and molecular pliancy, ligands of type **54**, **56** exhibit excellent chiral recognition in asymmetric syntheses.

The synthetic routes to the '*trans*-spanning' 2,11-bis(phosphinomethyl)-benzo[*c*]phenanthrene donor system **57** have been summarized in a recent review by Venanzi and coworkers[171].

Introduction of hetero aromatic units into the C_n bridges renders diphosphines either tridentate chelating or binucleating ligands. Their syntheses involve the reaction of the corresponding dihalides with organophosphides R_2PM (M = Li, Na) (**58.1**–**58.3**)[172–174],



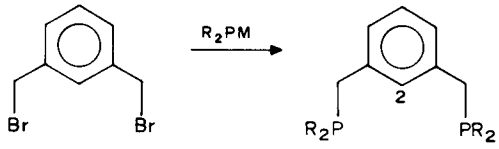
(70)



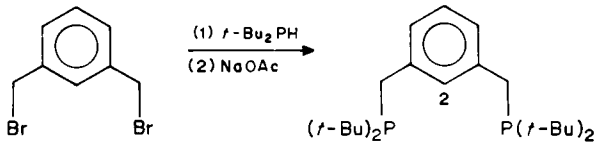
(71)

60[176]) or bifunctional organolithium derivatives with chlorophosphines R_2PCl (**59**)[175] (equations 70,71).

Ligands containing *m*- and *p*-phenylene units as part of the C_n backbone have been synthesized using standard methods (equations 72 and 73)[177–180]. The ligands with *m*-phenylene units undergo internal metallation at $C_{(2)}$ if the appropriate substrates are used.



(72)

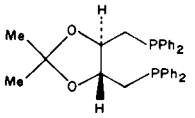


(73)

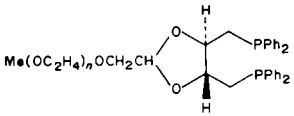
d. Chiral bidentate phosphine ligands. Since the early work of Dang and Kagan[181] in 1971 on diop (**63**), asymmetric syntheses using chiral transition metal phosphine complexes as catalysts has assumed a steadily increasing importance in organic chemistry. Rational structural modification of the chiral phosphines employed as ligands has been performed to improve the optical yields. As a result, an extended number of these ligands with different structures are now available. Their syntheses and applications have been discussed in detail in excellent reviews[182–186]. Therefore, only some recent developments will be reported here.

The linear P_2N_2 ligands **65.1**[187] and **65.2**[188] (Table 7) were synthesized by reaction of (*o*-aminophenyl)diphenylphosphine or (*o*-dimethylaminophenyl)phenylchlorophosphine

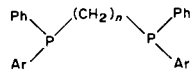
TABLE 7. Chiral bidentate phosphines



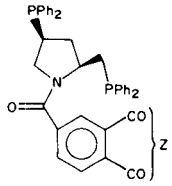
diop
(63)[181]



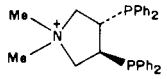
(64) ($n = 5, 16$)[189]



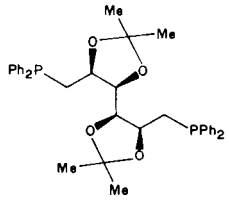
(65.1) ($n = 3$; Ar = o-$NH_2C_6H_4$)[187]
(65.2) ($n = 2$; Ar = o-$NMe_2C_6H_4$)[188]



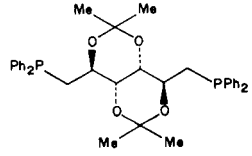
(66.1) $Z = (OH)_2$[190]
(66.2) Z = OH, $NH(CH_2)_2SO_3Na$[190]



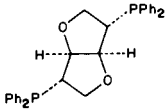
(67)[191]



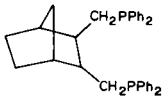
(68)[192]



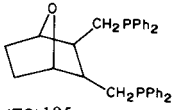
(69)[192]



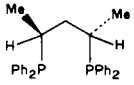
(70)[193]



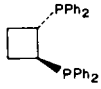
(71)[194]



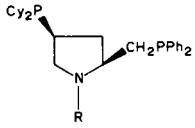
(72)[195]



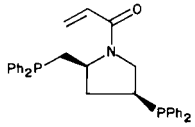
(73)[196]



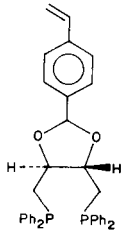
(74)[197]



(75)[198]



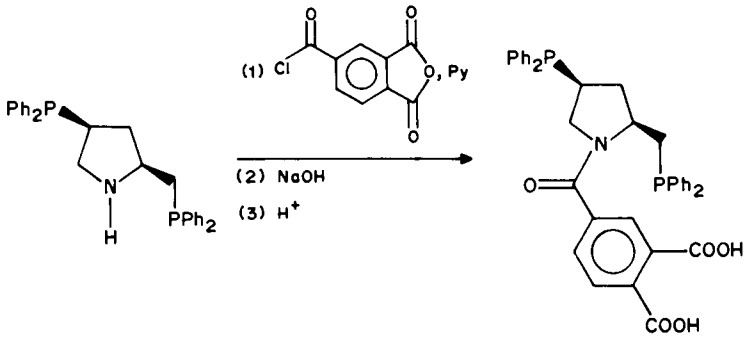
(76)[199,200]



(77)[200,201]

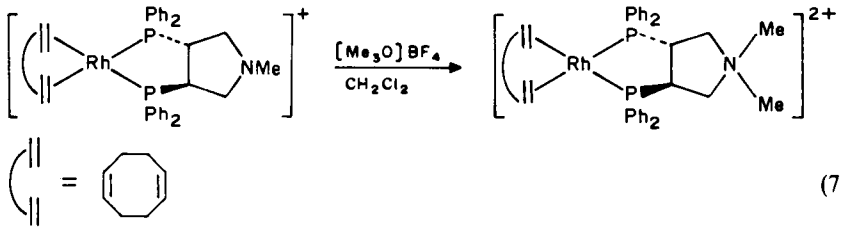
with lithium and subsequent treatment of the organolithium phosphides obtained with $Cl(CH_2)_nCl$ ($n = 2$ or 3). They form *racemic* and *meso* isomers. **65.1** may bind in a tridentate or tetradentate mode to transition metals.

Water solubilization of catalysts has become an area of increasing interest. It may be achieved by modifying known chiral phosphine ligands by introduction of groups bearing COOH or SO_3H substituents (**66.1**, **66.2**)[190], polyethylene glycol chains (**64**)[189] or quaternization of NR groups of ligands **67** already bound to a transition metal[191] (equations 74 and 75).



(74)

(**66.1**)



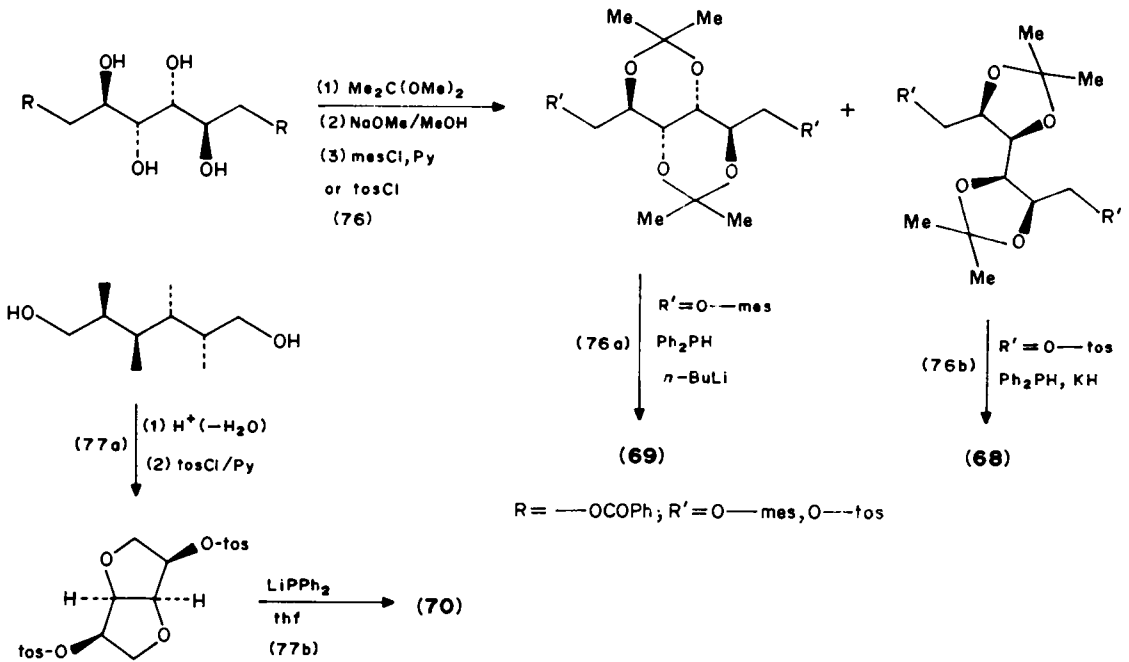
(75)

Using starting materials from the 'chiral pool' such as mannitol, novel chiral ligands containing two dioxolane rings are accessible (**68**, **69**[192], **70**[193]) in fair yields (equations 76, 77).

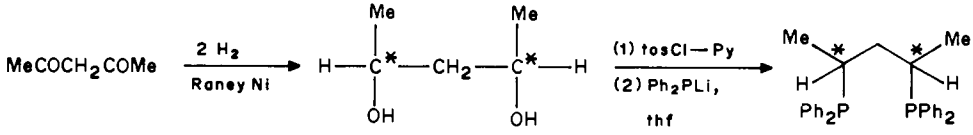
In order to test the effect of heteroatoms in the norbornane backbone on the catalytic activity of chiral phosphines **72**[195], the oxa analogue of **71**[194] has been synthesized in a multi-stage synthesis including Diels–Alder addition of furan to fumaryl chloride. After hydrolysis, hydrogenation and $LiAlH_4$ reduction, the 2,3-bis(hydroxymethyl)-7-oxanorbornane thus obtained is tosylated and subjected to reaction with Ph_2PNa.

Asymmetric heterogeneous hydrogenation of acetylacetone with a Raney nickel catalyst modified with a mixture of (*RR*)-or (*SS*)-tartaric acid and NaBr was applied to the preparation of both enantiomers of 2,4-bis(diphenylphosphino)pentane (**73**)[196] (equation 78).

The 4-hydroxypyrrolidine carboxylate was used as a starting material for the synthesis of unsymmetrically substituted 1,4-ditertiary phosphines with a 2,4-pyrrolidine bridge (**75**[198]). In a key step of this synthetic procedure, the phenyl substituents of one $Ph_2P(O)$ group are hydrogenated using $H_2/Rh-Al_2O_3$, a $(C_6H_{11})_2P(O)$ unit being formed (equation 79).

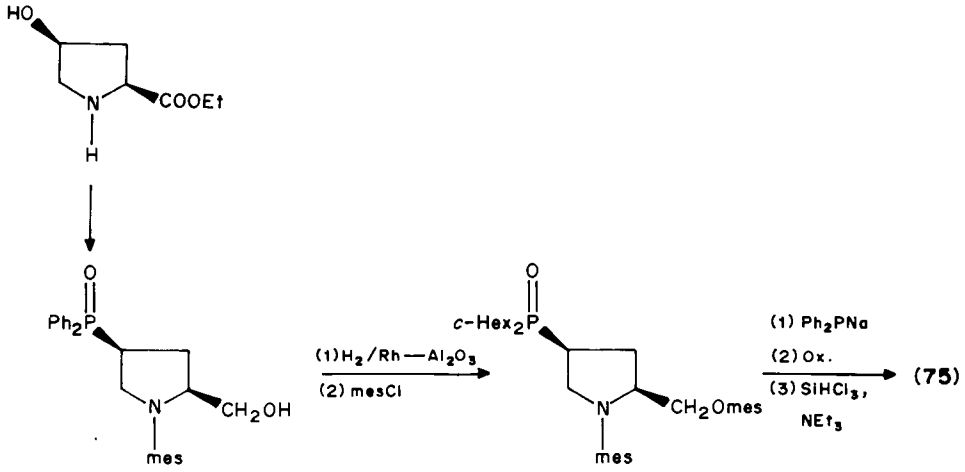

(1) Me2C(OMe)2
(2) NaOMe/MeOH
(3) mesCl, Py
or tosCl
(76)
(76a)
R'=O—mes
Ph2PH
n-BuLi
(69)
(76b)
R'=O—tos
Ph2PH, KH
(68)
(77a)
(1) H+(−H2O)
(2) tosCl/Py
LiPPh2
thf
(77b)
(70)
R= —OCOPh; R'=O—mes, O—tos

(76–77)



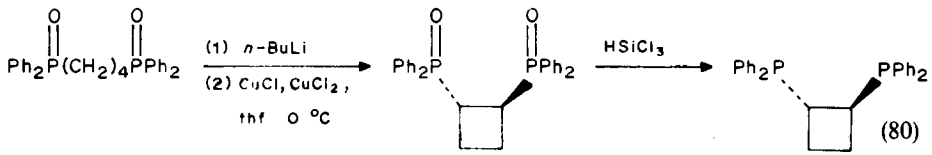
(73)

(78)



(79)

Copper-catalysed cyclization of $Ph_2P(O)(CH_2)_4P(O)Ph_2$ affords the racemic dioxide of **74**[197] (equation 80). After separation with L(−)-dibenzoyltartaric acid, the pure enantiomers of the phosphine oxides are reduced with $HSiCl_3$ to the bidentate phosphines **74**.



(80)

(74)

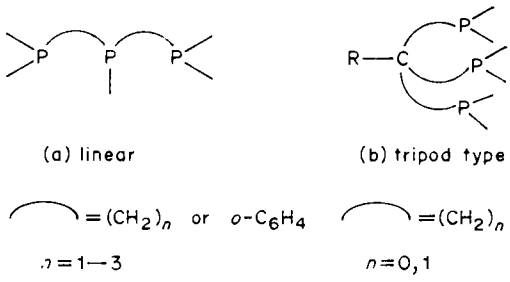
To overcome problems associated with separating the product from the catalyst in homogeneous asymmetric catalysis, the chiral ligands have been attached to cross-linked polymers[202]. Phosphine ligands bearing vinyl groups (e.g. **76**, **77**) were copolymerized with suitable monomers such as hydroxyethyl methacrylate, *N*,*N*-dimethylacrylamide, styrene or divinylbenzene[199–201].

B. Tridentate Phosphines

Over the past two decades, a large number of tridentate phosphine ligands with PC skeletons of different topologies have been reported. A perusal of the literature, however,

reveals that the synthetic approaches used for their preparation are based mainly on reactions well established in phosphorus chemistry, the most important of which have already been mentioned in the introductory remarks in Section II.

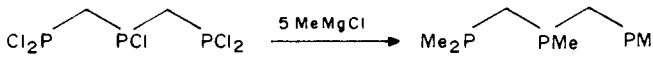
The phosphorus atoms in tridentate phosphines may be inter-connected (a) linearly or (b) branched tripod-like, leading to ligands with different coordination chemistry.



The chemistry of oligodentate phosphines was pioneered by Chatt and coworkers[203] in the 1960s and the progress in this area has been reviewed in a series of reviews[6–8,100,204,205].

1. Linear tridentate phosphines

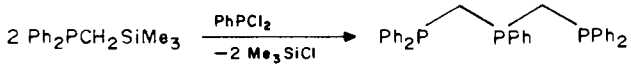
The methylene bridged derivatives **78.1**[206–208] and **78.2**[22] (Table 8) have the potential for binding three metal atoms in a row or coordinate to a bimetallic unit in a 'folded-in' manner and form a chelate ring about one metal atom (see Section III.F). The tridentate chlorophosphine $Cl_2PCH_2PClCH_2PCl_2$[206,207], Me_2PCH_2Li[208] or $Ph_2PCH_2SiMe_3$[22] may be used as key starting materials (equations 81–83) for their syntheses.



(81)

(**78.1**)

$$2Me_2PCH_2Li \xrightarrow{MePCl_2} \textbf{78.1} \qquad (82)$$



(83)

(**78.2**)

Base-catalysed (**79.3**[88], **79.4**[89,100], **79.5–79.7**[73], **79.9**[56], **79.10**[99,211], **83.2**[217]) or free radical-initiated (**79.2**[209], **79.11**[210], **80.1**[213], **80.2**[214], **80.4**[213,216], **82.1–82.3**[69]) addition of primary or secondary phosphines to vinyl or allyl phosphorus compounds $CH_2{=}CH(CH_2)_nX$ [$X = PR_2$, $P(S)R_2$, $P(O)R(OR')$, $P(O)(OR')_2$; $n = 0, 1$) have been widely employed for the syntheses of tridentate ligands containing $\succ P(CH_2)_nP\prec$ backbones ($n = 2, 3$) (equations 84 and 85). $LiAlH_4$ reduction of the addition products of unsaturated phosphinates or phosphonates to primary or secondary phosphines affords tridentate phosphines with PH functions in terminal and/or medial positions (equations 86, 87 and 89). Addition products of unsaturated phosphine sulphides [e.g. $RP(S)(CH{=}CH_2)_2$] to

TABLE 8. Tridentate phosphine ligands

$R^1P[(CH_2)_nPR^2_2]_2$

No.	n	R^1	R^2
78.1[206-208]	1	Me	Me
78.2[22]	1	Ph	Ph
79.1[73]	2	H	Me
79.2[209]	2	H	Ph
79.3[88]	2	Me	H
79.4[89,100]	2	Ph	H
79.5[73]	2	Me	Me
79.6[73]	2	Ph	Me
79.7[73]	2	Me	Ph
79.8[210]	2	*c*-Hex	Ph
79.9[56]	2	*neo*-Pen	*neo*-Pen
79.10[99,211,212]	2	Ph	Ph
79.11[210]	2	Ph	*c*-Hex
80.1[213]	3	Ph	H
80.2[214]	3	Me	Me
80.3[69a,93,215]	3	Ph	Ph
80.4[213,216]	3	Ph	Me
80.5[69a]	3	Me	Ph
80.6[214]	3	*t*-Bu	Me
80.7[93]	3	Ph	*c*-Hex

$R^1P[(CH_2)_3PR^2H]_2$

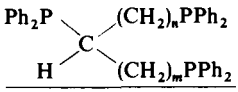
No.	R^1	R^2
81.1[213]	Me	Me
81.2[213]	Ph	Ph
81.3[213]	Ph	Me

$R^1_2P(CH_2)_3PMe(CH_2)_2PMeH$

No.	R^1
82.1[69]	Me
82.2[69]	*i*-Pr
82.3[69]	Ph

$R^1_2(PCH_2)_nPR^2(CH_2)_2PR^3_2$

No.	n	R^1	R^2	R^3
83.1[100]	2	Me	H	H
83.2[217]	2	Me	Ph	Ph
83.3[215]	3	Ph	Ph	Ph
83.4[215]	3	*c*-Hex	Ph	Ph

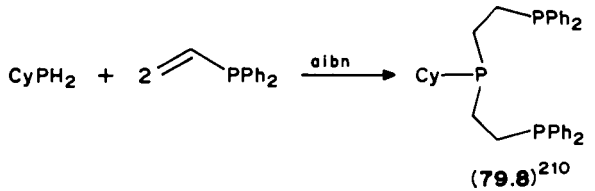


No.	n	m
84.1[218,219]	0	1
84.2[58,59]	1	2

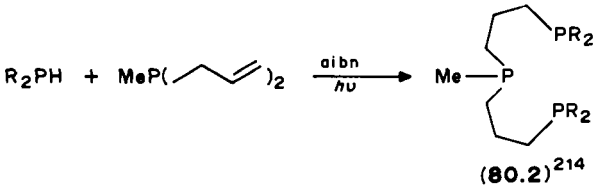
$R^1C[(CH_2)_nPR_2]_3$

No.	n	R	R^1
85.1[220]	0	Me	H
85.2[221,222]	0	Ph	H
86.1[21,223]	1	Et	Me
86.2[21,223]	1	Ph	Me

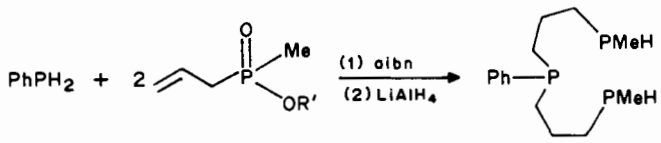
secondary phosphines may be desulphurized with either $LiAlH_4$ or sodium in boiling dioxane (equation 88). Using the diisopropylvinyl phosphonate $CH_2{=}CHP(O)(OR')_2$ ($R' = i$-Pr) as a synthon, the tertiary secondary primary phosphine **83.1**[100] was obtained by the sequence of reaction in equation 89.



(79.8)[210] (84)

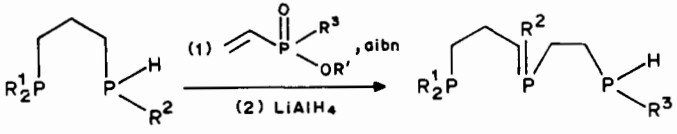


(80.2)[214] (85)



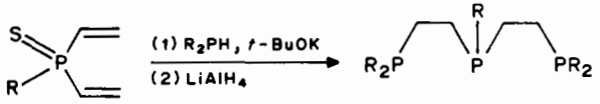
(86)

(81.3)[213]



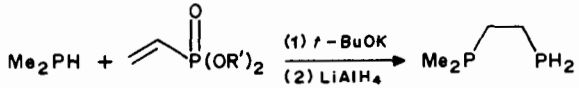
(87)

(82.1—82.3)[69]



(88)

(79.5)—(79.7)[73]



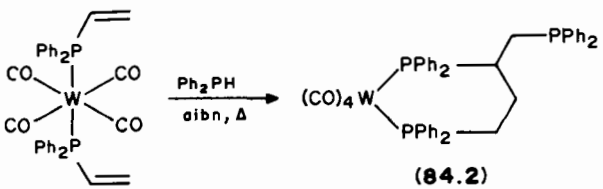
R' = *i*-PrO

(89)

(83.1)[100]

Addition of the vinylic ditertiary phosphine $CH_2{=}C(PPh_2)_2$ to primary or secondary phosphines yields interesting types of ligands, e.g. **84.1**[218,219], containing both P—C—P and P—C—C—P skeletons in the same molecule. This structure readily permits the study of the competition between the formation of four- and five-membered chelate rings.

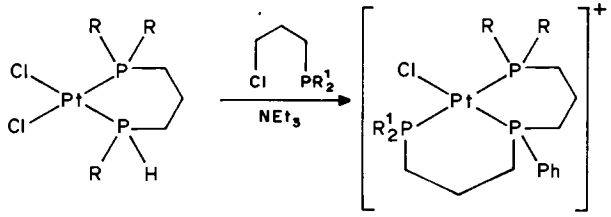
Template-mediated addition of vinylphosphines to primary or secondary phosphines offers an interesting and novel synthetic approach to new polydentate phosphine ligands and permits the control of the number of metal sites to which the ligand coordinates[58,59,212,215] (equation 90).



(90)

(84.2)

An alternative synthetic route to tridentate ligands (**80.3**[69a,93,215], **80.5**[69a], **80.7**[93]) is based on the reaction of ω-chloroalkylphosphines, e.g. $Cl(CH_2)_3PPh_2$, with organolithium phosphides, $PhPLi_2$[93] or $Ph_2P(CH_2)_3PRLi$[69a]. This type of reaction has been used for the template mediated synthesis of **80.3**, **83.3** and **83.4**[215] employing NEt_3 as a base (equation 91).



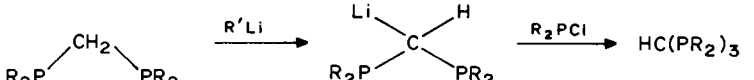
(91)

By base-catalysed addition of neomenthylphenylphosphine to phenyldivinylphosphine, the optically active tridentate ligand $PhP\{(CH_2)_2P(neo\text{-}Men)Ph\}_2$[224] has been obtained.

2. *Tripod-type tridentate phosphines*

Owing to their special geometry, the tripod-type ligands of type **86** favour facial coordination of one transition metal. Methylidenetrisphosphines **85**, however, should preferably function as capping tridentates for M_3 units, thus stabilizing trigonal faces formed by transition metal atoms in cluster compounds.

The ligands **86.1** and **86.2** (Table 8) are obtained by reaction of $RC(CH_2Cl)_3$ with the corresponding phosphides[21,223]. For the syntheses of the methylidenetrisphosphines, methylenebisphosphines $R_2PCH_2PR_2$ (R = Me, Ph) may be used as starting materials. *C*-Metalation at the bridging CH_2 group affords the organolithium compounds $R_2PCHLiPR_2$, which on reaction with R_2PCl yield the tripod-type ligands $HC(PR_2)_3$[220–222] (equation 92).



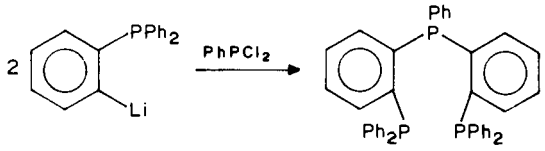
(85.1, 85.2) (92)

C-Lithiated phosphines are valuable reactive intermediates for the synthesis of a range of bi- and tri-dentate phosphine ligands[225] (e.g. **88**). This area has been reviewed by Abicht and Issleib[37c].

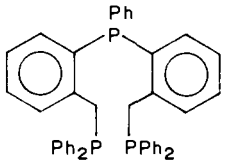
The *o*-phenylene-bridged tridentate phosphine ligand **87**, originally synthesized by Hartley *et al.*[226], may be obtained in satisfactory yields by reaction of $Ph_2P(o\text{-}LiC_6H_4)$ with phenyldichlorophosphine (equation 93)[37].

C. Tetra- and Poly-dentate Phosphines

Although of great potential in the stabilization of both high and low transition metal oxidation states, hydrides, nitrogen complexes and polynuclear arrangements with defined intermetallic distances, polydentate phosphines have so far received only sparse attention. This may be due to the intricate preparative routes involved in their syntheses. Aspects of developments in this field have been reviewed[100,204,205] and attempts have been made to systematize the different topologies of polydentate phosphines by use of graph theory[227,228].



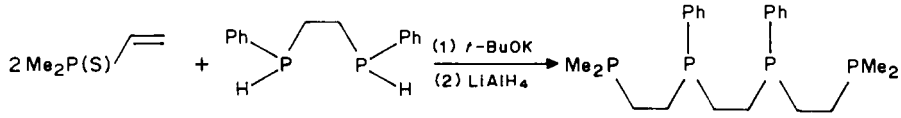
(87) (93)



(88)

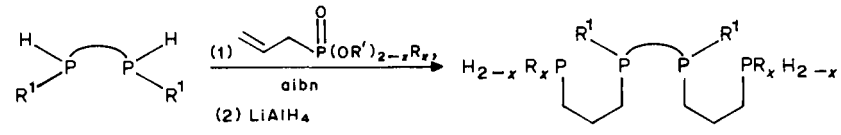
1. *Linear tetratertiary phosphines*

Free radical-initiated[229] or base-catalysed addition[73,99,100,204,211,230] of diphenylvinylphosphine to the disecondary phosphines $PhHP(CH_2)_nPPhH$ ($n = 2,3$) yield the tetratertiary phosphines **89.2** and **89.3** (Table 9). For the synthesis of **89.4**, the methylated analogue of **89.2**, $Me_2P(S)CH{=}CH_2$ (a 'protected' form of dimethylvinylphosphine) is made to react with $HPhP(CH_2)_2PPhH$. Reduction of the intermediate phosphine sulphide with $LiAlH_4$ in boiling dioxane affords the tetratertiary phosphine[73] (equation 94).



(89.4) (94)

PH-functional tetradentate phosphines have been prepared by free radical-initiated or base-catalysed addition of vinyl- or allyl-phosphorus compounds, $CH_2{=}CH(CH_2)_nP(O)(OR')_{2-x}R_x$ ($R' = i\text{-Pr}$; $n = 0$, 1; $x = 0$, 1) to disecondary phosphines followed by $LiAlH_4$ reduction (equation 95)[82,89,233]. Owing to the reactivity of the terminal PH-functional groups, these phosphines are versatile starting materials for the synthesis of a variety of derivatives (equation 96)[232,233]:



$x = 0, 1$; $R' = i\text{-Pr}$; $R, R^1 = Me, Ph$

(90.1, 90.2)

$\frown = (CH_2)_n$; $n = 2,3$ (95)

TABLE 9. Tetra- and poly-dentate phosphines

$[R^1_2P(CH_2)_mPR^2]_2(CH_2)_n$

No.	*m*	*n*	R^1	R^2
89.1[231]	1	3,6 10	*i*-Pr	*i*-Pr
89.2[99,211,230]	2	2	Ph	Ph
89.3[229]	2	3	Ph	Ph
89.4[73]	2	2	Me	Ph
89.5[232,233]	3	2	Me	Me
89.6[232,233]	3	3	Me	Me
89.7[231]	3	1	*i*-Pr	*i*-Pr

$[HRP(CH_2)_3PR^1]_2(CH_2)_n$

No.	*n*	R	R^1
90.1[82]	3	Ph	Ph
90.2[82,233]	3	Me	Me
90.3[82]	3	H	Ph
90.4[82]	3	H	Me
90.5[233]	3	*t*-Bu	Me
90.6[233]	2	Me	Me
90.7[89]	$[H_2P(CH_2)_2PPh]_2(CH_2)_2$		

$P[(CH_2)_nPR_2]_3$

No.	*n*	R
91.1[89]	2	H
91.2[73]	2	Me
91.3[56]	2	*neo*-Pen
91.4[99,211,234]	2	Ph
91.5[214]	3	Me, Et
91.6[235]	4	Me

$P(o\text{-}C_6H_4PR_2)_3$

No.	R
92.1[226,236]	Ph
92.2[237]	Me

$P(o\text{-}C_6H_4CH_2PPh_2)_3$ (**93**)[225]

$[Ph_2P(CH_2)_2PPh(CH_2)_2]_2PPh$ (**94**)[238]

$[R_2P(CH_2)_2]_2P(CH_2)_2PPh$ with $R_2P(CH_2)_2$ on the PPh

(**95.1**)[73] R = Me
(**95.2**)[238] R = Ph

$[[Et_2P(CH_2)_2]_2P]_2CH_2$
(**96**)[239]

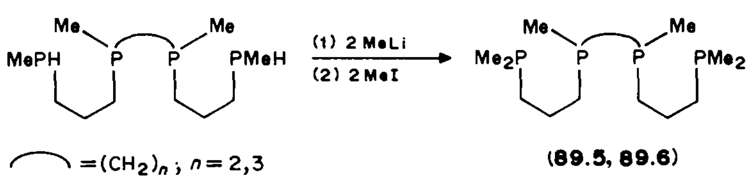
$[[R_2P(CH_2)_2]_2PCH_2]_2$
(**97.1**)[73] R = Me (**97.2**)[99] R = Ph

$[[Ph_2P(CH_2)_2]_2PCH_2]_2\text{—}p\text{-}C_6H_4$
(**98**)[240]

$P[(CH_2)_2P[(CH_2)_2PPh_2]_2]_3$
(**99**)[238]

$PhP[CH_2CH(PPh_2)_2]_2$
(**100**)[218,219]

$P[CH_2CH(PPh_2)_2]_3$
(**101**)[218,219]

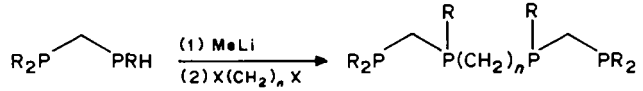


(96)

(89.5, 89.6)

Tetradentate phosphine ligands with the PC sequences PC_3PCPC_3P, $PCPC_nPCP$ (**89**) have been synthesized by alkylation reactions of the phosphides R_2PCH_2PRLi or

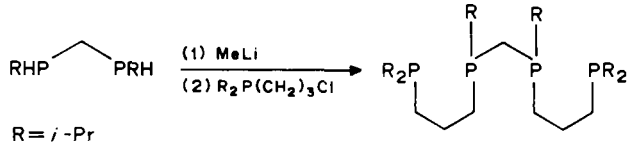
$RLiPCH_2PRLi$ with $R_2P(CH_2)_3Cl$ or α,ω-dihaloalkanes, respectively (equations 97 and 98)[231].



(97)

(89.1)

R = *i*-Pr; X = Cl; *n* = 3, 6, 10



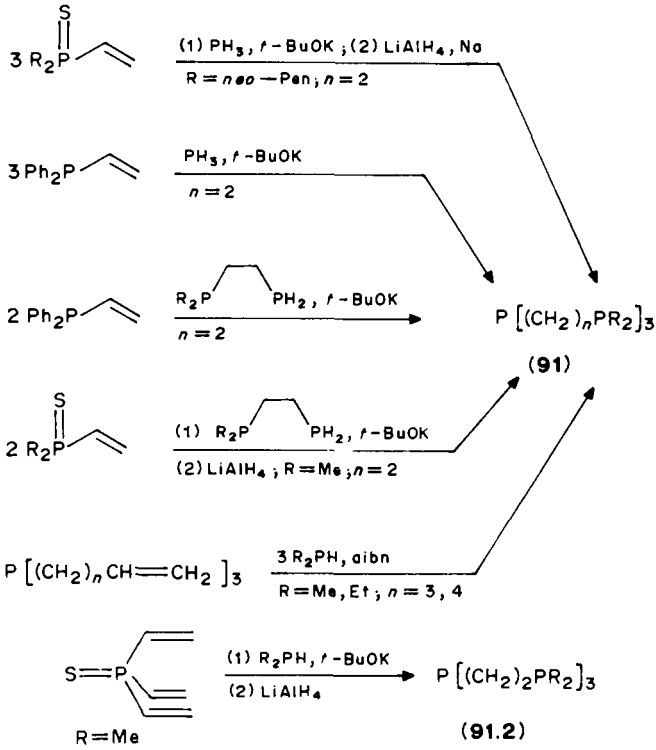
(98)

R = *i*-Pr

(89.7)

2. *Tripod-type tetradentate phosphines*

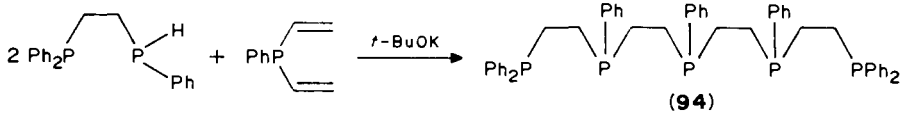
Owing to their special topology and flexibility, tetradentate tripod type ligands with $-(CH_2)_n-$bridging units are ideally suited for stabilizing trigonal bipyramidal coordination at transition metals. The synthesis of these ligands involves the addition of olefinic phosphorus compounds to PH_3[56,89,99,234] or primary tertiary[70,73] or secondary phosphines[73,99,214,235] (equations 99–104).



Tripodal tetratertiary phosphines containing rigid backbones impose trigonal bipyramidal coordination geometry on transition metals. The methyl analogue of **92.1**[236] has been obtained by reaction of 2-$LiC_6H_4PMe_2$ with triphenyl phosphite[237]. Abicht and Issleib[225] reported the synthesis of the more flexible tripod ligand **93** from *o*-$LiC_6H_4CH_2PPh_2$ and PCl_3.

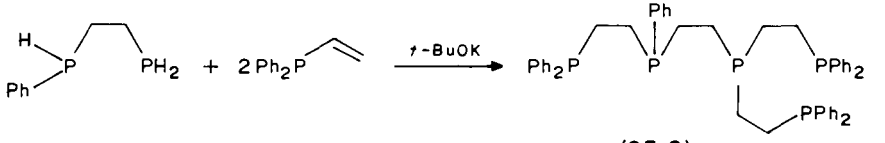
3. Poly-dentate phosphines

Open-chain or branched polydentate phosphines are accessible in good yields by addition of vinyl- or divinyl-phosphines to PH_3[218,219], primary[73,218,219], diprimary[239], secondary ($R_2P(CH_2)_2PPhH$)[238] or primary secondary phosphines[73]. The linear pentatertiary phosphines **94** (Table 9)[238] was thus obtained by base-catalysed addition of $Ph_2P(CH_2)_2PPhH$ to phenyldivinylphosphine (equation 105).



(94)

(105)



(95.2)

(106)

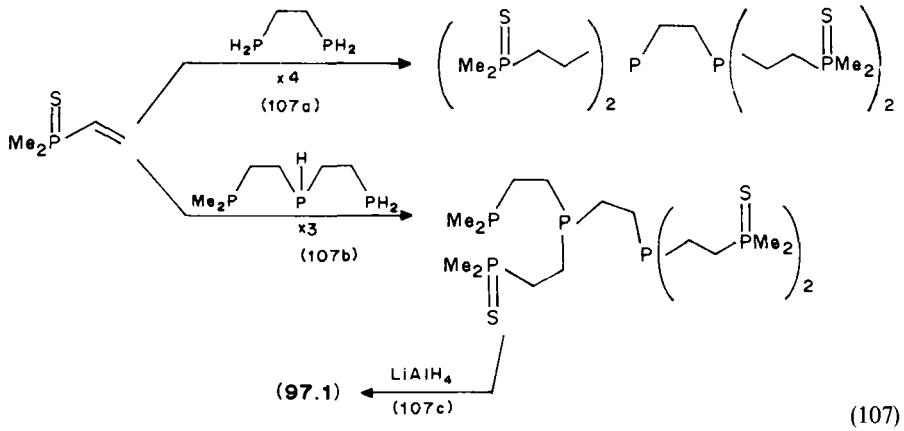
By variation of the reactands the branched isomer of **94**, **95.2** (equation 106) and the polytertiary phosphine **99** are accessible[238]. Alternatively, the hexatertiary phosphine **96**[239], capable of binding two phosphine-chelated metal atoms in close proximity, has been synthesized in 75–85% yield by free radical-initiated addition of the monovinylphosphine $Et_2PCH{=}CH_2$ to the diprimary phosphine $H_2PCH_2PH_2$.

1,1-Bis(diphenylphosphino)ethene was employed by McFarlane and coworkers[218,219] as a building block in syntheses of new type of ligands by addition of P—H bonds to C=C double bonds. The polyphosphorus ligands **100** and **101** obtained by base-catalysed addition of $(Ph_2P)_2C{=}CH_2$ to PH_3 or $PhPH_2$, respectively, contain both PCP and PCCP skeletons in the same molecule. These ligands therefore have the potential to coordinate one or more transition metals in different modes.

The hexatertiary phosphine **98**[240] with a *p*-xylylene spacer group between the bridge head P atoms of the two $P(CH_2CH_2PPh_2)_2$ units was obtained by base-catalysed addition of $Ph_2PCH{=}CH_2$ to the diprimary phosphine *p*-$PH_2CH_2C_6H_4CH_2PH_2$. The synthesis of the methylated hexatertiary phosphine **97.1**[73] by addition of four equivalents of $Me_2P(S)CH{=}CH_2$ to $H_2P(CH_2)_2PH_2$ (equation 107a) followed by $LiAlH_4$ reduction failed owing to insufficient solubility of the intermediate tetrasulphide of **97.1**. These difficulties could be circumvented employing the trisulphide obtained according to equation 107b in the $LiAlH_4$ reduction (equation 107c).

D. Macrocyclic Phosphines containing P—C_n—P Bonding

The first preparation of a macrocyclic ring system containing four phosphorus atoms (**99.1**–**99.3**) was carried out by Horner *et al.* in 1975[241]. In recent years, increasing interest



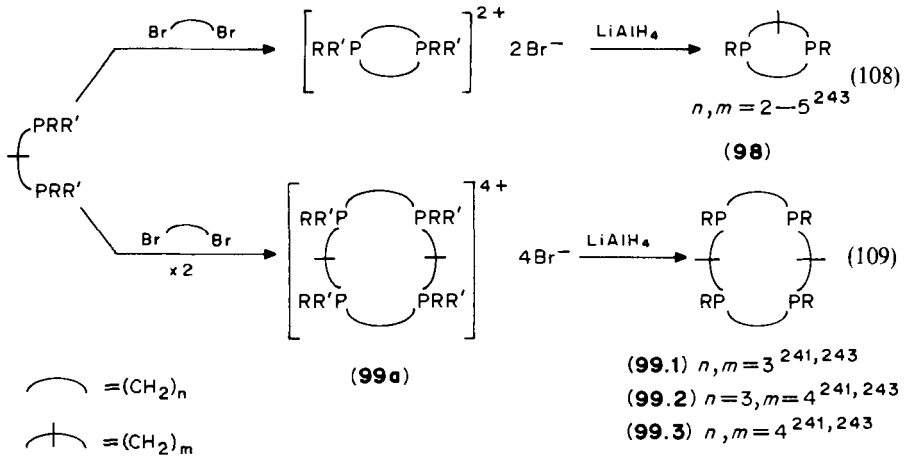
(107)

has been devoted to the synthesis of these stereochemically versatile ligands, which are strongly binding towards soft transition metals.

In a review of the syntheses of macrocyclic complexes Melson[242] summarized the literature up to 1979. A recent review[7] covers some aspects of macrocyclic phosphines chemistry.

Different synthetic approaches have been used for the macrocyclization of mono-, bi-, tri- or open-chain tetra-dentate phosphines, bearing good leaving groups at phosphorus (such as the benzyl group; see below) or PX functionalities (X = H, Li). Alternatively, phosphines with functional groups (*C*-halogen, γ-carbonyl groups) in the side-chains may be engaged in the ring-closure reactions. Reactions of types (a)–(e) will be discussed in this Section:

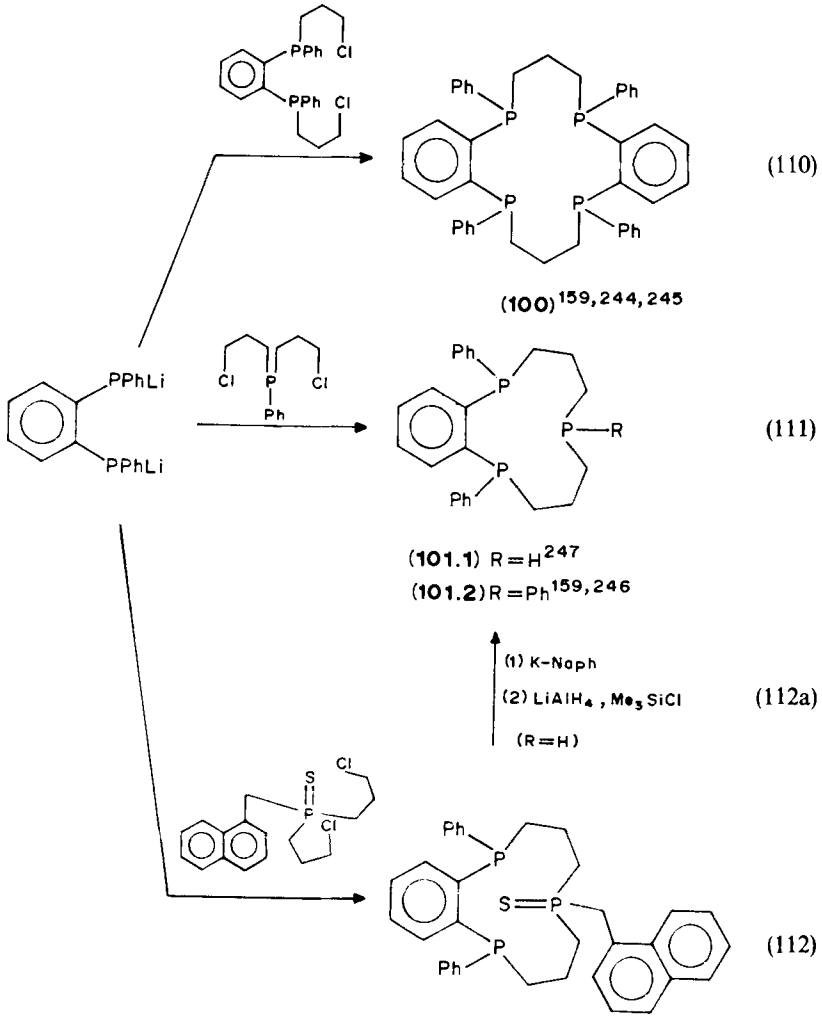
a. Reactions of ditertiary phosphines bearing at least one benzyl group per phosphorus atom with α,ω-dibromoalkanes in dilute solutions (**98, 99.1–99.4**)[241,243] followed by reduction with $LiAlH_4$ (equations 108 and 109).



(108)

(109)

b. Alkylation of disecondary phosphines or their alkali metal derivatives with α,ω-halogenfunctional mono- or bidentate phosphines under high dilution conditions (**100**[159,244,245], **101.1**, **101.2**[159,246,247]) (equations 110–112).
c. Template-mediated alkylation of disecondary or diprimary phosphines with reactive α,ω-dihalogen compounds (**102**[248,249], **103**[250]) (equations 113 and 114).
d. Metal-assisted addition of α- or β-diketones or α,ω-keto functional bidentate phosphines to disecondary or diprimary phosphines (**104**[251,252], **105**[253]) (equations 115 and 116).
e. Addition of allyl- or vinylphosphines to complexes of disecondary phosphines (**106**[254,255], **107**[256]) (equations 117 and 118).



The ring-closure reactions 108–112 afford 7–20-membered bidentate or macrocyclic tri- and tetra-dentate phosphines **98**–**99.3**[241–243] and **100**–**101.2**[159,244–247] in only moderate overall yields.

Only one isomer (C_s symmetry) of **101.2** was isolated. The phenyl substituents on the *o*-phenylene diphospha unit are *cis* occupying pseudo-equatorial position in a conformation with a dihedral angle of 100.3° between the benzo ring and the plane defined by the three phosphorus atoms (Figure 1).

Of the five possible isomers (three *meso* and two *dl* pairs) of **100**, two (a and b, Figure 1) were isolated from the macrocyclization reaction (equation 110). X-ray structural analysis revealed these to be *cis, cis, cis* (**100a**) and *cis, trans, cis* (**100b**)[244,245].

Using a 1-naphthylmethyl substuituent as a protecting group for the PH function, the 11-membered ditertiary secondary phosphine **101.1** has been synthesized (equation 112)[247].

In order to overcome problems associated with the low-yield ring-closure step in equations 108–112, template-type reactions have been employed in the syntheses of macrocyclic phosphines. This procedure was originally proposed by Horner and Kunz[257] in 1971 and later (1977) used by Del Donno and Rosen[248,249] in a multi-stage synthesis of **102** (equation 113). In the first single-stage syntheses of macrocyclic tetradentate

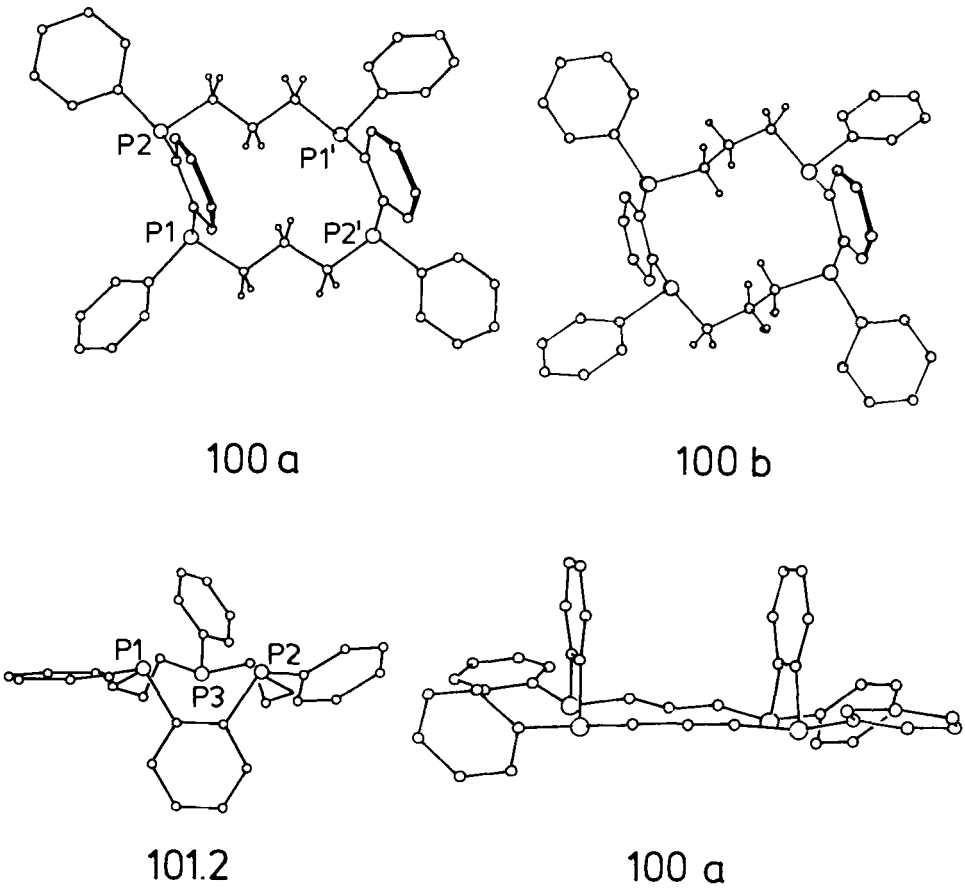
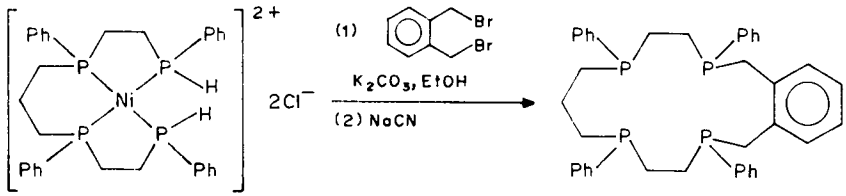


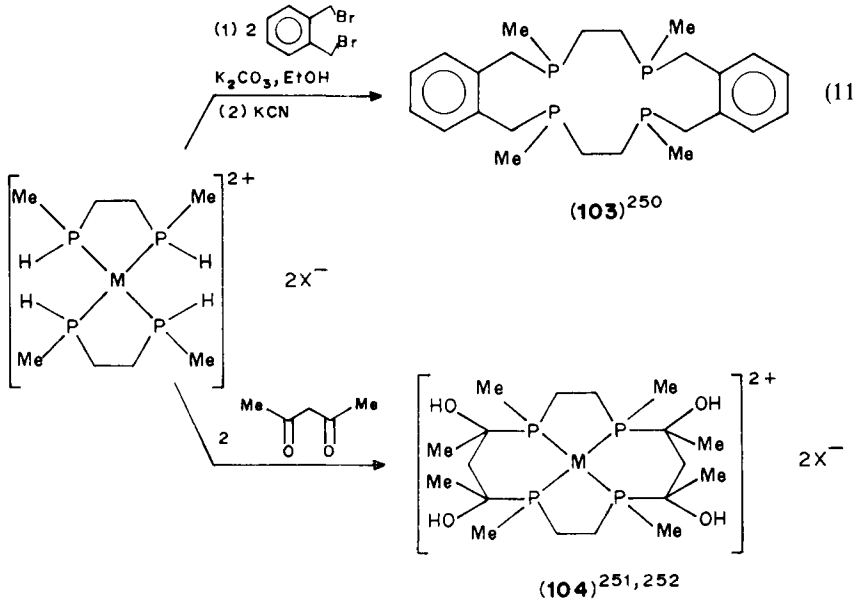
FIGURE 1. Diastereoisomers (a,b) of **100** and **101.2**. **100a** is shown in side and top view.



(102)[248,249]

(113)

phosphines and their complexes (**103**[250], **104**[251,252]), disecondary or diprimary phosphines were used a starting materials. Template-mediated macrocyclization was achieved by P-alkylation with dihalides (equation 114) or through addition of β-diketones to the PH groups of $[M\{HMeP(CH_2)_2PMeH\}_2]Cl_2$ (equation 115).



(103)[250]

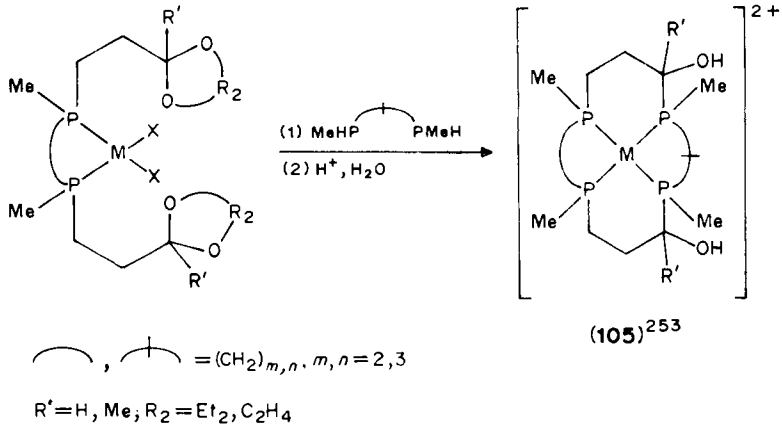
(114)

(104)[251,252]

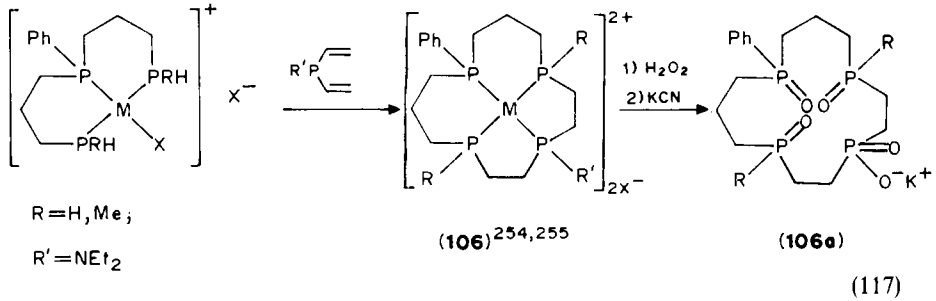
(115)

Bis(tertiary)phosphines with protected carbonyl groups in γ-position to phosphorus, $\{(RO)_2R'CCH_2CH_2PMe\}_2(CH_2)_m$($m = 2,3$; R = Et, 2R = C_2H_4; R' = H, Me) (L) form complexes $[MX_2L]$ (M = Ni, Pd, Pt, X = Cl, Br). The halides X may be replaced by secondary phosphines, $HMeP(CH_2)_nPMeH$, leading to a template in which after cleavage of the CO-protecting groups with H^+/H_2O the macrocyclic ring system is formed through addition of the PH-bonds to the carbonyl groups[253] in quantitative yield (equation 116).

Transition metal-mediated addition of olefinic bonds to PH functions has been used successfully for the syntheses of macrocyclic tetradentate phosphine ligands **106** and their oxides **106a**[254,255] (equation 117).

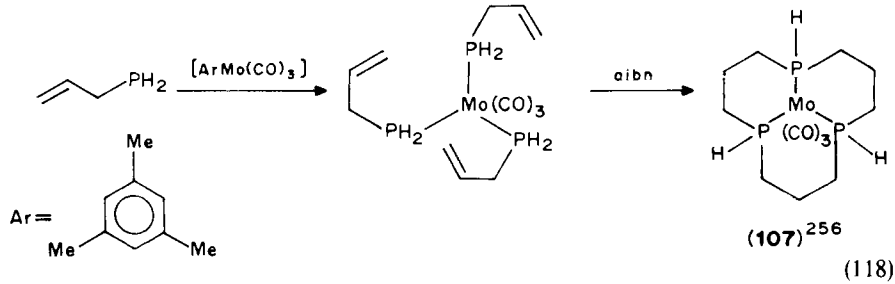


(116)



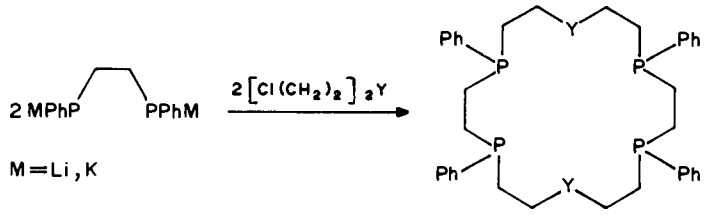
(117)

In elegant work Diel *et al.*[256] were able to cyclize allylphosphine to a 12-membered tridentate macrocyclic phosphine (**107**) using $Mo(CO)_3$ as a template (equation 118).



(118)

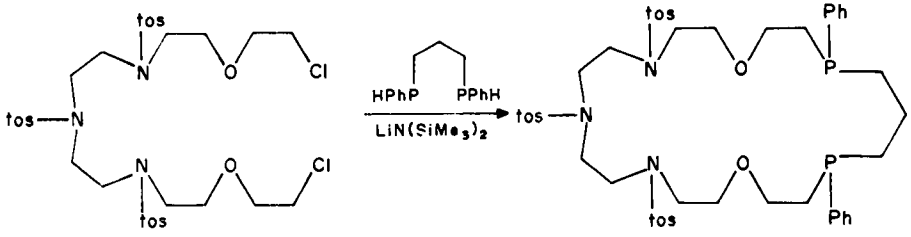
The first crown ether-type tetraphosphorus macrocycle (**108.1**) and its sulphur (**108.2**) and dinitrogen analogues (**108.3**) were synthesized by Ciampolini and coworkers[258–260] in moderate yields by macrocyclization of $MPhP(CH_2)_2PPhM$ (M = Li, K) with $\{Cl(CH_2)_2\}_2Y$(Y = O, S, PrN) (equation 119). All five isomers of **108.1** have been isolated by ion-exchange chromatography using SP Sephadex C-25 support on aqueous solutions of the nickel(II) derivatives.



(108.1)[258] Y=O
(108.2)[259] Y=S
(108.3)[260] Y=PrN

(119)

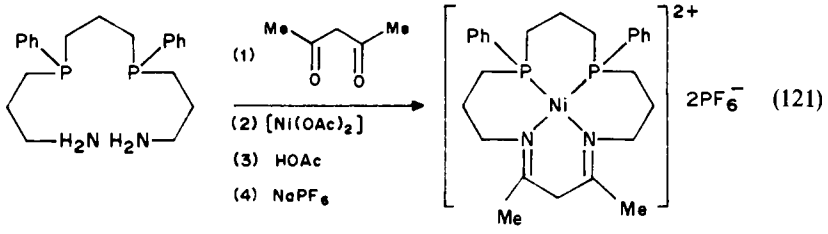
In a multi-stage synthesis Lippard's group[261] obtained oxa- and aza-phosphands (**109**) related to **108.1**–**108.3** by high-dilution condensation of the linear α,ω-dichloro functional diethylenetriamine (with *p*-tolylsulphonyl protecting groups) and 1,3-bis(phenylphosphino)propane using lithium bis(trimethylsilyl)amide as a base (equation 120).



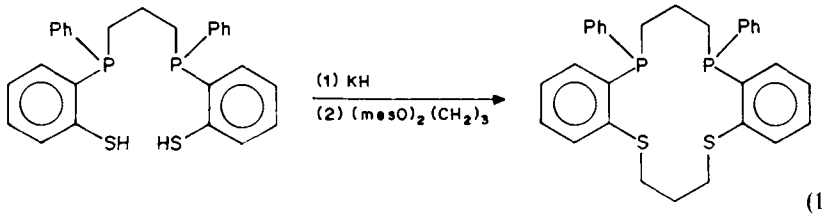
(109) (120)

The syn (*meso*) and anti (*racemic*) diastereomeric forms of **109** have been separated via complexation to nickel(II). Detosylation was achieved with sodium naphthalenide in presence of *t*-BuOH at −45 °C.

Tertiary or secondary phosphines with NH_2 or SH groups in the side-chains are versatile starting materials for the template syntheses of macrocyclic phosphines with the P_2N_2[262–264] (**110**) or P_2S_2 donor set[265] (**111**), respectively. Ring formation is effected by condensation with β-diketones (equation 121)[262] or alkylation with bifunctional alkylation reagents (equation 122)[265].

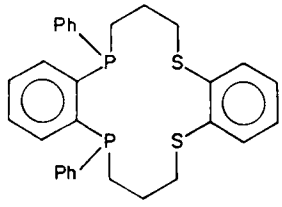


(110) (121)



(111) (122)

Macrocycle **112**, the isomer of **111**, has been obtained by high-dilution condensation of o-$C_6H_4(PPhLi)_2$ with o-$C_6H_4(S(CH_2)_3Cl)_2$[244]. Related macrocycles incorporating the o-$C_6H_4(AsMe)_2$ moiety have also been reported[266].



(112)

III. REACTIVITY OF BI- AND POLY-DENTATE PHOSPHINES WITH P—C_n—P BONDING

Phosphines, although weaker bases, are in general much stronger nucleophiles than amines of comparable structure. The reactivity of phosphines is therefore governed to a great extent by their nucleophilicity, which depends strongly on the nature of the substituents at phosphorus. Phosphines have a dual reactivity, however. They can act as σ-Lewis bases and as π-acceptors by virtue of the vacant phosphorus 3d orbitals. This biphilic character[267] accounts much for the general reactivity pattern of phosphorus(III) compounds in Main Group and transition metal chemistry. By a cooperative interplay of steric and electronic properties of their donor groups, polydentate phosphine ligands may increase the nucleophilicity of the Lewis acid centre to which they are bound, the coordination mode being subtly determined by steric factors, e.g. the spatial demand of the substituents at the P atoms. For monodentate phosphine ligands PR_3 or $PR^1R^2R^3$ bonded to nickel (Ni-P distance 228 pm), steric effects have been described by Tolman[7,268] in terms of the 'cone angle θ' obtained from X-ray crystallographic data and molecular models (Figure 2).

For bidentate and polydentate phosphine ligands, the intrinsic geometry of the ligand skeletons, i.e. their flexibility and connectivity, seems, however, to be of greater importance than the steric demand of the individual donor groups, as will be shown later in this section. There are, however, cases where the nature of the terminal substituents at phosphorus seems to be of significance, as has been shown for the bidentate ligands of type **29** with long, flexible alkylene binding units[112,113]. According to the work of McAuliffe and his group[115,116] the coordination chemistry of these ligands is governed, however, by the length of the $(CH_2)_n$-chain.

After discussion of the nucleophilic reactivity of bi- and poly-dentate phosphines towards Main Group electrophiles, some relevant aspects of their transition metal coordination chemistry are presented.

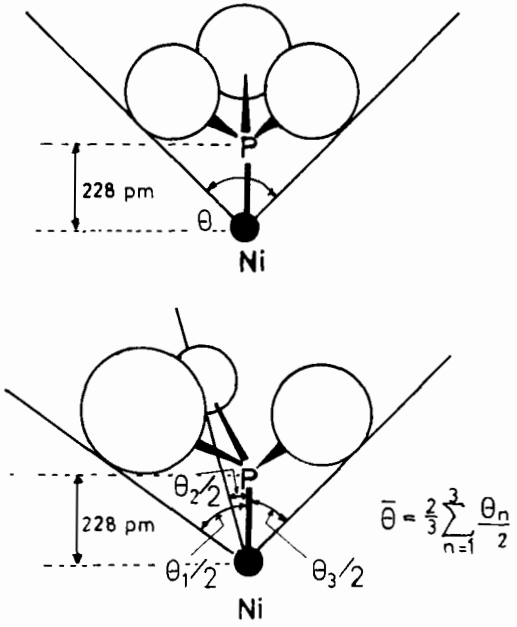
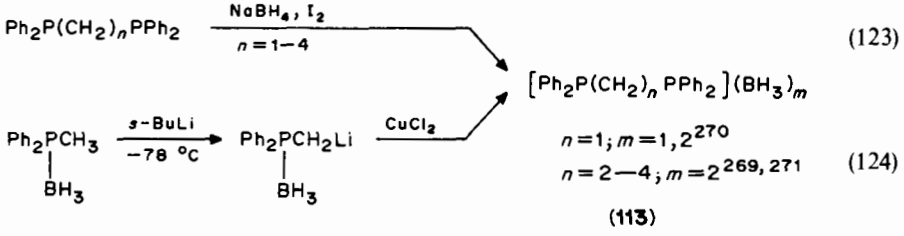


FIGURE 2. Definition of the cone angles θ or $\bar{\theta}$ for ligands PR_3 or $PR^1R^2R^3$, respectively.

A. Borane Adducts, Phosphinoboranes

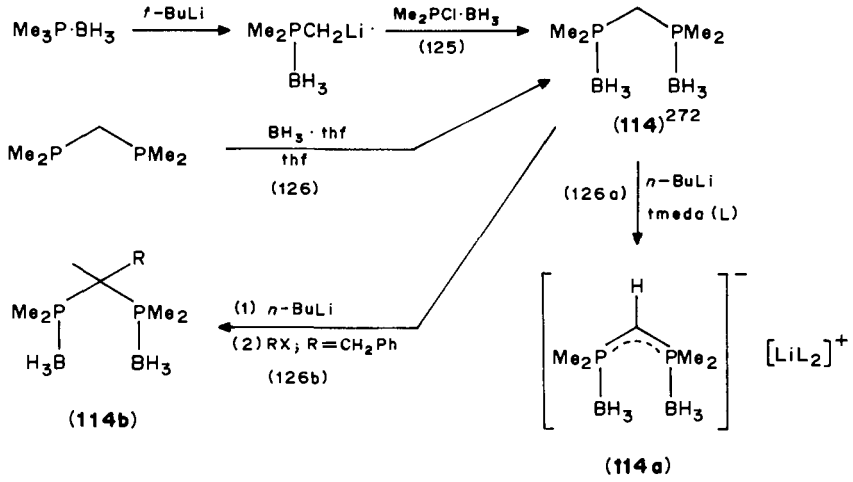
The formation of Lewis acid–base adducts between phosphines and borane is well established. New procedures have been developed for the syntheses of BH_3 adducts of bidentate phosphines. The borane adducts **113** were prepared in high yields by reaction of $(Ph_2P)_2(CH_2)_n$ with $NaBH_4/I_2$[269,270] (equation 123) or oxidative C—C coupling of $Ph_2PCH_2Li \cdot BH_3$ with $CuCl_2$[271] (equation 124). Alternatively, borane adducts of ditertiary phosphines are accessible also by P–C coupling reactions, as indicated for **114** in equation 125[272]. Compound **114** can be obtained, however, in a simpler way by reaction of $Me_2PCH_2PMe_2$ with BH_3·thf (equation 126).



(123)

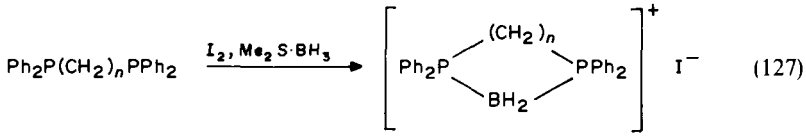
(124)

The compounds $R_2PCH_2Li \cdot BH_3$ (R = Me, Ph) are prepared by deprotonation of the corresponding phosphine borane adducts $R_2PCH_3 \cdot BH_3$[271,272]. Similarly, deprotonation of **114** with *n*-BuLi leads to **114a**. Compounds **114** can be converted into its *C*-alkyl derivative **114b** by alkylation of $(Me_2PCHLiPMe_2)(BH_3)_2$ with RX (equation 126b).



(125-126)

Cyclic boronium iodides of type **115**[269,270] are formed if the ditertiary phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) are treated with monoiodoborane, which may be generated *in situ* from $Me_2S{\cdot}BH_3$ and I_2 (equation 127).



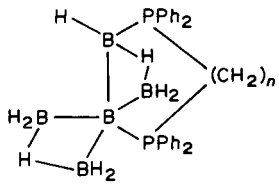
(127)

$n = 1$[270]

$n = 2$—4[269]

(115)

Bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1,2$) add to pentaborane-9 without degradation of the B_5 cluster unit. The complexes, e.g. **116**, may be considered as derivatives of the hypho-$B_5H_{11}^{2-}$ anions[273]. Even with excess $Ph_2P(CH_2)_nPPh_2$ (= L), no formation of BH_3L was observed, whereas monodentate phosphines such as Me_3P cause a breakdown and rearrangement of the B_5 cluster structure[274].

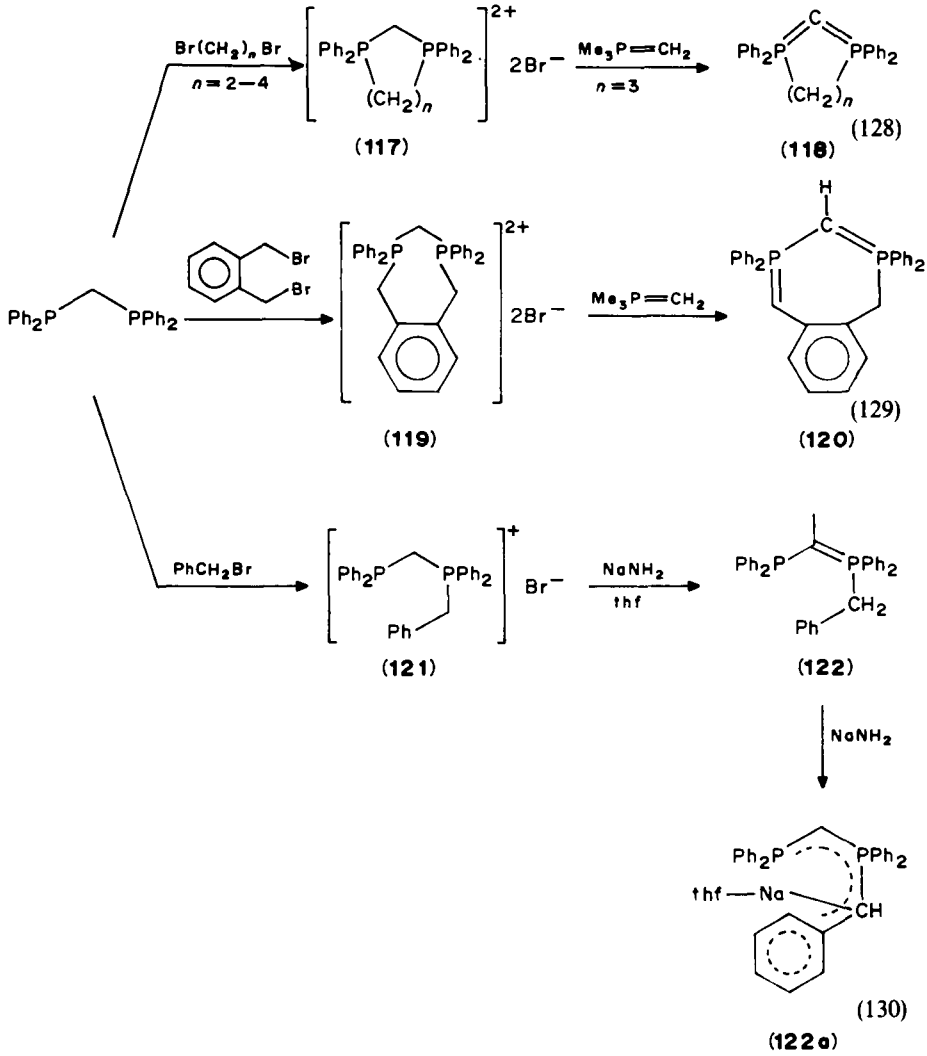


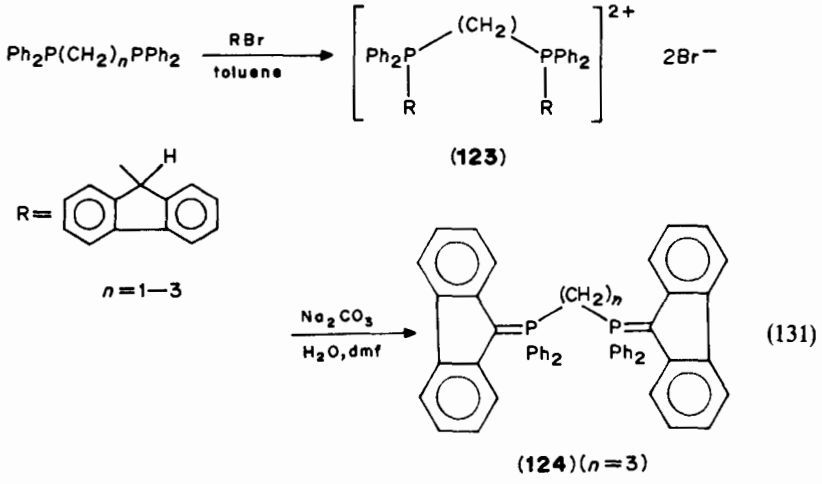
$n = 1,2$

(116)

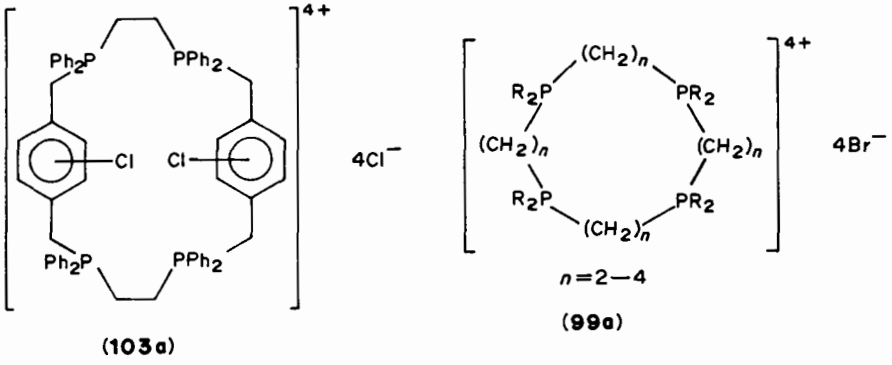
B. Nucleophilic Reactions at Carbon

Ditertiary phosphines react with mono- or bi-functional halides to form open-chain or cyclic phosphonium salts, respectively (**117**[275], **119**[276], **121**[277], **123**[278]). The quaternization of $R_2PCH_2PMe_2$ (R = Me, *t*-Bu, Ph) with MeI and $Br(CH_2)_nBr$ ($n = 1,2$) was studied by Karsch[279]. No cyclic phosphonium salts were formed with $Br(CH_2)_2Br$, however. Deprotonation of bifunctional quaternary phosphonium salts at the α-position using $NaNH_2$, KH, Na_2CO_3 or $R_3P{=}CH_2$ affords ylids (e.g. **122**[277], **124**[278]) or ring-strained carbodiphosphoranes, or double ylids (e.g. **118**[275], **120**[276]), which have been studied extensively by Schmidbaur's group. The ylid **122** may be deprotonated further with $NaNH_2$ to yield a novel organosodium compound (**122a**)[277] (equations 128–131).

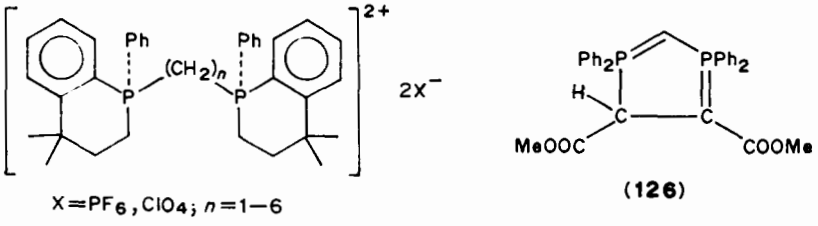




The formation of tetrafunctional phosphonium salts (e.g. **99a**[241,243]) from bidentate phosphines has been employed as a key step in the syntheses of macrocyclic phosphines (e.g. **99**) (see Section II,D).



Macrocyclic phosphonium salts (e.g. **103a**) with xylylene bridges were obtained in high yields by reaction of p-xylylene dihalides with $Ph_2P(CH_2)_2PPh_2$ by Berlin *et al.*[280]. Recently the same group reported the syntheses of chiral bis(phosphonium) salts (**125**).



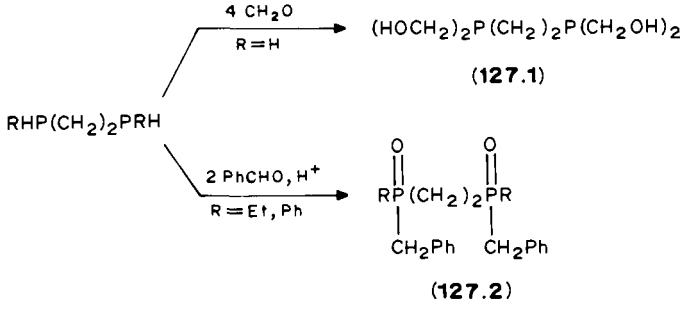
The diastereoisomers could be separated by crystallization and the enantiomers were obtained in pure form via the silver hydrogen dibenzoyl tartrates[281].

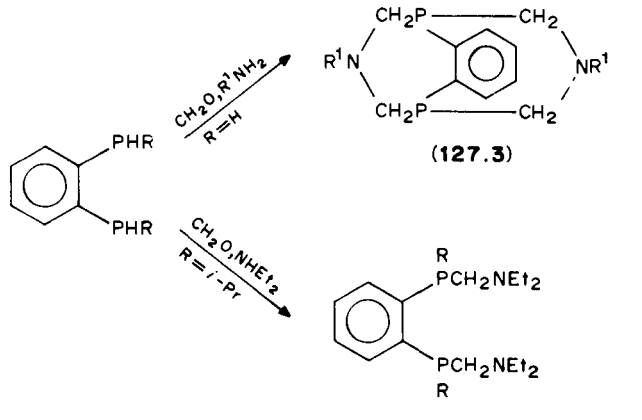
If the organo halides employed bear electronegative groups at carbon then the nucleophilic attack of the phosphine is directed towards the halogens; reactions of this type will be discussed in section D.

Tertiary bidentate phosphines behave as nucleophiles towards activated carbon—carbon and carbon—oxygen multiple bonds. Thus $Ph_2PCH_2PPh_2$ reacts with dimethylacetylene dicarboxylate to form the 5*H*-diphosphole **126**[282]. This topic has been reviewed[283,284].

Primary and secondary phosphines add to olefins (and acetylenes) in a straightforward manner by hydrogen transfer. The anti-Markownikoff products are formed preferentially. Free radical sources (such as aibn), strong bases (such as *t*-BuOK), acids and UV light are used as initiators. These reactions have widely been used in the syntheses of bi- and poly-dentate ligands with P—C_n—P bonding (see Section II).

PH-functional bidentate phosphines generally react with aldehydes and ketones to form compounds having new P—C—O bonds. Thus formaldehyde with the diprimary phosphine $H_2PCH_2CH_2PH_2$ gives **127.1**[285]. If aromatic aldehydes, however, are employed in these addition reactions, the hydroxyalkylphosphines formed initially rearrange to the phosphine oxides (e.g. **127.2**[286]) (equations 132a and 132b). The general topic has been surveyed by Wolfsberger[287].





Mannich-type reactions involving diprimary or disecondary phosphines, e.g. $H_2P(CH_2)_nPH_2$ ($n = 1$–4), *o*-$(PH_2)_2C_6H_4$ or *o*-$(PRH)_2C_6H_4$ (R = Ph, *i*-Pr, *n*-Bu, Et) yield the α-aminomethyl derivatives, e.g. **127.3** and **127.4**[288] (equations 132c, 132d). A review treating the general topic has appeared recently[40].

C. Formation of Oxides, Sulphides and Selenides

Bidentate and polydentate phosphines generally react with oxygen or sulphur and many oxygen- and sulphur-containing compounds to form the phosphine oxides or sulphides, the driving force being the high P=O and P=S bond energies. The general topic has been reviewed[289,290].

While the syntheses of the dioxides and disulphides of ditertiary phosphines are straightforward, the formation of the monoxides and monosulphides[291] needs careful control of the reaction conditions. Selective monooxidation or monosulphurization of ditertiary phosphines is only possible if the phosphorus atoms differ in their basicities as in $Me_2PCH_2PPh_2$, the monosulphide of which, $Me_2P(S)CH_2PPh_2$, may be obtained by direct sulphurization[279]. Selective monoselenation is possible, however, just by a proper choice of the reactants (selenium or, less good, KSeCN and ditertiary phosphine)[292] (equation 133).

$$Ph_2PCH_2PPh_2 \xrightarrow[\text{(or KSeCN)}]{Se} Ph_2P(Se)CH_2PPh_2 \qquad (133)$$

(128.1)

For a deliberate synthesis of the monoxides, monosulphides and monoselenides of the methylenebisphosphines **128.1**–**128.3**, P–C coupling reactions between $Ph_2P(X)CH_2Li$ and R^1R^2PCl[25,291,292] have been used (equation 134). Owing to the juxtaposition of the Ph_2P and PR^1R^2 groups, intramolecular sulphur transfer from the less basic to the more basic P atom occurs on heating of the monosulphides. Further oxidation of the monosulphides with sulphur yields the disulphides of the methylenebisphosphines.

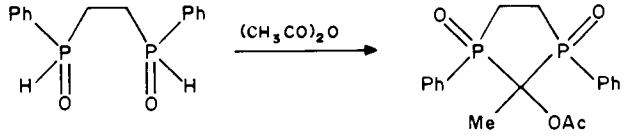
$$Ph_3P{=}X \xrightarrow[-PhH]{MeLi} Ph_2P(X)CH_2Li \xrightarrow{R^1R^2PCl} Ph_2P(X)CH_2PR^1R^2 \xrightarrow[X=S]{\Delta} Ph_2P(X)CH_2PR^1R^2 \qquad (134)$$

(128.2) **(128.3)**

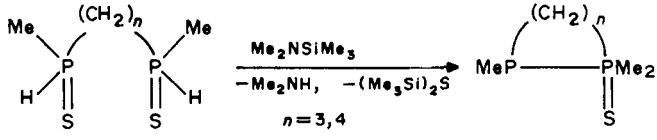
X = O; $R^1 = R^2$ = Ph

X = S; R^1, R^2 = Me, *i*-Pr, Ph

By oxidation of disecondary phosphines $RHP(CH_2)_nPRH$ (R = Ph, Me; $n = 1$–4, 6) with O_2 or S_8 under careful conditions, the secondary phosphine oxides or sulphides may be obtained[28,293,294] in fair yields. The diastereoisomers of the oxides **129** and the sulphides **131** are useful precursors for the syntheses of five- or six-membered ring systems (**130**, **132**) (equations 135 and 136).



(129) **(130)** (135)



(131) (132) (136)

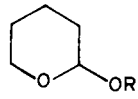
D. Nucleophilic Attack on Halogen

Like their monodentate analogues, bidentate and polydentate phosphines react vigorously with halogens to give phosphoranes or halophosphonium salts. Thus $Ph_2P(X_2)(CH_2)_2PPh(X_2)$ (X = Br, I) is obtained by reaction of $Ph_2P(CH_2)_2PPh_2$ with Br_2 or I_2, respectively (equation 137)[295].

$$Ph_2P(CH_2)_2PPh_2 \xrightarrow[CH_2Cl_2,\ 0°C]{X_2} Ph_2P(X_2)(CH_2)_2PPh_2(X_2) \quad (137)$$

(133)

This compound is probably of ionic structure $[Ph_2P(X)(CH_2)_2PPh_2(X)]^{2+}\ 2X^-$ (**133**) and may be employed for the conversion of alcohols (ROH) or their tetrahydropyranyl ethers **134** to the corresponding halides, RX.

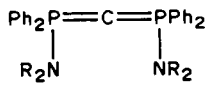


(134)

Interestingly, direct fluorination of bidentate and tridentate phosphines at phosphorus is possible without P—C bond breaking. Oligofunctional fluorophosphoranes [e.g. $F_2Ph_2P(CH_2)_nPPh_2F_2$, $\{F_2Ph_2P(CH_2)_n\}_2PPhF_2$, $n = 2, 3$] were obtained in fair yields. The elemental fluorine employed was diluted with N_2, He or Ar using $CFCl_3$ as a solvent[296]. Carbonyl difluoride may be used in some cases instead of elemental fluorine for the synthesis of bifunctional difluorophosphoranes from bidentate phosphines[297].

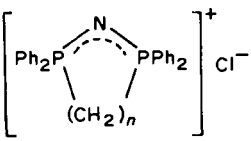
The reaction between bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–3) or $Ph_2PCH(SiMe_3)PPh_2$ and polyhalogenoalkanes in the presence of substrates such as NH_3, NHR_2 or ROH has been studied[299–301]. As in the combination CCl_4/PPh_3/substrate, which is being increasingly applied in organic chemistry as a mild halogenating and condensation reagent, it is now clear that the phosphines initially attack at the 'positive' halogen[298].

Amino-substituted carbodiphosphoranes (**135**) have been obtained by deprotonation of $[(R_2N)Ph_2PCH{=}PPh_2(NR_2)]^+Cl^-$ formed in the reaction between $Ph_2PCH_2PPh_2$/CCl_4 and NR_2H[299]. Whereas the ethylene and propylene bridged diphosphines ($n = 2,3$) with CCl_4/NH_3 form cyclic five- or six-membered phosphinimino phosphonium cations (**136a**), $Ph_2PCH_2PPh_2$ under the same conditions reacts with cleavage of the PCP skeleton to give **136b**[301].

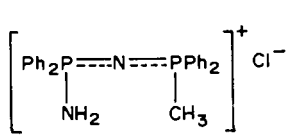


(135)

R = Me, Et, Pr, n-Bu



(136a) $n = 2,3$

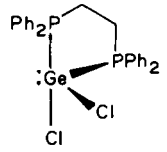


(136b)

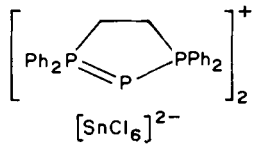
E. Miscellaneous Reactions with Group III–V Electrophiles

The Lewis acid–base interaction between $AlCl_3$ or $Al(OR)_3$ [$R = CH(CF_3)_2$] and bidentate phosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1,2$) or *cis, trans*-$Ph_2PCH{=}CHPPh_2$ has been studied[302]. No chelate formation was observed with $Ph_2P(CH_2)_nPPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, only 1:1 and 1:2 complexes being formed. Similarly, $GeCl_2$ forms a 1:1 and 1:2 complex with $Ph_2P(CH_2)_2PPh_2$. The 1:1 adduct **137** has been shown to have a structure intermediate between a half chelate and ylid[303] with pseudo-trigonal bipyramidal coordination at germanium.

Reduction of PCl_3 with $SnCl_2$ in the presence of $Ph_2P{\cdot}(CH_2)_2PPh_2$ yields the unusual cation **138**, which may be considered as a chelate complex of P^{+} [304].

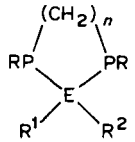


(137)



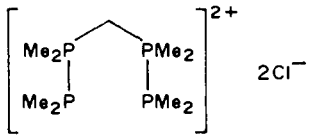
(138)

A wide range of 1,3-diphosphorinanes (**139**, $n = 3$) and 1,3-diphospholanes (**139**, $n = 2$) have been prepared from the alkali metal phosphides, $RMP(CH_2)_nPRM$ ($n = 2, 3$; R = Ph, *n*-Bu[64,305]) and the corresponding halides (E = Si, Ge, Sn; R^1, R^2 = alkyl, aryl; E = P; R^1 = lone pair). The bidentate nucleophile $Me_2PCH_2PMe_2$ reacts with Me_2PCl to form the diphosphonium cation **140**[279].



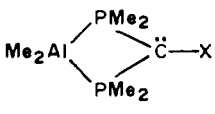
E=Ge, Si, Sn
E=P, R^1=lone pair

(139)



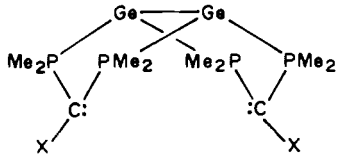
(140)

As mentioned earlier (Section II.A.2), phosphino methanides $[R_2PCXPR_2]^-$ (X = H, $SiMe_3$, PMe_2; R = Me, Ph) behave as ambidentate ligands offering two different sites (P or C) for attack by electrophiles. Preferably they coordinate to Lewis acid centres via their P atoms, although, there are some examples showing an intimate balance between P and C coordination governed by steric effects and hard–soft acid–base interactions. Recently a



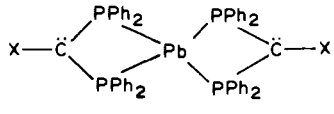
X=$SiMe_3$, PMe_2

(141)



X=$SiMe_3$

(142)



X=$SiMe_3$

(143)

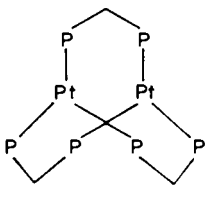
series of novel phosphino methanide complexes have been synthesized and their crystal structure has been determined. In addition to aluminium(III) (**141**)[306], germanium(I) (Ge—Ge bond) (**142**), mixed valence germanium(I)/germanium(II) [Ge(I)-Ge(I)-Ge(II)-Ge(I)-Ge(I)][307,308], tin(II)[309] and lead(II) complexes (**143**)[310] were reported to have unusual structures.

F. Coordination to Transition Metals

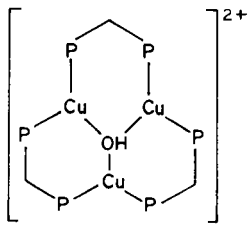
The coordination chemistry of mono-, bi- and poly-dentate phosphine ligands has been repeatedly reviewed in the past[8-11] and a recent review has appeared[7]. Therefore, only selected aspects of this topic will be discussed here in order to show trends of interest and the development in this area of coordination chemistry.

1. Bidentate ligands

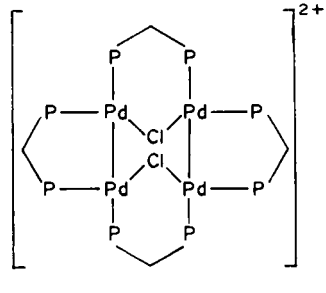
The coordination chemistry of PCP ligands has been extended. Owing to their small bite angle, these ligands are capable of binding two transition metals in close proximity and hence promote or enforce metal metal bonding. In addition to the well known A-frame complexes[11,311], the ligands $R_2PCH_2PR_2$ (P⌒P) may form triply bridged bimetallic complexes (**144**)[312] and tri- or tetra-metallic complexes (**145**[313] or **146**[314]). Recently, bimetallic PCP-bridged 'cradle-type' complexes have been reported[315,316] (e.g. **147**[315]).



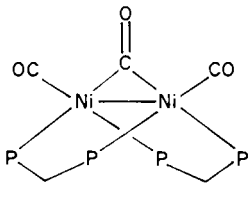
(**144**)



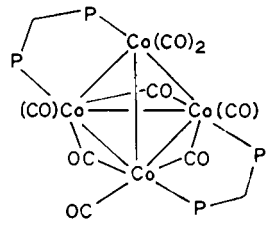
(**145**)



(**146**)

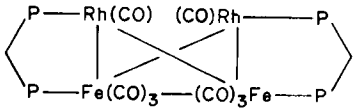


(**147**)

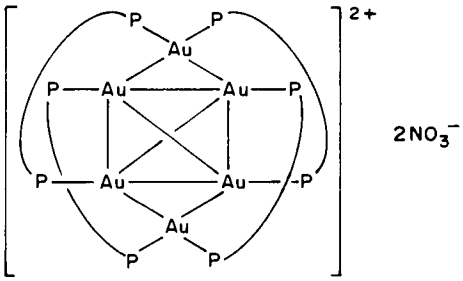


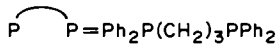
(**148**)

Reaction of $[Co_2(CO)_8]$ with the ligands $R_2PCH_2PR^1_2$ (R,R^1 = Me, Ph) affords a tetranuclear cluster compound stabilized through PCP edge bridging (**148**)[317]. There are more examples in the literature showing the capability of bidentate ligands $Ph_2P(CH_2)_nPPh_2$ of stabilizing cluster compounds by the formation of bridges between adjacent transition metal atoms[318-320] (**149**[318], **150**[320]).



(149)

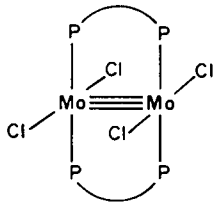




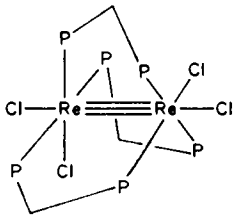
(150)

Ligand bridging and chelating of tetracobalt clusters with bidentate phosphines, $Ph_2P(CH_2)_nPPh_2$[321], in addition to metal—metal bond making and breaking in binuclear complexes[322], have been reviewed. Whereas bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ possessing short carbon backbones ($n = 1$, 2) react with the cluster $[Co_4(CO)_{10}(\mu_4\text{-}PPh)_2]$ to form disubstituted derivatives $[Co_4(CO)_8(\mu_4\text{-}PPh)_2\{Ph_2P(CH_2)_nPPh_2\}]$, the homologues with longer alkylene chains ($n = 3,4$) afford monosubstitution products $[Co_4(CO)_9(\mu_4\text{-}PPh)\{Ph_2P(CH_2)_nPPh_2\}]$ under electron-transfer chain catalysis at 25 °C[321].

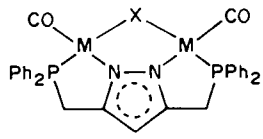
The ligands $R_2P(CH_2)_nPR_2$ coordinate to metal–metal multiple bonds in different modes. Thus doubly or triply P—C_n—P bridged complexes ($n = 1$, 2) were obtained by reaction of $K_4[Mo_2Cl_8]$ or $(NBu_4)_2[Re_2Cl_8]$ with these ligands (**151**, **152**[323,324]). For a review, see ref. 325 and Chapter 15.



(151)[324]



(152)[323]



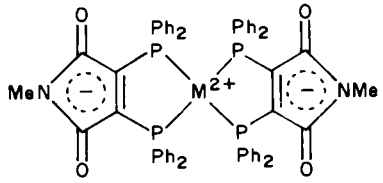
(153)

Bidentate ligands with long flexible backbones [$R_2P(CH_2)_nPR_2$, e.g. **29.4**, **29.5**[112,113]] are capable of spanning *trans* positions in square-planar complexes. The large ring chelates formed with these ligands are stabilized by sterically demanding end-groups R at P (e.g. *t*-Bu)[326]. With $n = 9$–12 mononuclear complexes are formed, e.g. *trans*-$[PdCl_2\ t\text{-}Bu_2P(CH_2)_nP(t\text{-}Bu)_2]$, but shorter methylene chains are not sufficiently long enough to span *trans* positions. Thus $t\text{-}Bu_2P(CH_2)_7P(t\text{-}Bu)_2$ leads to a binuclear 20-atom ring complex *trans*-$[Pd_2Cl_4\{t\text{-}Bu_2P(CH_2)_7P(t\text{-}Bu)_2\}_2]$ which appears to be indefinitely stable in solution.

The chelating and ligand bonding modes of bidentate phosphines in square planar complexes were discussed by Minahan *et al.*[327]. Ligands such as **57.1** or **57.2** with a rigid backbone functioning as a spacer for the two phosphorus atoms impart preference for the formation of linear P—M—P units. This effect has been found, however, to be small compared with the energy required to change the coordination geometry from tetrahedral to square planar or trigonal planar to linear[171,328,329].

The introduction of a pyrazole unit into the C_n bridge of a ditertiary phosphine results in a binucleating ligand system which forms stable bimetallic complexes with defined M—M distances (**153**[330]).

The bidentate 2,3-bis(diphenylphosphino)maleic anhydride and its derivatives (**34.2**) have low-lying π^* acceptor orbitals. They may be occupied by a metal—ligand electron transfer on coordination or by chemical or electrochemical reduction[331–333]. Complexes containing the radical anion $[\mathbf{34.2}]^{-\cdot}$, e.g. **154** (which are square planar) have been reported[331].



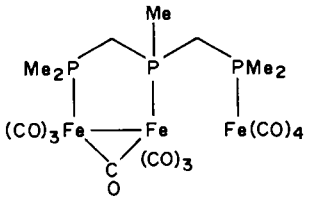
M = Pd, Pt

(154)

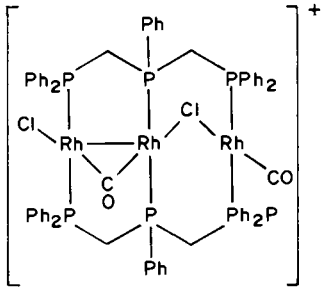
2. *Tri- and tetra-dentate ligands*

Linear tridentate ligands $R_2PCH_2PRCH_2PR_2$ (R = Me, Ph, **78.1**, **78.2**) are capable of binding three transition metals in close proximity, thus promoting metal—metal bonding (**155**[206], **156**[334]). Owing to the flexibility and the low steric demand of the substituents, the ligands **78.1** and **78.2** can bind also in a 'folded-in' manner to bimetallic units (**157**[335]). Both ligands also have the potential of bidentates forming six-membered chelate complexes[206,336].

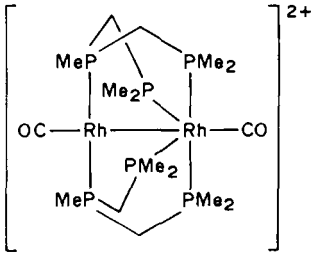
The ligands $[R_2P(CH_2)_n]_{3-m}PR_m$ with $m = 0,1$ and $n = 2,3$ preferentially form mononuclear complexes with five- or six-membered chelate ring systems. Their stability is governed by the connectivity of the P atoms as pointed out by Mason and Meek[8] and more recently by Dahlenburg[337].



(155)



(156)

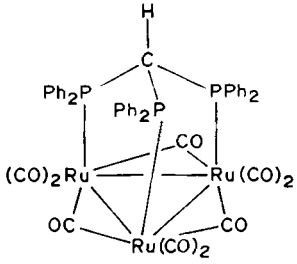


(157)

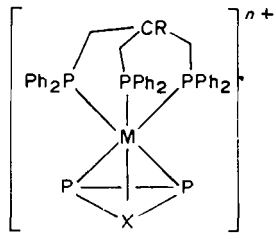
Owing to the multiple chelate effect, linear tetradentate phosphines of type **89** (Table 9) form extremely stable nickel(II), palladium(II), platinum(II), iron(II) and zinc(II) complexes of square-planar (pyramidal), octahedral and tetrahedral geometry[82,233,338].

The complexation mode of linear tetradentate ligands may be controlled by the donor sequence in the PC skeleton. Whereas the ligands **89.3**–**89.6** and **90.1**–**90.6** (Table 9) preferentially form mononuclear complexes,[73,82,232,233,338] **89.1** is binucleating[231]. It has been shown that the binuclear rhodium(I) complexes formed by the two diastereoisomers of **89.2** show different reactivity towards hydrogenation[339]. An open-mode dimeric nickel complex, $[Ni_2Cl_2\{(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2\}]^{2+}$, has been obtained by reaction of the novel binucleating hexaphosphine **96** with $NiCl_2{\cdot}6H_2O$[340].

Tridentate tripod ligands of type **85** and **86** differ in their 'bite angle'. Whereas **85** may be complexed to triangular faces of three transition metals found in cluster **158**[341], **86** preferentially occupies facial coordination sites in mononuclear complexes, e.g. **159**[342–344].



(158)

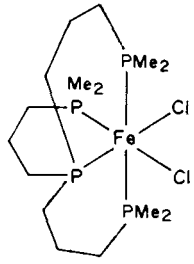


X=P; $n=0$

X=S, Se; $n=1$

M=Co, Rh, Ir

(159)



(160)

The classical tetradentate tripod ligands **92** with the *o*-phenylene backbones and **91** with the $(CH_2)_n$ backbones ($n = 3$, 4) differ considerably in flexibility. Whereas **92** is predetermined sterically to occupy ligand positions in a trigonal bipyramidal complex, tetra-dentates of type **91** may form *cis* octahedral complexes[214,235,345], e.g. **160**[337].

3. Macrocyclic tri- and tetra-dentate phosphine ligands

Macrocyclic tri- and tetra-dentate phosphine ligands show an enhanced stability compared with their open-chain analogues. Thermodynamic (entropy and enthalpy

changes) and kinetic effects contribute to this higher stability summarized as 'macrocyclic effect'. This has been outlined elsewhere[7,242] and will not be discussed further here.

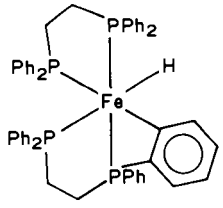
The strong macrocyclic effect of the ligands **99, 104** and specially **105** has so far prevented the demetallation of their complexes, which would be the last step in the template syntheses of these ligands. Increasing ring size, however, obviously destabilizes these complexes. Thus the ligands **103** could be removed from the metal by KCN[250].

4. Reactions at coordinated phosphine ligands

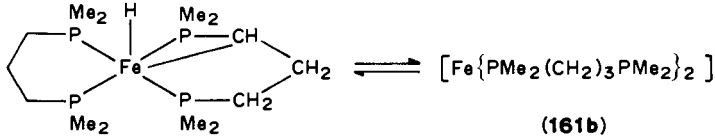
Coordination of a phosphine ligand to a transition metal is generally associated with a change in the polarity and reactivity of the bonds to phosphorus and those within the backbones and substituents. Template syntheses of polydentate phosphine ligands, for instances, make use of the increased reactivity of the P—H bond in complexes of primary and secondary phosphines. This has already been discussed in section II.D.

Numerous examples are also known, however, for P—C bond activation within the coordination sphere of transition metal phosphine complexes. Thus heating of *cis*-$[\{Ph_2P(CH_2)_2PPh_2\}_2FeC_2H_4]$ causes *o*-metallation of a PhP group, **160** being formed[346]. Activation of C—H bonds in the $(CH_2)_n$ backbones ($n = 1, 3, 5$) of $R_2P(CH_2)_nPR_2$ coordinated to transition metals has also been observed.

These comprise reactions at the CH_2 bridge in $Ph_2PCH_2PPh_2$ complexes[347] (see also Section IIA.1), the reversible intramolecular CH addition equilibrium process in

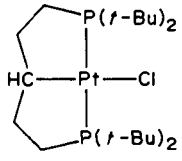


(160)

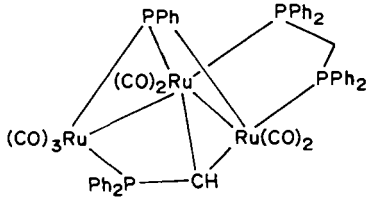


(138)

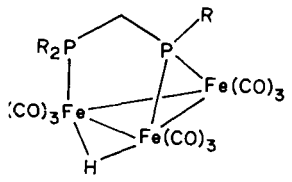
(161a) **(161b)**



(162)



(163)



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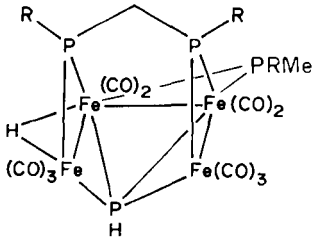

(165)

$[Fe\{Me_2P(CH_2)_3PMe_2\}_2]$[348] (**161a**⇌**161b**) (equation 138) and cyclometallation observed on reaction of t-$Bu_2P(CH_2)_5P(t$-$Bu)_2$ with $PtCl_2$ yielding **162**[349]. This topic has been reviewed[350,351].

Oxidative addition reactions of ditertiary phosphines, e.g. **1.9**, to $[Ru_3(CO)_{12}]$[352] or PH functional methylenebisphosphines to $[Fe_2(CO)_9]$[353–356] result in P—C and P—H bond cleavage, clusters containing μ_2-phosphido and μ_3-PR or μ_4-PR phosphinidene bridges being formed (**163**–**165**).

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The Chemistry of Organophosphorus Compounds
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CHAPTER 9

Chemistry and ligating properties of phospha-alkynes and their derivatives

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I. HISTORICAL BACKGROUND

Compounds containing tervalent phosphorus with coordination number 1 and 2 have played an important role in the development of phosphorus chemistry over the past decade. Just as adherence to the octet rule delayed the discovery of the inert gas compounds, progress in the search for phosphorus compounds of low coordination number was influenced by the so-called 'double-bond rule', which stated that elements having a principal quantum number greater than two would not be likely to form $p\pi$–$p\pi$ bonds with other elements or themselves[1,2]. This theoretical prediction was subsequently disproved when Gier[3] successfully synthesized the first phospha-alkyne, HC≡P, in 1961 by passing PH_3 through a low-intensity electric arc between graphite electrodes, however the compound was only stable at low temperatures and for many years remained a chemical curiosity.

More recently, the chemistry of phospha-alkenes, $R_2C{=}PR'$ and phospha-alkynes, RC≡P, (R, R' = alkyl, aryl, silyl, H, halogen) containing phosphorus and carbon double and triple bonds, respectively, has rapidly expanded, as have tervalent compounds containing P=P and P=N bonds, and reviews of these compounds have appeared[4-11]. This chapter concerns some recent developments in the chemistry and ligating ability of phospha-alkynes and their derivatives. Several groups, particularly those of Appel[5], Becker[11], Regitz[12] and Nixon[13], have been involved in the development of this type of compound. A fuller account of the coordination chemistry of phospha-alkynes appears elsewhere[14].

II. SYNTHETIC ROUTES TO PHOSPHA-ALKYNES

Fifteen years after the report of HC≡P by Gier[3], the gaseous phospha-alkynes MeC≡P and FC≡P were synthesized by Hopkinson *et al.*[15], suggesting that a family of RC≡P compounds should exist. A major breakthrough was the seminal report by Becker *et al.*[16] of the first very thermally stable phospha-alkyne Bu^{t}C≡P and rapid development followed.

To date the following phospha-alkynes have been prepared: HC≡P[3,13,17]; MeC≡P[15,17-19]; FC≡P[20,21]; $CF_3C{\equiv}P$[21]; N≡CC≡P[21-23]; N≡CC≡CC≡P[22]; HC≡CC≡P[22,24]; $H_2CCHC{\equiv}P$[22,25]; PhC≡P[22,26]; $Me_3SiC{\equiv}P$[27]; $Bu^tC{\equiv}P$[16]; TriptC≡P[28]; AdC≡P[29]; $2,4,6\text{-}Bu^t{}_3C_6H_2C{\equiv}P$[30,31]; $Pr^iC{\equiv}P$[32]; $Bu^tCH_2C{\equiv}P$[32]; $MeC(CH_2)_5C{\equiv}P$[32]; and $MeC(CH_2)_4C{\equiv}P$[32]. The following synthetic routes were used.

A. Via Thermal Elimination of HX (X = Cl, F)

This method utilizes flow-pyrolysis techniques at temperatures of ca 1000 °C involving elimination of HX (X=Cl, F) from suitable halophosphine precursors (equation 1)[13,15,18,19,21,22,24,25].

$$RCX_2PY_2 \xrightarrow[-2XY]{1000\,^\circ C} RC{\equiv}P \qquad (1)$$

X = H, Y = Cl or F; Y = H, X = Cl or F; R = H, Me, F, CF_3, $NCNC_2C$—, HCC—, H_2CCH—, Ph)

Recently, it has been shown[23] that R'C≡P, (R' = Ph) can be synthesized directly (albeit in low yield) by co-pyrolysis of R'Me and PCl_3 (equation 2)

$$PCl_3 + R'Me \xrightarrow{\Delta} R'C{\equiv}P + 3HCl \qquad (2)$$

Most of the phospha-alkynes obtained by thermal elimination of HCl or HF were not isolated pure but were detected and fully characterized by microwave and/or photoelectron spectroscopy. A brief report[17] suggests that pure HC≡P and MeC≡P can be obtained and in higher yield (ca 30%) by flash vacuum thermolysis (FVT) of dichlorophosphines followed by careful subsequent removal of HCl on a solid base (equation 3), but this route has not yet been confirmed independently.

$$RCH_2PCl_2 \xrightarrow[R = H, Me]{750\text{–}900\,^\circ C/10^{-3}\ mmHg} RC{\equiv}P \qquad (3)$$

R = H, Me

B. Via Base-induced Elimination of HF

An important observation was that when CF_3PH_2 vapour is allowed to pass slowly over solid KOH at room temperature, high yields of FC≡P are obtained by elimination of 2 mol of HF (equation 4)[20]. The reaction is easily monitored by ^1H, ^{19}F and ^{31}P NMR spectroscopy and the intermediate phospha-alkene $CF_2{=}PH$ is also isolable. The phospha-alkyne is stable for long periods at −78 °C and also at room temperature and low pressure, and has been studied spectroscopically.

$$CF_3PH_2 \xrightarrow[-HF]{KOH} CF_2{=}PH \xrightarrow[-HF]{KOH} FC{\equiv}P \qquad (4)$$

C. Via Thermal Elimination of Me_3SiCl

This synthetic route[26,27] gives a good yield of $Me_3SiC{\equiv}P$ and PhC≡P by elimination (at ca 700 °C) of chlorotrimethylsilane from appropriate vicinal chloro- and trimethylsilyl-substituted phospha-alkenes (equation 5).

$$\begin{matrix} R \\ Me_3Si \end{matrix}\!\!>C{=}PCl \xrightarrow[-Me_3SiCl]{\Delta,\ 700\,^\circ C} RC{\equiv}P \qquad (5)$$

R = Me_3Si, Ph

D. Via Elimination of Hexamethyldisiloxane from $RC(OSiMe_3)=PSiMe_3$ (R = Alkyl or Aryl)

This important route discovered[16] for $Bu^tC{\equiv}P$ in 1981 has been the main method for the synthesis of a number of thermally stable phospha-alkynes and has been extended in more recent work by Regitz and coworkers[29,32]. Hexamethyldisiloxane is readily eliminated from the appropriate phospha-alkene precursor (equation 6). Initially, solid NaOH or KOH was used to catalyse the elimination of $(Me_3Si)_2O$; however, alternative procedures are sometimes preferable and these are discussed below.

$$Me_3SiP{=}C(OSiMe_3)(R) \xrightarrow[-(Me_3Si)_2O]{} RC{\equiv}P \qquad (6)$$

R = Bu^t[16], Tript[28], Ad[29], 2,4,6-$Bu^t_3C_6H_2$[30], Pr^i[32], Bu^tCH_2[32], $MeC(CH_2)_5$[32], $MeC(CH_2)_4$[32]

1. *Using solid KOH or NaOH in the presence of a solvent*

Variable yields of $Bu^tC{\equiv}P$ and AdCP are formed on addition of small amounts of solid KOH or NaOH to a solution of the appropriate phospha-alkene in 1,2-dimethoxyethane at room temperature (equation 7).

$$Me_3Si{\sim}P{=}C(OSiMe_3)(R) \xrightarrow[-(Me_3Si)_2O]{\text{dme, NaOH(s), RT}} RC{\equiv}P \qquad (7)$$

R = Bu^t[16], Ad[30]

2. *Via addition of a phospha-alkene to NaOH at 110–160 °C in the absence of a solvent*

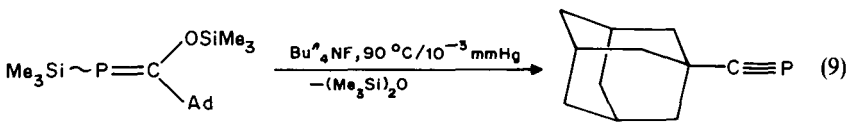
Slow addition of certain phospha-alkene precursors to small amounts of solid NaOH at 110–160 °C *in vacuo* gives high yields of phospha-alkynes (equation 8).

$$Me_3Si{\sim}P{=}C(R)(OSiMe_3) \xrightarrow[-(Me_3Si)_2O]{\text{NaOH, 110–160 °C/10}^{-3}\text{ mmHg}} R{-}C{\equiv}P \qquad (8)$$

R = Bu^t[33], Ad[33], Pr^i[32], Bu^tCH_2[32], $MeC(CH_2)_5$[32], $MeC(CH_2)_4$[32]

3. *Via use of $Bu^n{}_4NF$ on kieselguhr in the absence of a solvent*

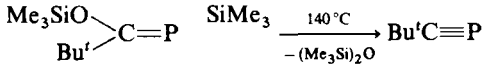
AdC≡P can be obtained in high yields by addition of $Bu^n{}_4NF$ on kieselguhr to the phospha-alkene precursor held at 90 °C *in vacuo* (equation 9)[29].



(9)

4. *Via thermal elimination of $(Me_3Si)_2O$ in the absence of a solvent*

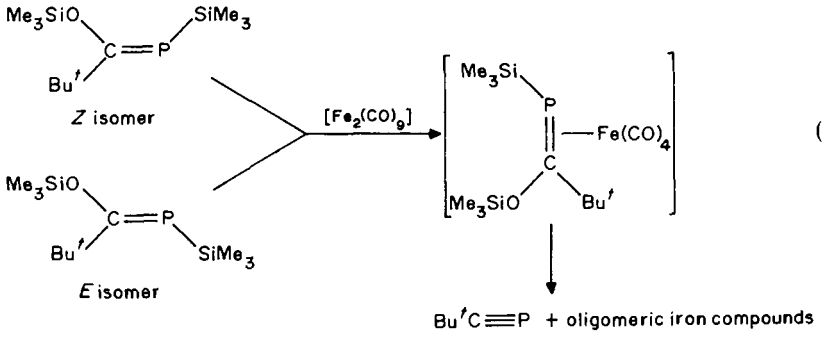
A recent report[34] has shown that high yields of $Bu^tC{\equiv}P$ can be achieved by heating the *Z* isomer of the phospha-alkene precursor at 140 °C in the absence of a solvent (equation 10).



(10)

Z isomer

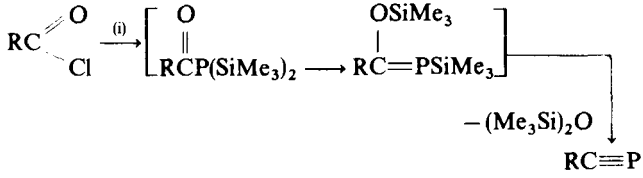
Interestingly, no $Bu^tC{\equiv}P$ was produced when the *E* isomer was heated under the same conditions. Both (*E*)- and (*Z*)-phospha-alkene precursors, however, can be converted into $Bu^tC{\equiv}P$ in high yields by treatment of a stoichiometric quantity of $[Fe_2(CO)_9]$ (equation 11). The reaction is proposed to proceed via an $[Fe(CO)_4(\eta^2\text{-phospha-alkene})]$ complex.



(11)

5. *Via single-step routes*

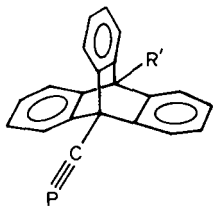
This method developed[28], for certain solid phospha-alkynes, involves treatment of acid chlorides with $P(SiMe_3)_3$ or $[LiP(SiMe_3)_2{\cdot}2thf]$ without separation of the phospha-alkene intermediates.



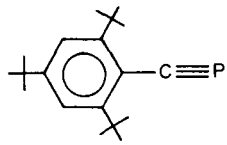
(12)

(i) $P(SiMe_3)_3$, Δ, dme, (– MeSiCl), or $[LiP(SiMe_3)_2.2thf]$, RT, (– LiCl) R = Tript, 2,4,6-$Bu^t{}_3C_6H_2$

The method has been particularly useful for synthesizing the two compounds shown below.



R' = H, Me, Cl



Phospha-alkynes formed by reaction 12 are subsequently isolated by column chromatography, in contrast to the previous methods which require fractional distillation.

III. THERMAL STABILITY OF PHOSPHA-ALKYNES

The thermal stability of phospha-alkynes, RC≡P, is dependent on the nature of the R group. Most of the gaseous RC≡P compounds (R = H, Me, F, Ph) are thermally unstable at room temperature. A recent report[17] suggests that the degree of purity of phospha-alkynes may play an important role in determining their apparent thermal stability. The thermal stability of RC≡P increases as the R group becomes bulkier and all the phospha-alkynes prepared by the method in Section II.D are thermally stable. Since $Bu^tC{\equiv}P$ is stable at room temperature and AdC≡P can be handled in air without decomposition, the chemistry of these two phospha-alkynes has been the most widely studied.

IV. STRUCTURAL AND BONDING ASPECTS OF PHOSPHA-ALKYNES

A. Structural Aspects

Microwave spectroscopy has been a powerful tool in the detection of the gaseous phospha-alkynes, RC≡P (e.g. R = H, Me, F, Ph)[35]. In 1964, the structure of the parent HC≡P was determined[36]. It was found to be a linear molecule whose formula was HCP rather than HPC. The molecular structures of several phospha-alkynes have been established by microwave spectroscopy[37]. Structural parameters are listed in Table 1; it is interesting that the P≡C bond distance (ca 1.544 Å) is essentially independent of the nature of the substituent at carbon.

TABLE 1. Selected data on phospha-alkynes, RC≡P, from microwave and He I photoelectron spectroscopy

Compound	d(X—C_{sp}) (Å)	d(C≡P) (Å)	Ionization potentials (eV) A[a]	B[b]	Ref.
HC≡P	1.0667	1.5421	10.79	12.86	36, 38
$CH_3C{\equiv}P$	1.465	1.544	9.89	12.19	18, 19
FC≡P	1.285	1.541	10.57	13.55	20, 39
$CF_3C{\equiv}P$	1.460	1.542	—	—	21
N≡CC≡P	1.382	1.547	—	—	40
HC≡CC≡P	1.382	(1.544)[c]	—	—	24
N≡CC≡C≡P	1.382	(1.544)[c]	—	—	41
$CH_2{=}CHC{\equiv}P$	1.432	(1.544)[c]	—	—	25
PhC≡P	1.467	(1.544)[c]	8.68 9.87	9.60 10.79	37, 42
$Me_3SiC{\equiv}P$	—	—	9.9	10.9	42
$Bu^tC{\equiv}P$	—	1.54	9.61	11.44	42, 43
AdC≡P	—	(1.54)[c,d]	—	—	44
2,4,6-$Bu^t{}_3C_6H_2C{\equiv}P$	—	1.516(13)[d]	—	—	45

[a]Assigned to C=P π orbital.
[b]Assigned to P lone-pair electron.
[c]Values in parentheses were fixed in the structural determination.
[d]Data from single-crystal X-ray diffraction studies; X = atom of group R linked to the C_{sp} carbon atom.

B. Bonding Aspects

Several phospha-alkynes have been investigated by He I and He II photoelectron spectroscopy (see Table 1). In all the spectra of these compounds, the band having the lowest ionization potential (i.p.) corresponds to the removal of an electron from a bonding π-orbital localized predominantly in the C≡P group. The second band has been assigned as arising from the removal of non-bonding electrons localized at the phosphorus atom.

Figure 1 shows a correlation for the first and second ionization potentials of four phospha-alkynes, FC≡P, HC≡P, MeC≡P and Bu^{t}C≡P, together with those for analogous nitriles, FC≡N, HC≡N, MeC≡N and Bu^{t}C≡N[37]. For the phospha-alkynes there is an overall shift to lower i.p., as is expected when N is replaced by the less electronegative P atom. The effect of changing the R group in both RC≡N and RC≡P series is similar[19,37].

The most important feature of Figure 1 is the increased π–n separation in the phospha-alkyne series compared with the analogous nitriles which is a quantitative indicator of the reduced overlap for a 2pπ–3pπ interaction relative to that for 2pπ–2pπ. The main effect is the destabilization of the π-bonding orbitals in the C≡P group. The separation of the π and n orbitals in the phospha-alkynes is of interest in connection with their behaviour as ligands towards transition metals (see below).

C. NMR Spectroscopy of RC≡P Compounds

^{31}P and ^{13}C NMR chemical shifts and coupling constants for several phospha-alkynes are listed in Table 2. The range of ^{31}P chemical shifts of RC≡P compounds is large (ca 300 ppm), lying between −45 ppm (R = $SiMe_3$) and −348 ppm (R = F) (relative to 85% H_3PO_4). In contrast, the range of ^{13}C chemical shifts for the sp-hybridized carbon atom in RC≡P does not differ so much (ca 50 ppm) and the signals occur at a lower field relative to $SiMe_4$.

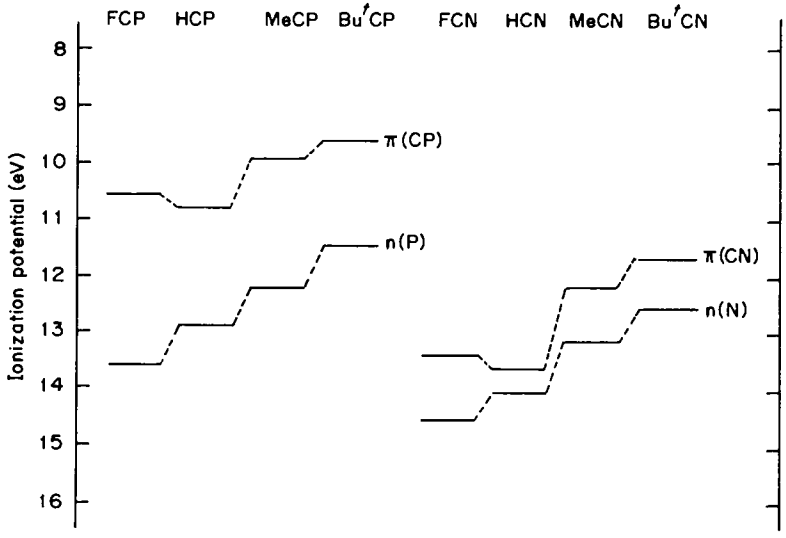
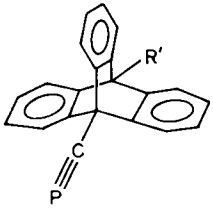


FIGURE 1. Orbital correlation diagrams for the first two ionization potentials of RC≡P (left) and RC≡N (right) (R = F, H, Me and Bu^t)[37].

TABLE 2. NMR parameters for phospha-alkynes

Compound	$\delta(^{31}P)$(ppm)[a]	$\delta(^{13}C)$(ppm)[b]	$^1J(CP)$(Hz)	Ref.
HC≡P	−173	154.0	54.0	17, 46
FC≡P[c]	−348	—	—	47
PhC≡P	−173	164.9	48.3	26
$Me_3SiC{\equiv}P$	−45	201.4	13.9	27
$Bu^tC{\equiv}P$	−209	184.8	38.5	16
$CH_3C{\equiv}P$	−201	170.8	49.0	17
AdC≡P	−208	184.7	39.0	29
$Pr^iC{\equiv}P$	−205	183.4	41.3	32
2,4,6-$Bu^t_3C_6H_2C{\equiv}P$	−107	168.7	53.2	30
$Bu^tCH_2C{\equiv}P$	−192	173.7	45.5	32
$Bu^t_2CHC{\equiv}P$	−207	—	—	48
$C_6H_{11}C{\equiv}P$	−203	—	—	48
$MeC(CH_2)_5C{\equiv}P$	−198	184.9	37.2	32
$MeC(CH_2)_4C{\equiv}P$	−207	184.9	37.9	32
				
R′ = H	−159	164.6	46.5	28
R′ = Me	−158	165.1	46.4	28
R′ = Cl	−155	163.3	46.7	28

[a]Relative to trimethylphosphite (TMP).
[b]Relative to tetramethylsilane.
[c]$\delta(^{19}F) = -96.6$ ppm ($CFCl_3$), $^2J(PF) = 182.0$ Hz.

It is interesting that the magnitude of the $^1J(PC)$ coupling constant (13.9–54.0 Hz; see Table 2) in phospha-alkynes is significantly smaller than the value for phospha-alkenes (50–100 Hz)[48,49]. A higher $^1J(PC)$ value is expected for RC≡P because of the higher s character of the P≡C triple bond (sp hybrid in contrast to sp^2 hybrid).

V. REACTIVITY OF PHOSPHA-ALKYNES

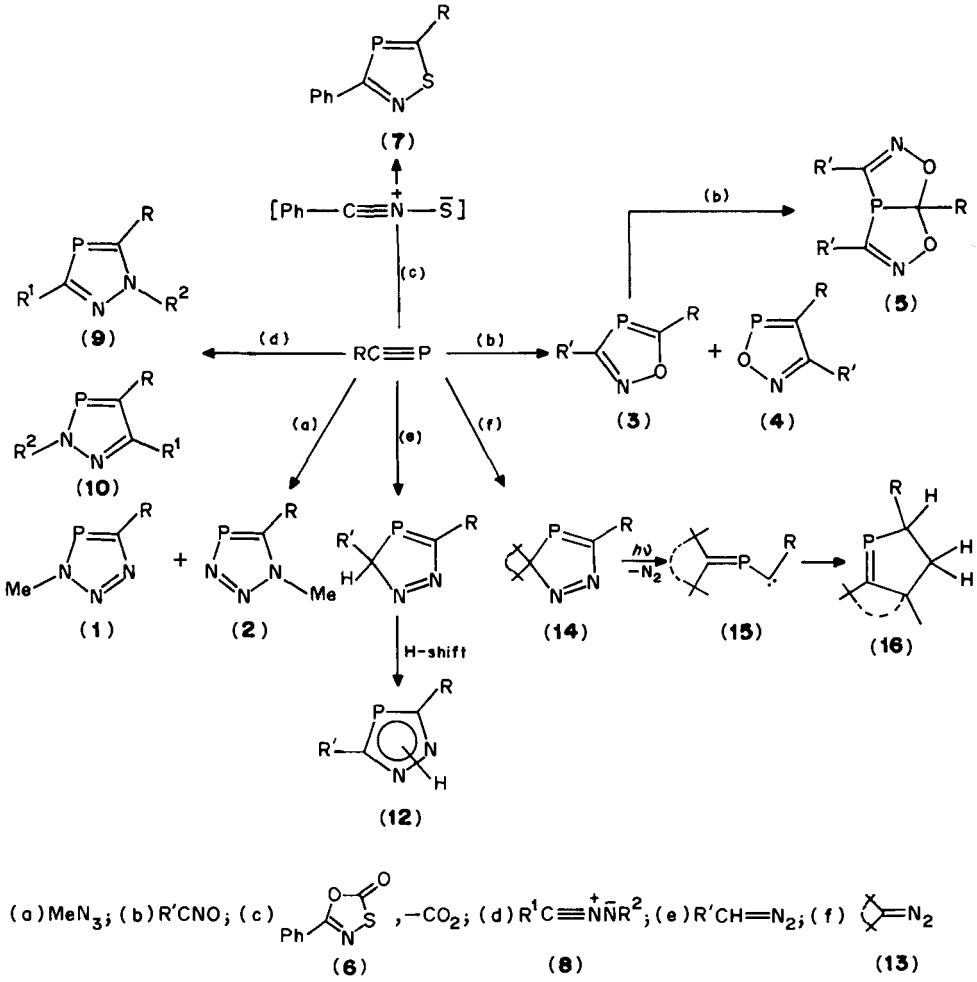
Since the development of synthetic routes to phospha-alkynes, there has been continuing interest in their chemical properties. Several research groups have been actively involved in utilizing the synthetic potential of phospha-alkynes[33,50] and their reactivity can be conveniently discussed in the following sections.

A. Cycloaddition Reactions

The synthetic potential of phospha-alkynes as useful building blocks in organophosphorus chemistry represents the most widely studied area. Four types of cycloaddition reactions, namely [3 + 2], [4 + 2], [8 + 2] and [2 + 1], have been established.

1. [3 + 2] Cycloaddition reactions

Phospha-alkynes readily undergo [3 + 2] cycloaddition reactions with 1,3-dipoles such as azides, nitrile oxides, nitrile sulphides and nitrile imines to afford a wide variety of

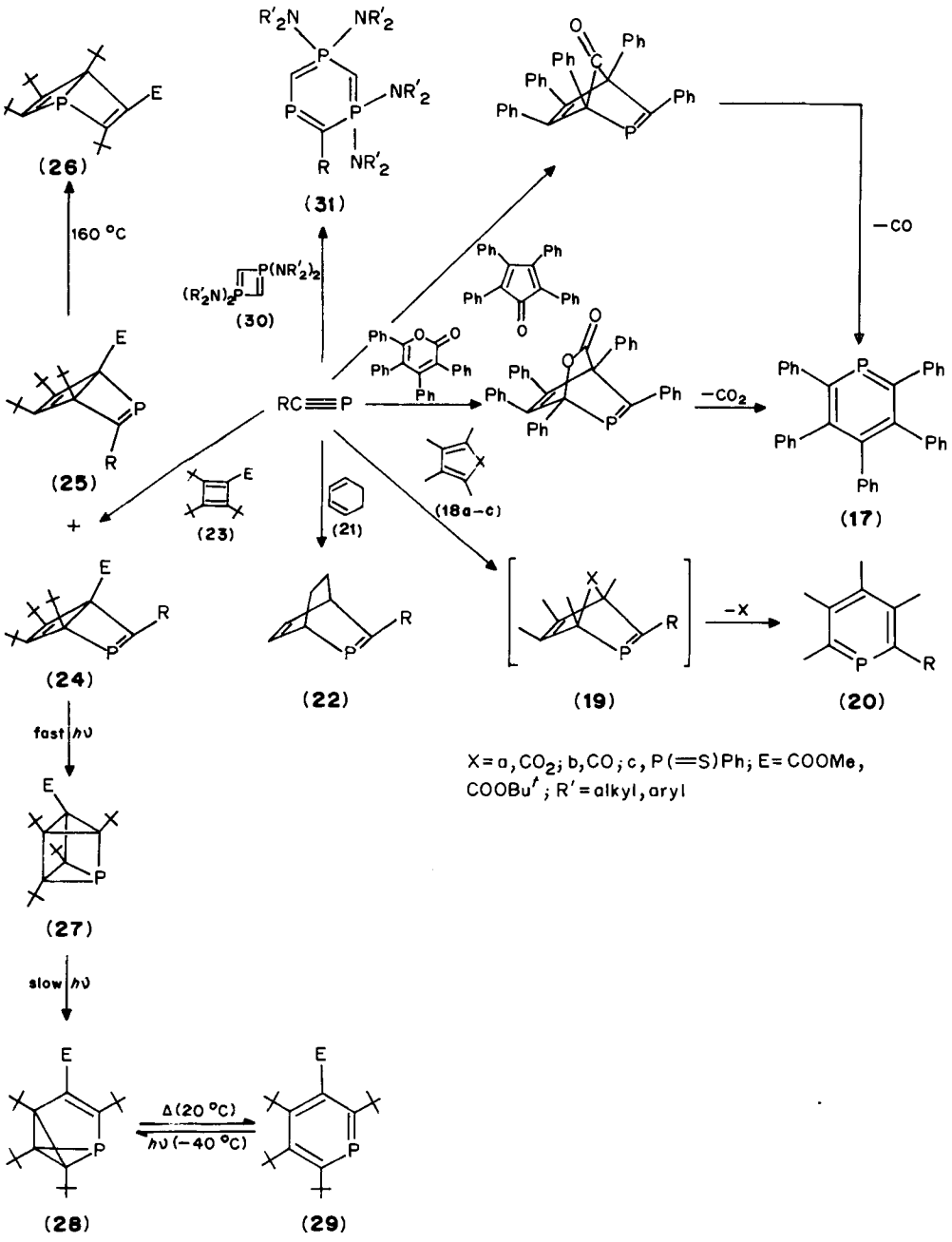


SCHEME 1. Some [3 + 2] cycloaddition reactions of RC≡P [R=H, Bu^t, Ad, Pr^i, Bu^{t}CH$_2$, MeC(CH$_2$)$_5$, MeC(CH$_2$)$_4$][33,50–53].

phospholes containing further heteroatoms. Some of the reactions are summarized in Scheme 1[33,50–52].

The [3 + 2] cycloaddition of methyl azide, MeN_3, with RC≡P [R = Ad, Pr^i, H Bu^{t}CH$_2$, MeC(CH$_2$)$_5$, MeC(CH$_2$)$_4$] resulted in the formation of 1,2,3,4-triazaphospholes (**1**[29,32,33] and **2**[32]). Likewise, reactions of RC≡P [R = Bu^t, Ad, Pr^i, Bu^{t}CH$_2$, MeC(CH$_2$)$_4$] with nitrile oxides, R'CNO [R' = Ph, 2,4,6-Me$_3$C$_6$H$_2$, 2,4,6-(MeO)$_3$C$_6$H$_2$, Bu^t, *p*-ClC$_6$HC$_6$H$_4$] afforded 1,2,4-oxazaphospholes (**3** and **4**). Further addition of R'CNO (R' = Bu^t, *p*-ClC$_6$H$_4$) to **3** led to the formation of the heterobicyclic product **5**[50].

The novel 1,2,4-thiazaphospholes **7** could be synthesized in high yields from the reaction of **6** with Bu^{t}C≡P[53] (Scheme 1). Similarly, addition of nitrile imines, R^{1}C≡$\overset{+}{N}\overset{-}{N}$R^2 (**8** R'



SCHEME 2. [4 + 2] cycloaddition reactions of RC≡P [R = Ph, Bu^t, Pr^i, Bu^{t}CH$_2$, Ad, MeC(CH$_2$)$_5$].

= Pr, R^2 = Me; R^1 = Me, R^2 = Ph; $R^1 = R^2$ = Ph) to $Bu^tC{\equiv}P$ gave 1*H*-1,2,4-diazaphospholes (**9**) and 2*H*-1,2,3-diazaphospholes (**10**)[53] and the diazo compounds, $R'CH{=}N_2$ (**11** R' = H, Bu^t, MeO_2C, PhCO) underwent smooth [3 + 2] cycloaddition to the phosphorus—carbon triple bond of $RC{\equiv}P$ [R = Ad, Pr^i, H, Bu^tCH_2, $MeC(CH_2)_5$, $MeC(CH_2)_4$] to give 1,2,4-diazaphospholes (**12**) (Scheme 1)[29,32,33,51-53].

A recent report[33] showed that the primary product **14** could be isolated from the reaction of **13** with $Bu^tC{\equiv}P$, which on photolysis generated the carbene **15** that which was subsequently converted into the phosphacyclopentene **16** (Scheme 1).

2. *[4 + 2] Cycloaddition reactions*

The [4 + 2] cycloaddition reaction involving a phospha-alkyne was first studied by treating $PhC{\equiv}P$ with an α-pyrone or cyclopentadienone to give the phosphabenzene **17**[54] (Scheme 2).

Analogous reactions were also carried out[55] using $Bu^tC{\equiv}P$. Diels–Alder reactions of $Bu^tC{\equiv}P$ with α-pyrones (**18a**) cyclopentadienones (**18b**) and phosphole sulphides (**18c**) resulted in the formation of the phosphabenzene **20** in high yields.

Bicyclic intermediates (**19**) could not be detected directly as they underwent spontaneous aromatization with elimination of the CO_2-bridge[55]. In contrast, bicyclic adducts of the type **22**, obtained from the reactions of $Bu^tC{\equiv}P$ with cyclohexadiene[56] (**21**) or anthracene could be isolated without difficulty. Scheme 2 summarizes some of the [4 + 2] cycloaddition reactions of phospha-alkynes studied so far.

Novel 2-phospha-Dewar-benzenes [**24** and **25**, R = Bu^t, Pr^i, Bu^tCH_2, Ad, $MeC(CH_2)_5$; E = CO_2Me, CO_2Bu^t] have been synthesized by treatment of the kinetically stabilized cyclobutadienes **23** with $RC{\equiv}P$ (Scheme 2)[57].

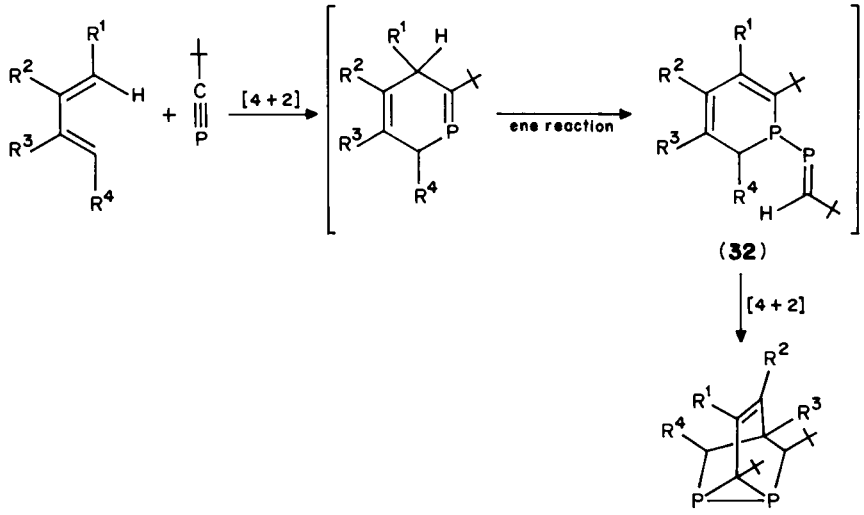
Compound **24** (R = Bu^t; E = CO_2Me, CO_2Bu^t) was thermally transformed smoothly to the 1-isomer **26**, whereas under photochemical conditions, an intramolecular [2 + 2] cycloaddition occurred to afford the phosphaprismane compound **27**. Further photolysis of the tetracycle **27** gave access to the phosphabenzvalene **28**, which was in thermal and photochemical equilibrium with the phosphabenzene **29**[33] (Scheme 2). Treatment of the diphosphete **30** with $Bu^tC{\equiv}P$ afforded the first $1\lambda^5$, $3\lambda^5$, $5\lambda^3$-triphosphabenzene derivative (**31**)[58].

A summary of the types of [4 + 2] addition reactions undergone by phospha-alkynes is shown in Scheme 2.

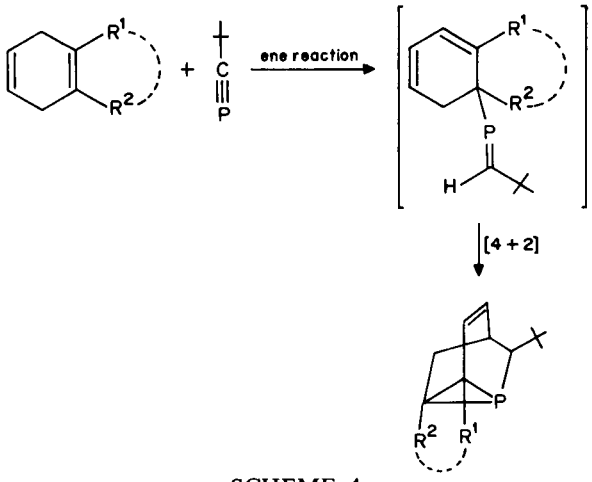
Recently, $Bu^tC{\equiv}P$ has been shown also to undergo Diels–Alder-type reactions with open-chain 1,3- and 1,4-dienes to give mono- and di-phosphatricyclo[3.2.1.$0^{2,7}$]oct-3-enes (Scheme 3)[59]. The products presumably involve an ene reaction of the initially produced Diels–Alder product to give (**32**, which undergoes a [4 + 2] cycloaddition. The first reaction step is not regiospecific but the ene reaction occurs specifically at the P=C double bond. The mechanism is supported by the observation that cyclo-1,4-hexadienes react with $Bu^tC{\equiv}P$ under comparable conditions (Scheme 4)[59].

The first examples of 1-aza-3-phosphabenzenes (**33**) were prepared[60] via regiospecific Diels–Alder reactions of 2-trifluoromethyl-4-methyl-6*H*-1,3-oxazin-6-one with $RC{\equiv}P$, (R = Bu^t, Ad) (Scheme 5). The initially formed cycloaddition products extrude CO_2 under the reaction conditions (80 °C, sealed tube, 3 days) and cannot be isolated.

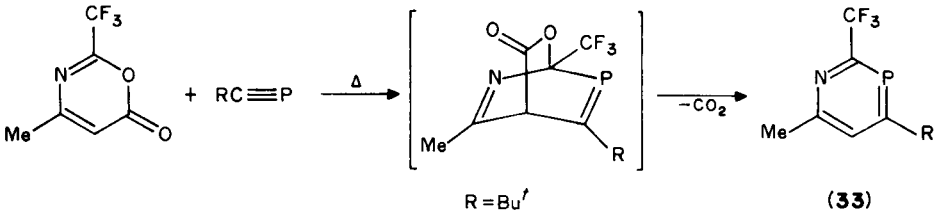
Interesting differences in the chemical behaviour of alkynes and phospha-alkynes with 1,3-azaphosphinines have been reported[61]. Alkynes react under mild conditions to afford the [4 + 2] heterobarralene cyclo-adducts **34**, which undergo cycloreversion to the corresponding substituted phosphinines (Scheme 6a). $Bu^tC{\equiv}P$, on the other hand, gives **36a** rather than **36b** (Scheme 6b). The tetracyclic triphosphane structure shown combines a 3*H*-pyrrole, a 1,3-diphosphacyclopropane, a 1,3-diphosphacyclobutane and a



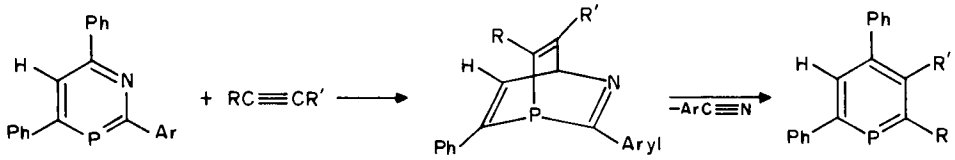
SCHEME 3



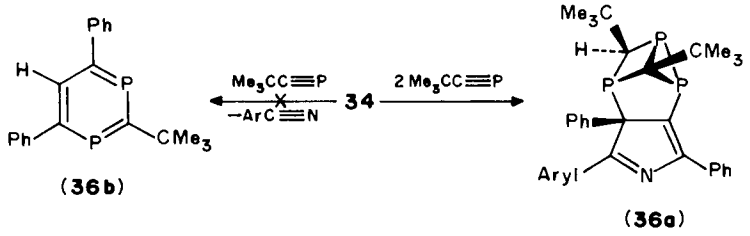
SCHEME 4



SCHEME 5



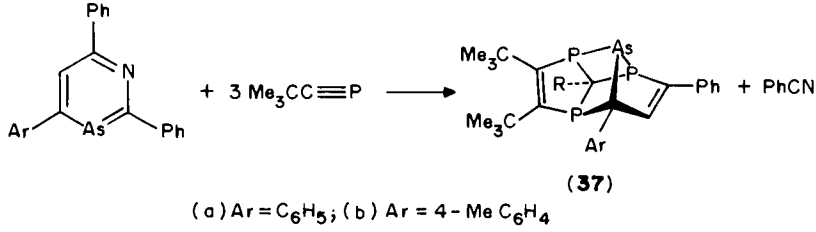
SCHEME 6a



SCHEME 6b

diphosphacyclopropane system. A reaction mechanism has been proposed but intermediates have not yet been isolated.

Surprisingly, 1,3-azaarsinines behave differently again with Bu^{t}C≡P at 120 °C in a sealed tube to give colourless crystalline compounds (**37**)[62]. A single-crystal X-ray structural analysis shows that **37** has the tetracyclic skeletal framework shown in Scheme 7a with all the phosphorus atoms and the arsenic atom being located in



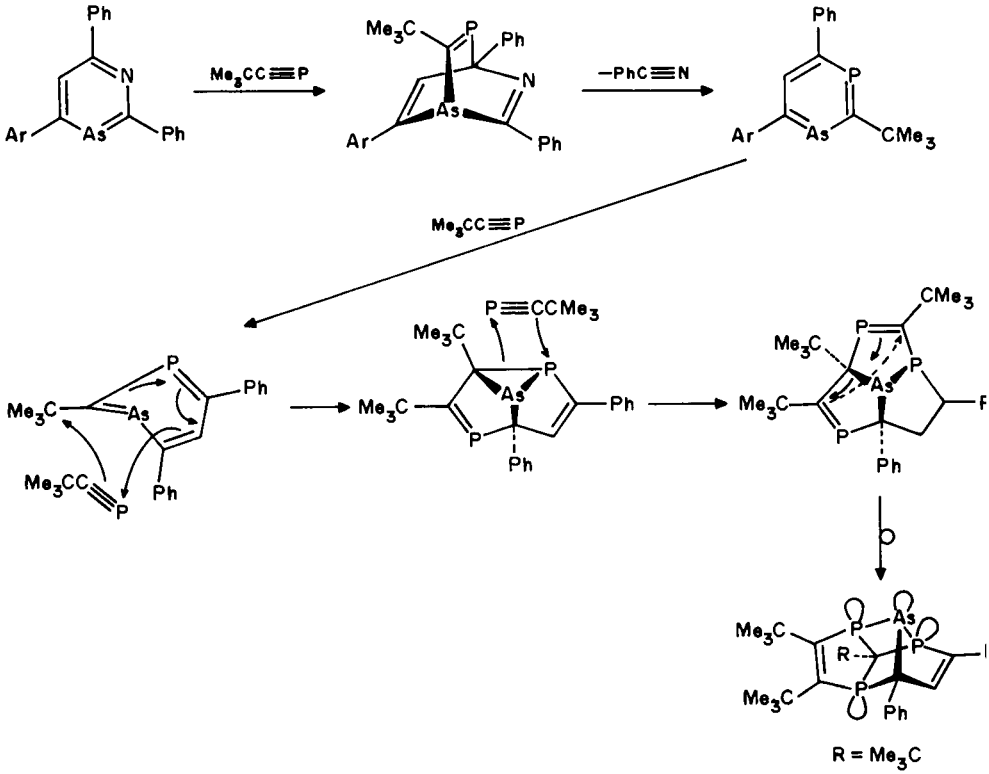
SCHEME 7a

bridgehead positions. These observations have been interpreted as arising from the decreased electrophilicity of the arsenic in the 1,3-azaarsinine, and the reaction mechanism in Scheme 7b is proposed.

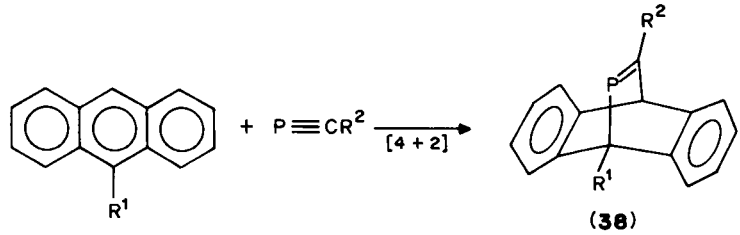
The previously unknown 2-phosphabarrelenes (**38**) are also obtained by Diels–Alder reactions of RC≡P (R = Bu^t, Ad) with various anthracenes (Scheme 8) and have been characterized by NMR spectroscopy[63].

3. An [8 + 2] cycloaddition reaction

The reaction involving [8 + 2] cycloaddition of PhC≡P to 8-methoxyheptafulvene led to the formation of the previously unknown 2-phospha-azulene (**39**) (equation 13)[64].

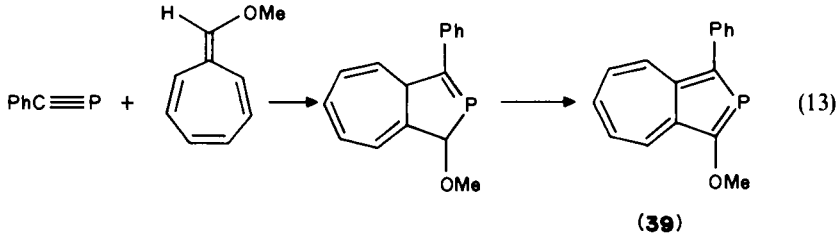


SCHEME 7b



(38)

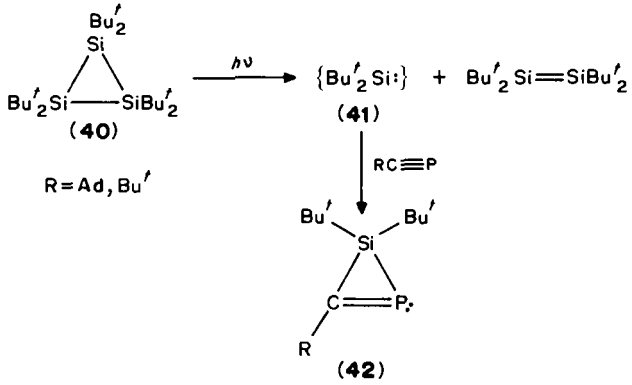
SCHEME 8



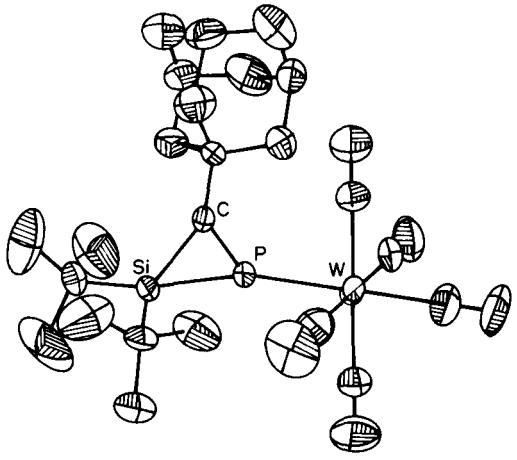
(39)

4. [2 + 1] Cycloaddition reactions

A recent report has shown that di-*tert*-butylsilanediyl (**41**), obtained by irradiation of hexa-*tert*-butylcyclotrisilane (**40**), undergoes [2 + 1] cycloaddition to the triple bond of RC≡P (R = Bu^t, Ad) to give novel phosphasilirenes (**42**), which can be η^1-complexed with [W(CO)$_5$][65] (Scheme 9). The X-ray structural analysis of the adamantyl analogue (**43**) confirms the novel three-membered ring system and the P—C distance is typical of phospha-alkenes[65].



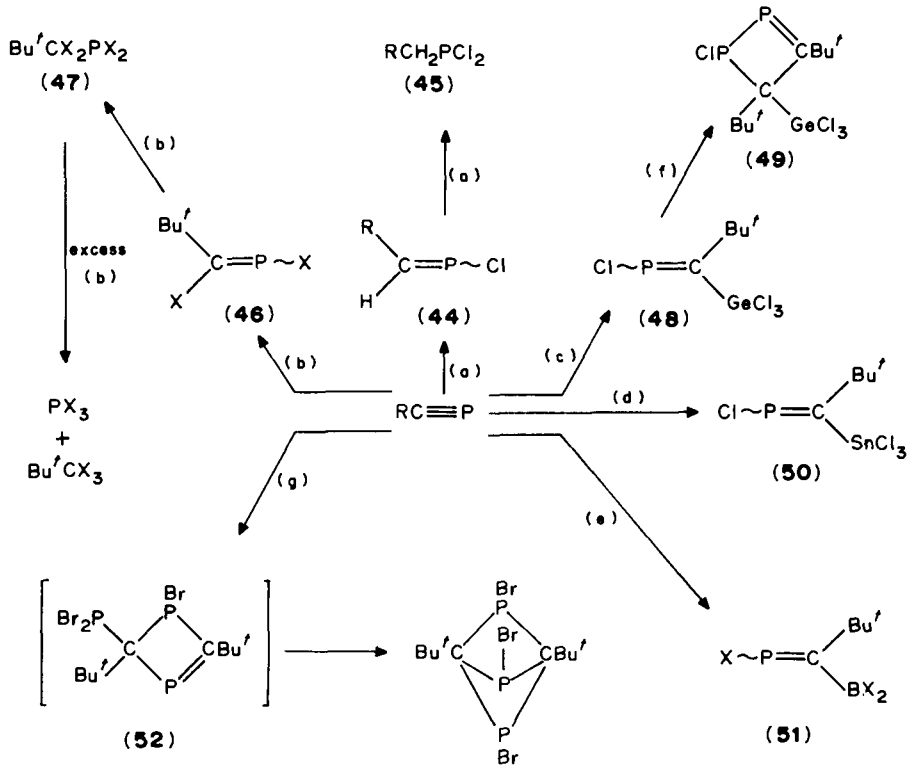
SCHEME 9



(43)

B. Reactions of Phospha-alkynes with Main Group Halides

Scheme 10 summarizes the reactions of phospha-alkynes with halides of several Main Group elements. In early studies, RC≡P (R = H, Ph) was reacted with hydrogen



(a) HCl, R = H, Ph; (b) X_2, X = Cl, Br, I, R = Bu^t; (c) $GeCl_4$, R = Bu^t; (d) $SnCl_4$, R = Bu^t; (e) BX_3, X = Cl, Br, R = Bu^t; (f) Bu^{t}CP; (g) PBr_3, R = Bu^t

SCHEME 10. Reactions of RC≡P with Main Group halides.

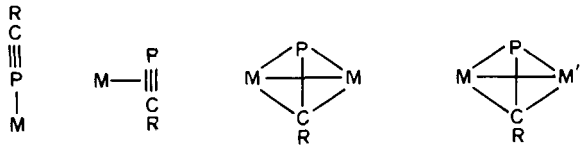
chloride to give chlorophospha-alkenes (**44**) and chlorophosphines (**45**), respectively[3,26]. These reactions had been used to confirm the identity of these phospha-alkynes, which were obtained in only small amounts.

Halogens, X_2 (X = Cl, Br, I), add in a stepwise fashion to the P≡C triple bond of Bu^{t}C≡P to afford the halogenophospha-alkenes (**46**) and subsequently the dihalogeno (1,1-dihalogenoalkyl)phosphine (**47**). The weak P—C single bond in **47** is cleaved to give PX_3 and Bu^tCX_3 with an excess of the halogen[11] (Scheme 10).

Interestingly, halides of Main Group elements, MX_n (M = Ge, Sn, B, X = Cl; M = B, X = Br; n = 3 or 4) also readily add across the triple bond of RC≡P (R = Bu^t) to afford the phospha-alkenes, ClP=C(Bu^t)MCl_3 [**48**, M = Ge; **50**, M = Sn] and XP=C(Bu^t)MX_2 (**51**, M = B, X = Br, Cl). Further treatment of Bu^{t}C≡P with **47** gave the 1,2-diphosphetene (**49**) (Scheme 10), the structure of which was confirmed by a single-crystal X-ray diffraction study. An analogous reaction with PBr_3 afforded the unusual cage compound **53**, which formed via the intermediate **52**[44,66].

VI. PHOSPHA-ALKYNE–TRANSITION METAL COMPLEXES

As mentioned earlier, photoelectron spectroscopic studies on a series of phospha-alkynes indicated that the HOMO is of the π-type and the π–n separation is greater than in the corresponding nitrile. This suggests that side-on (η^2-) coordination of the RC≡P ligand to a metal centre might be preferred to P-ligation. In mono- and di-nuclear metal systems, the following ligation modes are expected and examples of all types A–D have subsequently been established (see below). The η^1-ligating mode has only recently been established in complexes which have special steric restrictions[67], and the favoured type of bonding is of the η^2-type.



(A) (B) (C) (D)

Most complexes reported involve ligated Bu^{t}C≡P or AdC≡P, except for a single report of complexes of type C (**54**), which were generated *in situ* by dehalogenation of $RCCl_2PCl_2$ by $[Co_2(CO)_8]$ (equation 14)[68].

Syntheses of a selection of η^2-complexes of type B are summarized in equation 15–18[69–71].

$$RCCl_2PCl_2 + [Co_2(CO)_8] \xrightarrow{thf} \left[\begin{array}{c} R \\ C \\ (OC)_3Co \quad Co(CO)_3 \\ P \end{array} \right] \qquad (14)$$

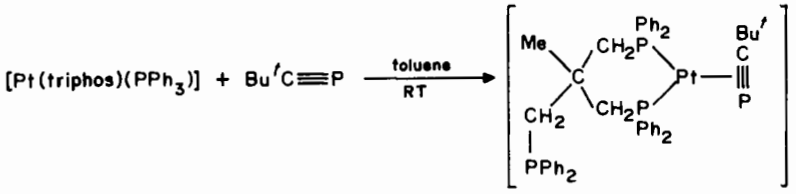
R=Ph, Me, Me_3Si

(**54**)

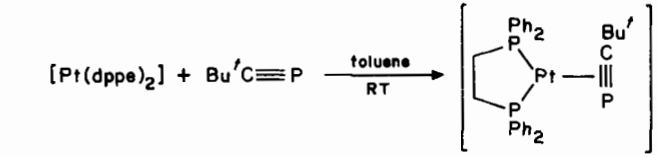
$$[Pt(cod)_2] + 2PR_3 \xrightarrow[RT]{Bu^tC\equiv P,\ hexane} \left[\begin{array}{c} R_3P \\ Pt \\ R_3P \end{array} \begin{array}{l} Bu^t \\ C \\ \equiv \\ P \end{array} \right] \qquad (15)$$

R=Me, Ph

$$[Pt(PPh_3)_2(C_2H_4)] + Bu^tC\equiv P \xrightarrow[RT]{toluene} \left[\begin{array}{c} Ph_3P \\ Pt \\ Ph_3P \end{array} \begin{array}{l} Bu^t \\ C \\ \equiv \\ P \end{array} \right] \qquad (16)$$

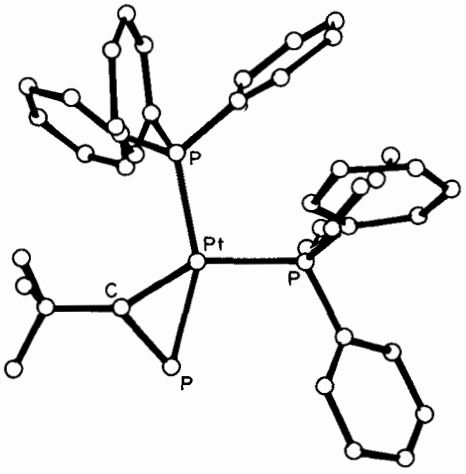


(17)



(18)

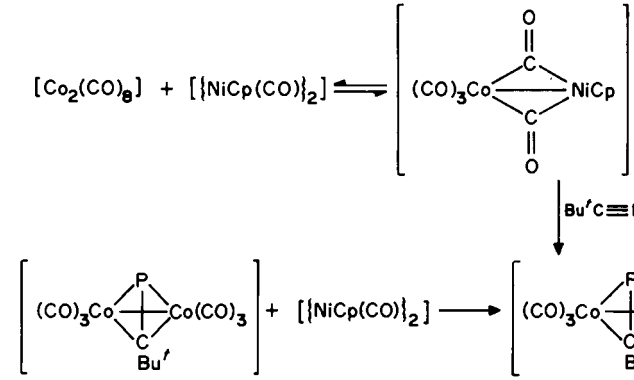
The molecular structure of $[Pt(PPh_3)_2(Bu^tC{\equiv}P)]$ (**55**) confirms the η^2-bonding mode and, as expected, the P—C bond is considerably lengthened on coordination. In complex **55**, the one-bond J(PtPalkyne) coupling constant (62 Hz) is the smallest so far recorded, reflecting the low s character of the Pt—P alkyne bond[69].



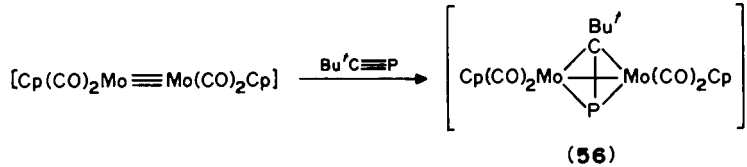
(**55**)

Several complexes of type C and D have been prepared by analogous reactions known for alkynes, namely by (i) treatment with $[Co_2(CO)_8]$ or $[CoNi(CO)_5Cp]$ or (ii) via addition of RC≡P across metal—metal multiple bonds (e.g. equations 19–22)[72,73]. The molecular structure of **56** is shown below[74].

The lone pair of electrons at phosphorus in B–D offer further ligating potential; thus complexes of type E and F are known from further interaction with other metal centres (equations 23–27)[75].

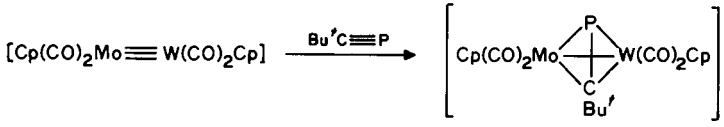


(19)

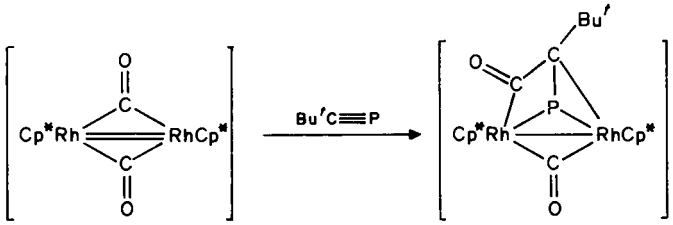


(20)

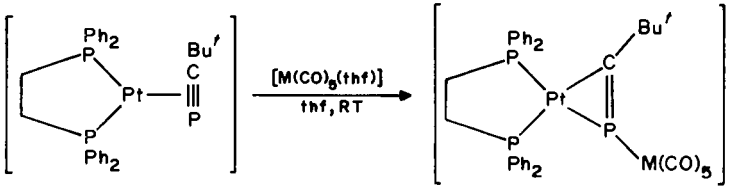
(56)



(21)

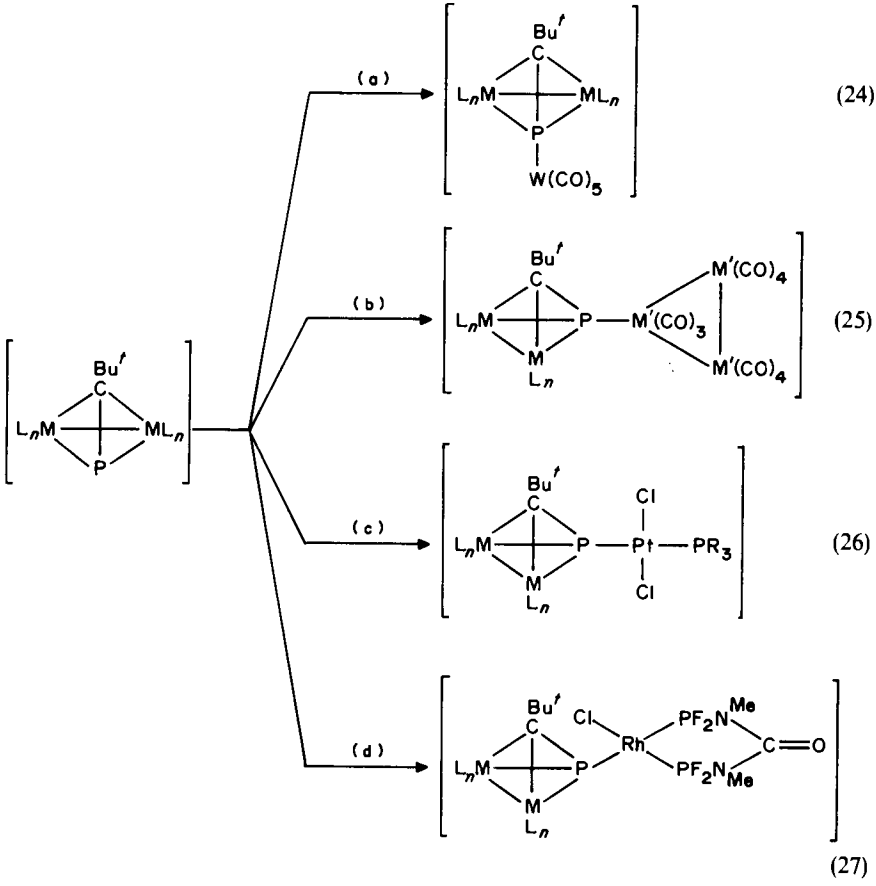


(22)



M = Cr, Mo, W

(23)



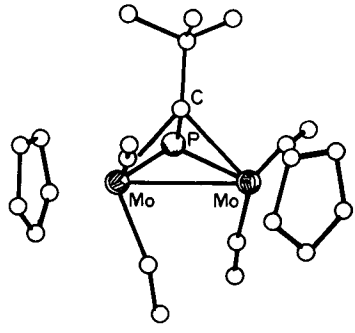
(24)

(25)

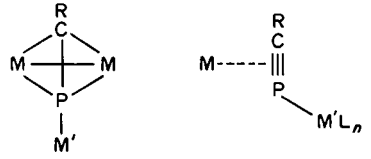
(26)

(27)

(a) $[W(CO)_5(Thf)]$, $ML_n = Co(CO)_3$, $Mo(CO)_2Cp$; (b) $[M'_3(CO)_{11}(MeCN)]$, $M' = Os$, Ru; $ML_n = Mo(CO)_2Cp$; (c) $[\{PtCl_2(PR_3)\}_2]$, R = alkyl, aryl; $ML_n = Mo(CO)_2Cp$; (d) $[\{RhCl[OC(NMePF_2)_2]\}_2]$, $ML_n = Mo(CO)_2Cp$

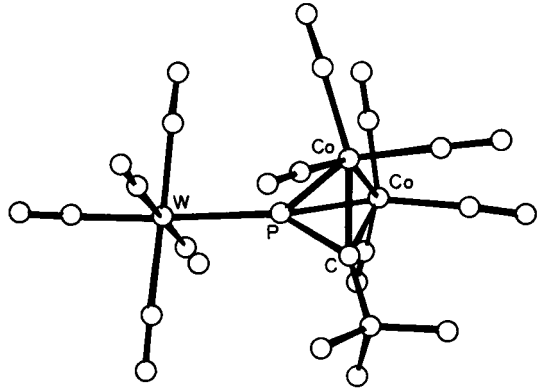


(56)

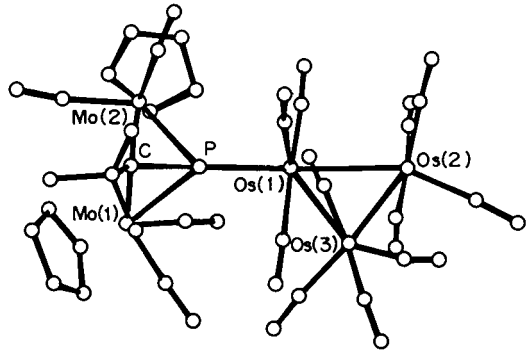


(E) (F)

Tri- and penta-metallic derivatives [72,76–78] have been synthesized and the molecular structures confirmed by X-ray studies. e.g. $[Co_2(CO)_6(\mu\text{-Bu}^t\text{CP})W(CO)_5]$ (**57**)[72], $[Mo_2(Cp)_2(CO)_4(\mu\text{-Bu}^t\text{CP})Os_3(CO)_{11}]$ (**58**)[76] and $[Mo_2(Cp)_2(CO)_4(\mu\text{-Bu}^t\text{CP})Fe(CO)_4]$ (**59**)[78].

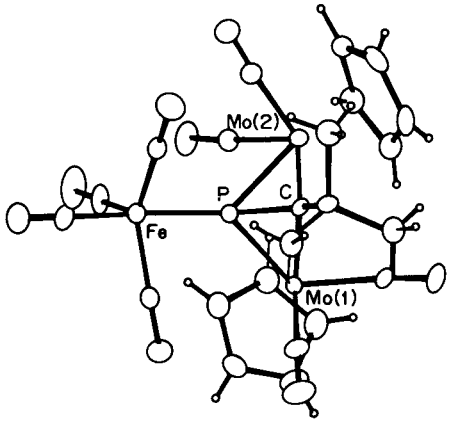


(**57**)

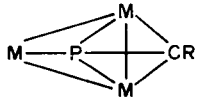


(**58**)

The trimetallic phospha-alkyne complex (type G), in which the RC≡P fragment transversely bridges an M—M bond to afford a μ_3-($\eta^2 - \perp$) ligating mode, has also been reported[79], e.g. $[Fe_2Pt(dppe)(CO)_6(Bu^tCP)]$ (**60**) is formed quantitatively from [Pt(dppe)Bu^{t}CP] and either $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ (equation 28).



(59)



(G)

$$[Pt(dppe)(Bu^tCP)] \xrightarrow[\text{or}\,[Fe_3(CO)_{12}]]{[Fe_2(CO)_9]} \left[\begin{array}{c} Ph_2 \\ P \\ Pt \\ P \\ Ph_2 \end{array}\right.\!\!\left.\begin{array}{c} Fe(CO)_3 \\ P \\ CBu^t \\ Fe(CO)_3 \end{array}\right] \quad (28)$$

(60)

Examples of phospha-alkynes utilizing both their P≡C bonds and phosphorus lone-pair electrons to form cluster metal systems involve pentametallic complexes of the type $[Pd_2M_3(PPh_3)_5(Bu^tCP)_3]$ (M = Pd, Pt), the molecular structure of which is shown with the phenyl groups of PPh_3 omitted for clarity[80]. It consists for a trigonal bipyramidal arrangement of the metal atoms with the two palladium atoms (which are bonded) occupying axial positions and the three platinum stellated atoms in equatorial sites.

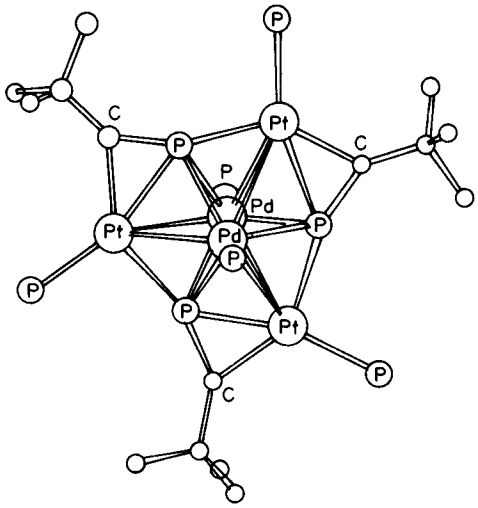
$$[Pt(PPh_3)_2(Bu^tCP)] \xrightarrow{[Pd(PPh_3)_4]} [Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3] \quad (29)$$

(61)

$$[Pd(PPh_3)_4] + Bu^tC{\equiv}P \xrightarrow[RT]{\text{toluene}} [Pd_5(PPh_3)_5(Bu^tCP)_3] \quad (30)$$

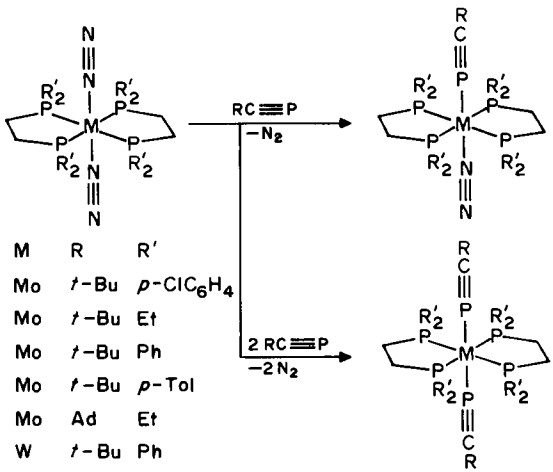
(62)

η^1-Bonded phospha-alkyne–metal complexes (type A) have been reported only recently by displacement of dinitrogen from *trans*-$[M(N_2)_2(R'_2PCH_2CH_2PR'_2)_2]$ (M = Mo, W)



(61)

(equation 31)[67]. The metal–phosphorus network exploited is such that only ligands that are long and thin can approach the metal and bind in the axial positions.



(31)

A single-crystal X-ray study on *trans*-[Mo(AdCP)$_2$($Et_2PCH_2CH_2PEt_2$)$_2$ (**63**) reveals (a) a linear seven-atom CCPMoPCC framework, (b) a short Mo—P alkyne bond distance and (C) a short P≡C bond distance which is comparable to that found in the free phospha-alkyne[67] (see Table 3).

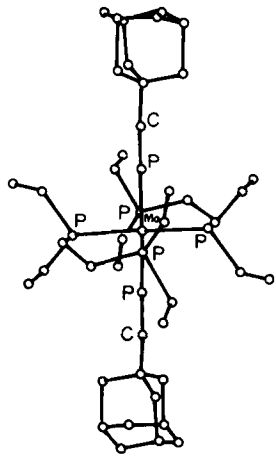
Some typical P—C bond lengths in RC≡P metal complexes are listed in Table 3.

Reactions of phospha-alkynes with metal complexes in high oxidation states lead to

TABLE 3. P—C bond lengths in some phospha-alkyne–transition metal complexes[a]

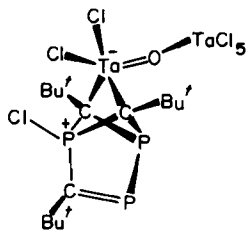
Complex	d(P—C)(Å)	Ref.
$[Pt(PPh_3)_2(Bu^tCP)]$	1.672(17)	69
$[Mo(dppe)_2(AdCP)_2]$	1.520(12)	67
$[Mo_2(Cp)_2(CO)_2(Bu^tCP)]$	1.719(3)	74
$[Mo_2(Cp)_2(CO)_2(Bu^tCP)W(CO)_5]$	1.733(12)	78
$[Mo_2(Cp)_2(CO)_2(Bu^tCP)Fe(CO)_4]$	1.719(5)	78
$[Mo_2(Cp)_2(CO)_2(Bu^tCP)Os_3(CO)_{11}]$	1.86(1)	76
$[Co_2(CO)_6(Bu^tCP)W(CO)_5]$	1.695(6)	72
$[Fe_2Pt(dppe)(CO)_6(Bu^tCP)]$	1.703(6)	79
$[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$	1.62(2)	80

[a] d(P—C) for free phospha-alkynes RC≡P = 1.540(3) Å.

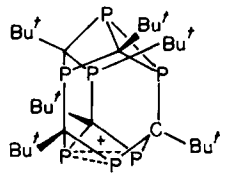


(63)

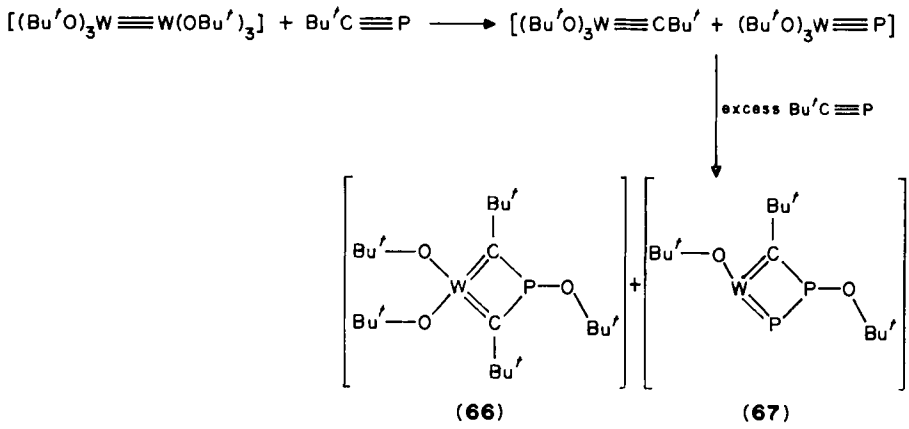
unusual products. Thus $TaCl_5$ gives the remarkable compounds **64** and **65** and $[W_2(OBu^t)_6]$ gives the 1-phospha-3-tungstena- (**66**) and 1,4-diphospha-3-tungstenacyclobuta-2,3-diene (**67**) complexes via trasnfer of Bu^{t}O from W to P (equation 32)[11,66].



(64)



(65)



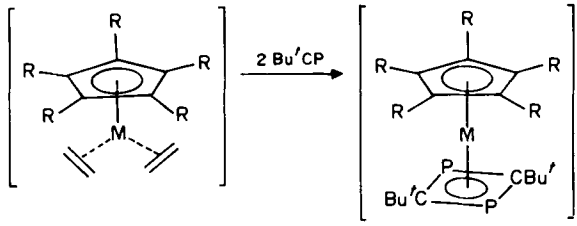
(32)

VII. USE OF PHOSPHA-ALKYNES IN THE SYNTHESIS OF PHOSPHORUS ANALOGUES OF η^4-CYCLOBUTADIENE-, η^5-CYCOPENTADIENYL-AND η^6-ARENE-TRANSITION METAL COMPLEXES

A major recent development in the chemistry of phospha-alkynes is their usefulness in the synthesis of phosphorus analogues of the well known η^4-cyclobutadiene-, η^5-cyclopentadienyl- and η^6-arene-transition metal complexes.

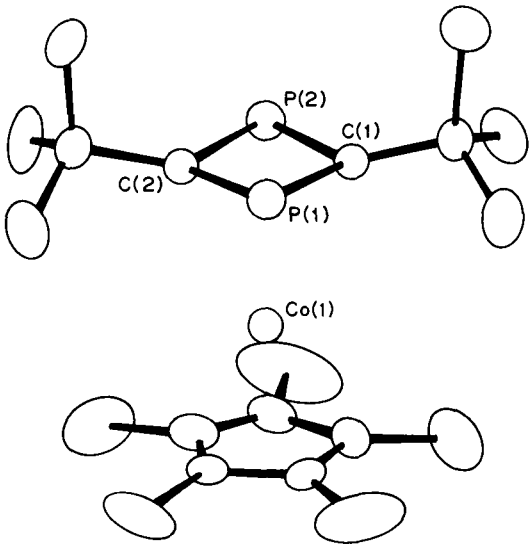
A. 1,3-Diphosphacyclobutadiene Complexes

First examples of this type of complex were reported by Maah *et al.*[81] and independently by Binger *et al.*[82]. The ready cyclodimerization of Bu'CP occurs on treatment with complexes of the type $[M(\eta^5\text{-}C_5R_5)(C_2H_4)_2]$ (R = H, M = Co, Rh; R = Me, M = Co, Rh, Ir) (equation 33)[81].



(33)

In $[Co(Cp^*)\{\eta^4(Bu^tCP)_2\}]$ (**68**), the η^4-diphosphacyclobuta-1,3-diene ring is essentially planar and all the P—C bond lengths are equivalent, indicating that in the complexed form the diphosphacyclobuta-1,3-diene ring is a square rather than a rectangle. This is similar to the behaviour of coordinated cyclobutadienes. Interestingly, the phosphorus—carbon bond length (1.801 Å) is, as expected, much longer than that of free Bu'CP (1.54 Å).



$P_{(1)}—C_{(1)}$ 1.80(1), $P_{(1)}—C_{(2)}$ 1.79(1), $P_{(2)}—C_{(1)}$ 1.82(1), $P_{(2)}—C_{(2)}$ 1.80(1), $Co_{(1)}—P_{(1)}$ 2.240(3), $Co_{(1)}—P_{(2)}$ 2.244(4), $Co_{(1)}—C_{(1)}$ 2.09(1), $Co_{(1)}—C_{(2)}$ 2.08(1) Å; $P_{(1)}—C_{(1)}—P_{(2)}$ 98.0(5), $P_{(1)}—C_{(2)}—P_{(2)}$ 98.7(5), $C_{(1)}—P_{(1)}—C_{(2)}$ 82.0(5), $C_{(1)}—P_{(2)}—C_{(2)}$ 81.0(5)°

(68)

An indenyl cobalt analogue is also known in which the P_2C_2 ring geometry is essentially identical with **68**. Analogous derivatives of $Me_2CHC{\equiv}P$ and $AdC{\equiv}P$ are also known[83,84]. Cyclodimerization of mixtures of $Bu^tC{\equiv}P$ and $AdC{\equiv}P$ also give the mixed [AdCPBu^{t}CP] ring system (equation 34).

Most recently it has been found[85] that although attempts at co-cyclodimerization of $Bu^tC{\equiv}P$ and $MeC{\equiv}CMe$ only gave ligated $[PCBu^t]_2$ and the arene Me_6C_6, the reaction between $[Co(Cp)(C_2H_4)_2]$ and $Me_3SiC{\equiv}CSiMe_3$ at $-30\,^{\circ}C$ followed by treatment of the resulting intermediate with $Bu^tC{\equiv}P$ gave a low yield of the previously unknown phosphacyclobutadiene complex **69** (equation 35).

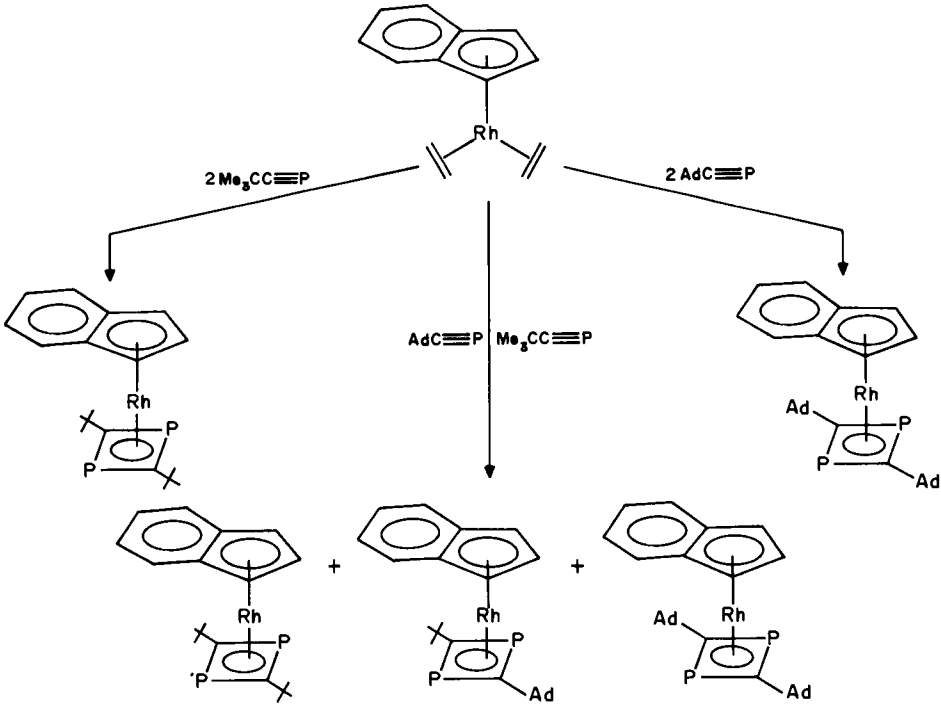
B. Metal Aggregates Containing Ligated 1,3-Diphosphacyclobutadienes

Novel bi- and tri-metallic complexes (**71** and **72**) have been characterized and syntheses of the remarkable hexametallic compounds **73a** and **73b** have also been reported[82,86] (equations 36 and 37).

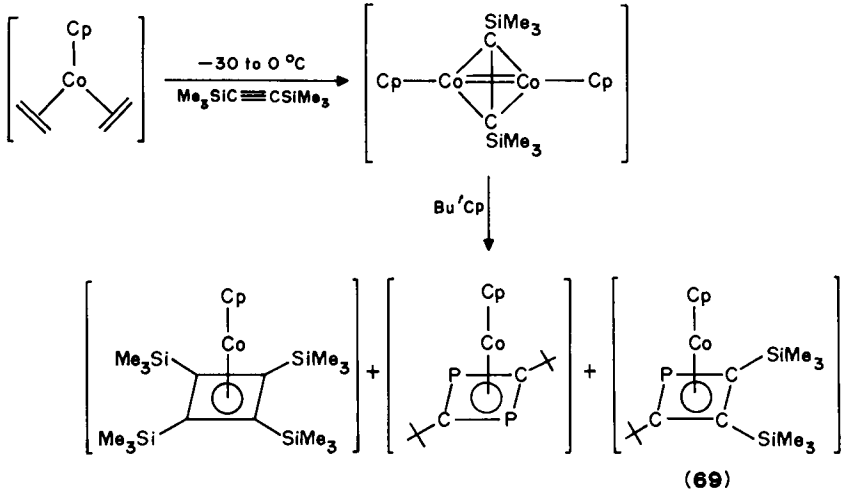
Zenneck and coworkers[87] have described mixtures of complexes containing phosphorus heterocycles by reaction 38. The cleavage of the P≡C triple bond in these systems is noteworthy.

In a recent attempt to synthesize examples of 2-metalla-1,4-diphosphacyclopentadiene complexes, Binger *et al.*[88] treated $Bu^tC{\equiv}P$ with $[Zr(\eta^5\text{-}C_5H_5)_2]$ generated *in situ* to afford the unusual bis (η^5-cyclopentadienyl)-1,3-diphosphabicyclo[1.1.0]butane-2,4-diylzirconium compound **74** (equation 39).

A single-crystal X-ray structural determination of **74** indicated that the phospha-alkyne has undergone dimerization to form the folded bicyclic ring system bonded to the metal by two Zr—C bonds.

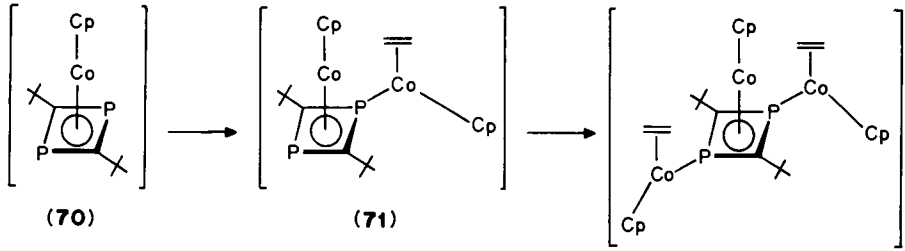

Rh
2 Me3CC≡P
2 AdC≡P
AdC≡P
Me3CC≡P
Ad
+
+

(34)

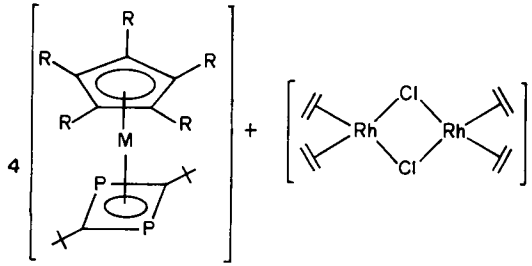

Cp
Co
−30 to 0 °C
Me3SiC≡CSiMe3
SiMe3
Bu'Cp
Me3Si
+
+

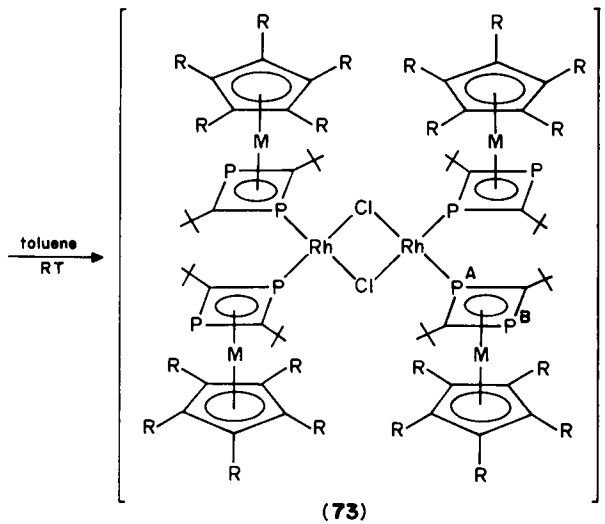
(69)

(35)

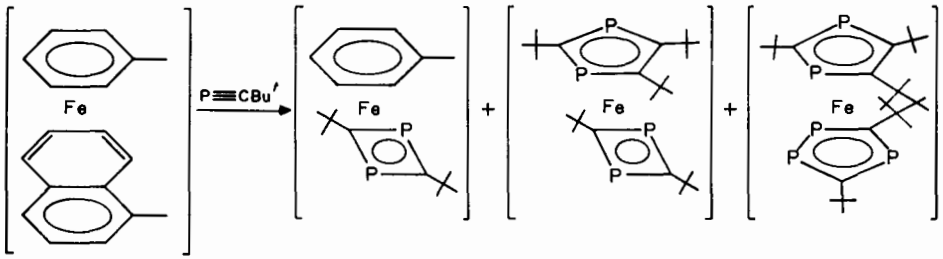

Cp
Co
P
(70)
(71)
(72)

(36)


4
R
M
P
Rh
Cl
+
M=Co, Rh


toluene
RT
R
M
P
Rh
Cl
A
B
(73)
(a) M=Co
(b) M=Rh

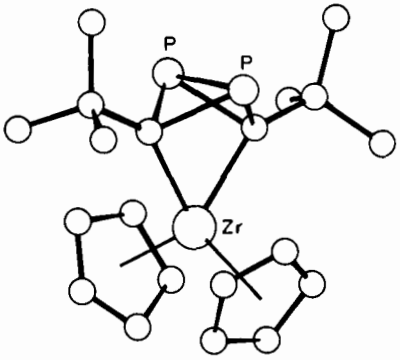
(37)



(38)

$$[Cp_2ZrCl_2] + 2\,P{\equiv}CBu^t \xrightarrow{Mg-HgCl_2} \left[Cp_2Zr\begin{smallmatrix}P\\P\end{smallmatrix}\right] \quad (39)$$

(74)



(74)

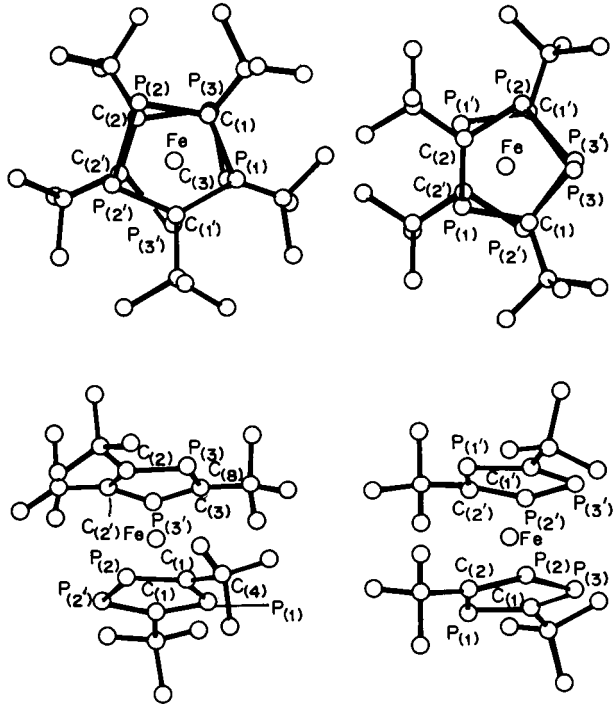
C. Tri-, Penta- and Hexa-phosphorus Analogues of Ferrocene

The synthesis of the triphosphacyclopentadienyl anion $[C_2R_2P_3]^-$ (R = Bu^t) has been reported from the reaction of Bu^{t}CP and Li[P(SiMe$_3$)$_2$][11,66]. The crystalline [Li(dme)$_3$][$C_2R_2P_3$], has been fully characterized by ^{31}P NMR spectroscopy and an unpublished single-crystal X-ray study. Subsequent studies suggested that a second anion, $[P_2C_3R_3]^-$, is also present in the reaction mixture[89].

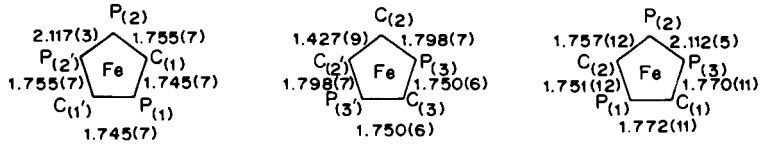
Penta- and hexa-phosphorus analogues of ferrocene have been obtained by treatment of the lithium salts of the $[P_3C_2R_2]^-$ and $[P_2C_3R_3]^-$ anions with $FeCl_2$ in monoglyme; they have been structurally characterized[89].

The remarkable green, air-stable, sublimable complexes [Fe(η^5-$C_2R_2P_3)_2$] (**75**) and [Fe(η^5-$C_2R_2P_2$)] (**76**) (R = Bu^t) have been fully structurally characterized by single-crystal X-ray diffraction studies. The sandwich structures (two views) are shown (top) together

with relevant bond length data (bottom). Analogous adamantyl compounds have also been prepared[89].



(75) (76)



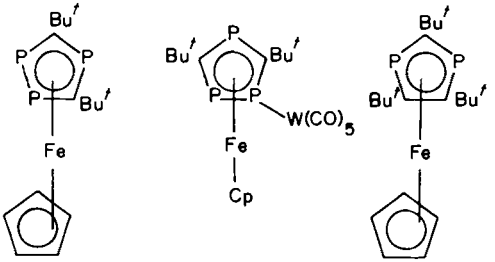
(75) (76)

Bond lengths to iron: (**75**) from $P_{(1)}$ 2.330(3), $P_{(2)}$ 2.360(2), $P_{(3)}$ 2.316(2), $C_{(1)}$ 2.208(7), $C_{(2)}$ 2.192(7), $C_{(3)}$ 2.242(9) Å; (**76**) from $P_{(1)}$ 2.330(3), $P_{(2)}$ 2.358(3), $P_{(3)}$ 2.359(3), $C_{(1)}$ 2.197(11), $C_{(2)}$ 2.222(12) Å

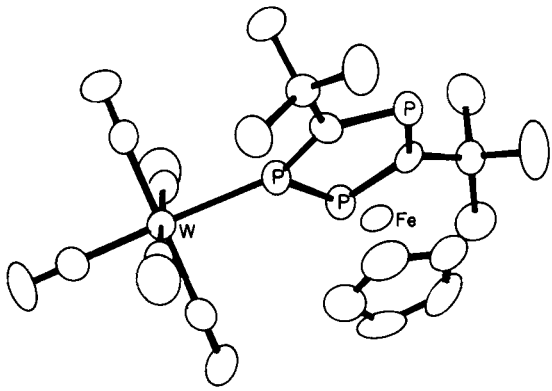
In both structures **75** and **76** the two η^5-bonded rings are eclipsed and the disposition of the rings minimizes inter-ring interactions of the organic groups.

More recently, the first paramagnetic sandwich compound, $[Cr(C_2R_2P_3)_2]$[90], was obtained and also compounds containing both η^5-C_5H_5(Cp) and η^5-$(C_2R_2P_3)$ or η^5-$(C_3R_3P_2)$ ring systems[91] **77** and **78**.

Further interaction of **77** with $[W(CO)_5(thf)]$ gives **78**, in which the tungsten is attached to one of the least sterically hindered phosphorus atoms of the η^5-$(C_2R_2P_3)$ ring. The molecular structure is shown[91].

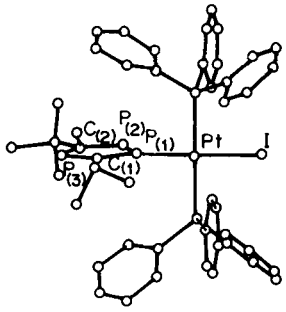


(77) (79) (78)



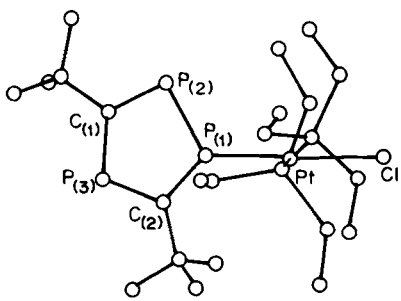
(79)

Electrochemistry and Mössbauer and photoelectron spectroscopic studies on these η^5-complexes indicate that the presence of phosphorus atoms in the rings exerts an overall electron-withdrawing effect on the transition metal atom[92].



$P_{(1)}$—$P_{(2)}$	2.010(11)	Å
$P_{(2)}$—$C_{(2)}$	1.73(4)	Å
$C_{(2)}$—$P_{(3)}$	1.81(4)	Å
$C_{(1)}$—$P_{(3)}$	1.69(1)	Å
$C_{(1)}$—$P_{(1)}$	1.76(4)	Å

(80a)

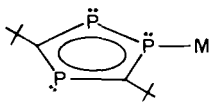


$P_{(1)}$—$P_{(2)}$	2.068(3)	Å
$P_{(1)}$—$C_{(2)}$	1.711(7)	Å
$P_{(2)}$—$C_{(1)}$	1745(7)	Å
$C_{(1)}$—$P_{(3)}$	1.726(7)	Å
$C_{(2)}$—$P_{(3)}$	1.740(8)	Å

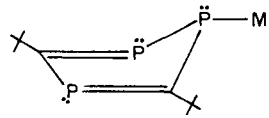
(80b)

The $(C_2R_2P_3)$ ring system also acts in an η^1-ligated fashion and the first example of this class of compounds is illustrated by **80a** and **80b**, $[PtX(PR'_3)_2(C_2R_2P_3)]$ (R = Bu^t; X = Cl, I; R′ = Ph, Et), whose structures indicate that one of the least sterically hindered phosphorus atoms is the donor site[93].

A feature of interest is the perfectly planar η^1-$C_2R_2P_3$ ring in both complexes, indicating that the nature of the bond between the ring phosphorus and the metal is of type H rather than I, and this is supported by the magnitude of ^1J(PtP) in **80b**, which is 2920 Hz. The complexes are also fluxional, the metal undergoing 1,2-shifts between the two adjacent P atoms of the ring[93].



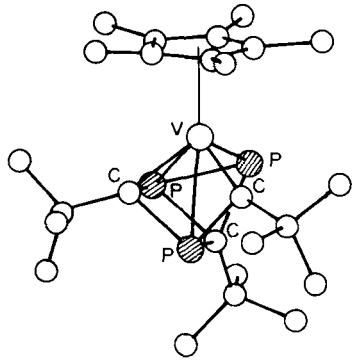
(H)



(I)

D. 1,3,5-Triphosphabenzene–Metal Complexes

First reports of metal-promoted cyclotrimerization of phospha-alkynes to give complexes containing 1,3,5-triphosphabenzene and its valence isomers have appeared recently. Treatment of a *tert*-butylphospha-alkyne with a source of the $[V(C_5Me_5)]$ fragment results in the formation of a dark-brown crystalline complex (**81**)[94].



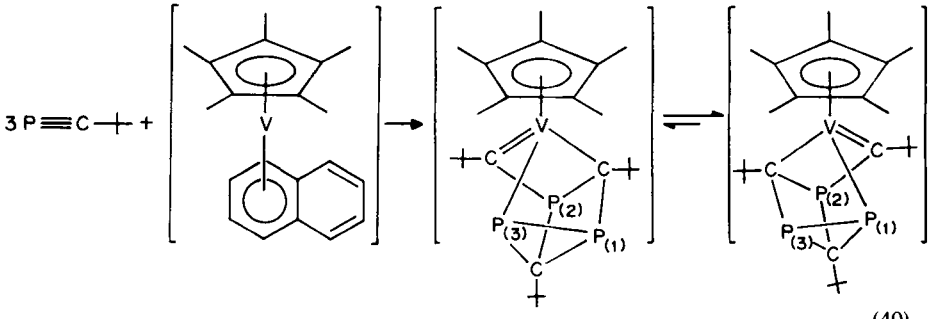
(81)

The ring system in **81** is derived from a 1,3,5-triphosphaprismane and the complex exhibits dynamic behaviour in solution (equation 40). At room temperature **81** reacts readily with 1 mol of carbon monoxide to give the dark-green complex **82**, which contains a ligated 1,3,5-triphospha-Dewar-benzene that has been fully structurally characterized by a single-crystal X-ray analysis[94].

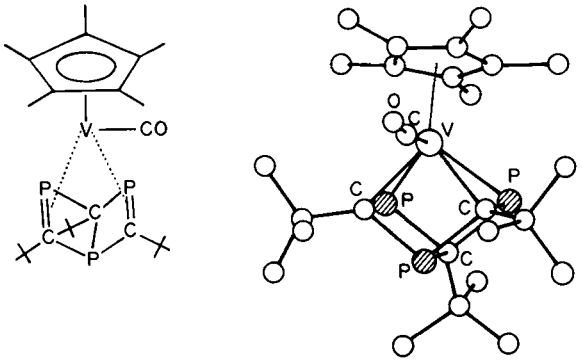
Treatment of cycloheptratrienemolybdenumtricarbonyl with Bu^{t}C≡P afforded the orange complex **83**, which has been formulated as a 1,3,5-triphosphabenzene derivative on the basis of spectroscopic data[95]. [*Added in proof*: This result has been questioned by other workers—see Ref. 14 for details.]

E. Other Metal Complexes Derived from Phospha-alkynes

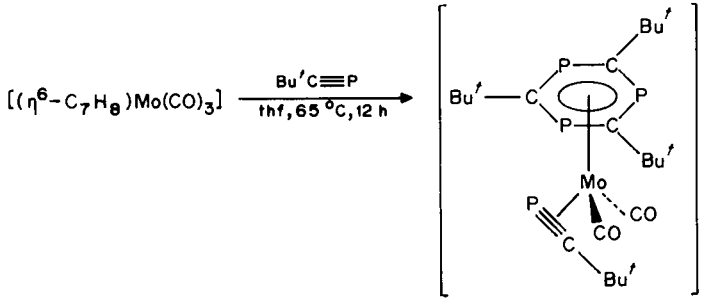
A variety of novel ligands generated from phospha-alkynes have recently been described. The coupling of two phospha-alkyne units via a carbonyl group to afford the



(40)



(82)

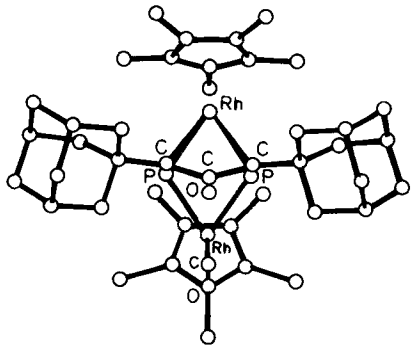


(83)

(41)

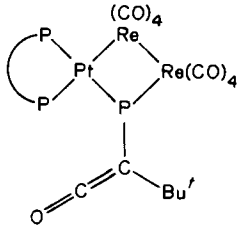
novel ligating unit P=CR(CO)CR=P (R = adamantyl or Bu') occurs on treatment with $[Rh_2(CO)_2(Cp^*)_2]$[96].

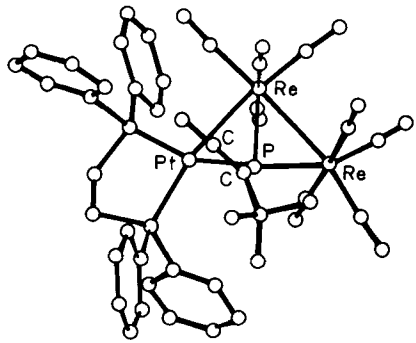
The solid-state structure of **84** shows that one rhodium atom is attached in an η^2-fashion to each of the P=C double bonds whereas the other rhodium is directly bonded to both phosphorus atoms.



(84)

Attack of carbon monoxide on the carbon of a single coordinated phospha-alkyne generates the unusual phosphinidene ligand RC(CO)P (R = Bu^t), which has been trapped in the complex $[Re_2Pt(CO)_9(dppe)(Bu^tC(O)P)]$ **85**[97].



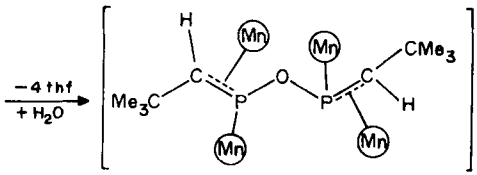


(85)

F. A Ligated Bis(phosphavinyl) Ether

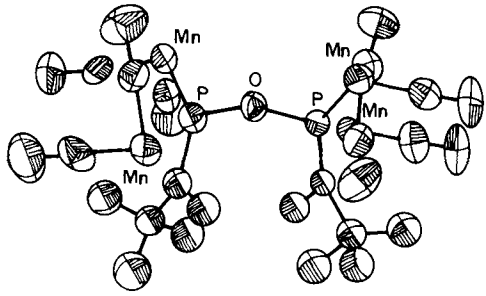
The remarkable bis(phosphavinyl)ether complex **86** containing four $[Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]$ fragments has been synthesized unexpectedly by addition of water to 2 mol of

$$4\,\mathrm{I}(\eta^5\text{-}C_5H_4Me)(CO)_2Mn\cdot thf\,\mathrm{I} + P{\equiv}CCMe_3 \xrightarrow[+H_2O]{-4\,thf} \text{(86)} \qquad (42)$$



Mn = $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2$

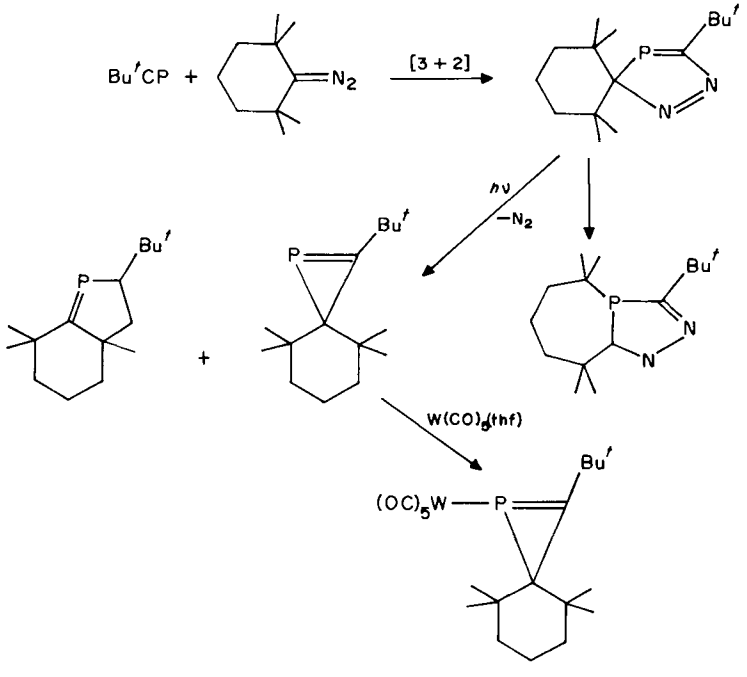
Bu^{t}C≡P during its reaction with the manganese carbonyl precursor (equation 42)[98]. Of the four manganese complex fragments, two are bonded to the phosphorus atoms and the other two to the P=C double bonds of the ligand.



(86)

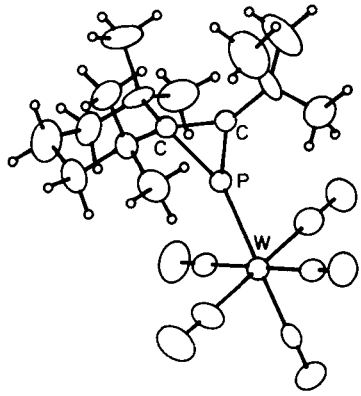
G. A 2*H*-Phosphirene Complex

The first example of a 2*H*-phosphirene complex resulted from treatment of Bu^{t}C≡P with a diazocyclohexane compound at −40 °C[99] (Scheme 11). The P=C bond length in **87**, 1.634(4) Å, is slightly shorter than that found in free or η^1-ligated phospha-alkenes.



(87)

SCHEME 11



(87)

VIII. NMR SPECTRA OF PHOSPHA-ALKYNE–METAL COMPLEXES

^{31}P NMR data and/or P—C bond distances in some phospha-alkyne–metal complexes are summarized in Table 4. It is interesting that there is a downfield shift (ca 100–150 ppm)

TABLE 4. ^{31}P NMR data for some phospha-alkyne–metal complexes

Compound	δ(P)(ppm)[a]	J(MP)(Hz)	Bonding type	Ref.
$[Pt(PPh_3)_2(Bu^tCP)]$[b]	−56.9	62[c]	B	69
$[Pt(dppe)(Bu^tCP)]$[b]	−53.3	166[c]	B	79
$[Pt(triphos)(Bu^tCP)]$[b]	−58.7	144[c]	B	70
$[Pt(PMe_3)_2(Bu^tCP)]$[b]	−74.8	151[c]	B	75
$[Pt\{(mes)P{=}CPh_2\}_2(Bu^tCP)]$[b]	−101.9	115[c]	B	70
$[Mo_2(Cp)_2(CO)_4(Bu^tCP)]$	−252.0	—	C	74, 77
$[Rh_2(Cp^*)_2(CO)\{Bu^tC(CO)P\}]$	+189	29[d]	C	74
$[Ni_2(Cp)_2(Bu^tCP)]$[b]	−188	—	C	73
$[Co_2(CO)_6(Bu^tCP)W(CO)_5]$	—	—	E	72
$[Mo_2(CO)_4(Cp)_2(Bu^tCP)Fe(CO)_4]$	−189.4	—	E	78
$[Mo_2(CO)_4(Cp)_2(Bu^tCP)W(CO)_5]$	−269.2	229[e]	E	78
$[Mo_2(CO)_4(Cp)_2(Bu^tCP)Os_3(CO)_{11}]$	−287.4	—	E	76
$[Mo_2(CO)_4(Cp)_2(Bu^tCP)Ru(CO)_{11}]$	−234.9	—	E	76
trans-$[PtCl_2(PBu_3)\{Mo_2(\mu\text{-}Bu^tCP)(CO)_4Cp_2\}]$[b]	−205.9	2033[c]	E	77
trans-$[PtCl_2(PPr_3)\{Mo_2(\mu\text{-}Bu^tCP)(CO)_4Cp_2\}]$[b]	−206.6	2034[c]	E	77
$[RhCl\{OC(NMePF_2)_2\}\{Mo_2(\mu\text{-}Bu^tCP)(CO)_4Cp_2\}]$[b]	−242.0[f]	140[d,f]	E	77
$[Fe_2Pt(dppe)(CO)_6(Bu^tCP)]$[b]	−192.8	128[c]	G	79
$[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$[b]	—	—	—	80
$[Re_2(CO)_8Pt(dppe)\{Bu^tC(CO)P\}]$[b]	+142	—	—	100
$[W(Bu^tCP)_2(dppe)_2]$	−157.9	354[e]	A	83

[a]Relative to TMP.
[b]Data refer to phosphorus of RCP moiety only; δ(P)($Bu^tC{\equiv}P$) = −209 ppm.
[c]^1J(PtP).
[d]^1J(RhP).
[e]^1J(WP).
[f]Estimated.

from that of the free Bu^{t}C≡P ligand [δ(P) = −209 ppm] on coordination in the η^2-bonded type (B) phospha-alkyne complexes. For other complexes (types C and D, no generalizations can be made although most of the ^{31}P NMR resonances lie in the high-field region. One important feature in the ^{31}P NMR spectra of these complexes is the magnitude of ^1J(MP) (M = ^{195}Pt, ^{183}W, ^{103}Rh) which reflects the s-character term in the coupling expression and can be diagnostic in structural elucidation. Low ^1J(MP) values [e.g. ^1J(PtP) = 62–166 Hz in bonding types B and F; ^1J(RhP) = 29 Hz in bonding type C] are observed when the Bu^{t}C≡P ligand is η^2-bonded to the metal atom. When the lone pair of electrons at the phosphorus atom of the coordinated RCP are directly involved in coordination towards the metal atom (type E, a higher ^1J(MP) would be expected [e.g. ^1J(WP) = 229 Hz; ^1J(PtP) = 2034 Hz).

IX. APPENDIX

Since submission of the manuscript in August 1988, the field of phospha-alkyne chemistry has developed remarkably, particularly with respect to their use in the synthesis of heterocyclic compounds, phospha-arenes and their valence isomers, and polycyclic compounds. The role of phospha-alkynes as ligands and as precursors to new types of ligands is also noteworthy as is their cyclodimerization in the coordination sphere of metals. Two major review articles covering these aspects have recently appeared: J. F. Nixon, *Chem. Revs.*, **88**, 1327 (1988), and M. Regitz and P. Binger, *Angew. Chem. Int. Edn.*, **27**, 1482 (1988).

A major international meeting PSIBLOCS (The Chemistry of Phosphorus, Silicon, Boron and Related Elements in Low Coordination Number) was held in Palaiseau, Paris, in August 1988 and a book entitled *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, by M. Regitz and O. J. Scherer: Thieme, Stuttgart 1989 (in press), also report the developing interest in this area.

Of special note are the recently reported cage compounds $P_5C_5B^t_5$ [R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organometal. Chem.*, **375**, C31 (1989), $P_6C_4Bu^t_4H_2$ (R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. C. S. Chem. Commun.*, 1989, 1047) and the novel cubane like compound $P_4C_4Bu^t_4$ (T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter, and M. Regitz, *Angew. Chem. Int. Edn.*, **28**, 1013 (1989)] which have been synthesized from Bu^{t}C≡P or its derivatives. The use of phospha-alkynes in the synthesis of organophosphorus compounds and their metal complexes seems likely to continue to produce a wide variety of novel compounds.

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The Chemistry of Organophosphorus Compounds
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CHAPTER **10**

Cyclic phosphines

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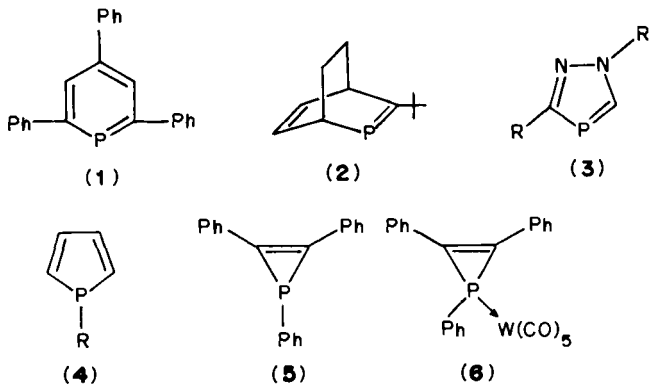
I. INTRODUCTION

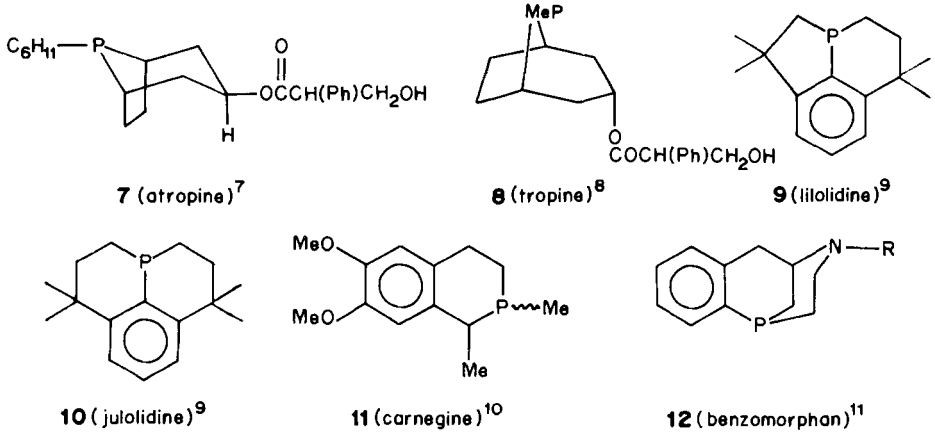
The first cyclic phosphine (1-phenylphospholane) was prepared as early as 1915[1], but only recently has this class of compounds received broad attention. Many valuable discoveries of new structural types and of unusual characteristics are being made, and the field is in a state of rapid development. Particularly exciting are discoveries of new unsaturated ring systems, where a double bond to phosphorus is present. The first example of this structural type was a 'phosphabenzene' (**1**; 2,4,6-triphenylphosphinine[2]), announced in 1967. This type of compound will be discussed in detail in section V. Only in the last few years has it been recognized that the C=P unit can be found in other stable molecules (e.g. **2**[3] and **3**[4]), and now many ring systems are being discovered regularly. Even cyclic phosphines with single bonds to phosphorus can have some surprising properties, such as in their conformational preferences or in striking NMR effects. When a phosphine grouping is attached to a carbon—carbon double bond, the possibility exists that electron delocaliz-

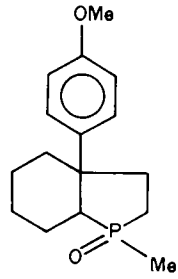


ation can be present, and in multiply unsaturated phosphines with $4n + 2$ π electrons, properties associated with 'aromaticity' might appear.

This notion has been responsible for a great amount of research, especially in the phosphole (**4**) family. Yet another aspect of contemporary cyclic phosphine chemistry is concerned with metal coordination complexes. These compounds have many valuable characteristics, but are now receiving attention as aids in the synthesis of new and unusual compounds, which result when operations are performed directly on the phosphine ligands. Some remarkable structures have been synthesized for the first time by this approach. An example is **5**, first made in 1982[5] in the form of a metal carbonyl complex (**6**); the free phosphine was then released in a decomplexation step[6], and proved to be surprisingly stable (half-life greater than 17 h at 90 °C in toluene).

The ready oxidizability of phosphines interferes with the development of practical uses for these compounds, other than as synthetic intermediates. Particularly lacking in the literature are data on biological properties of cyclic phosphines. However, there is detectable activity arising in this area, and some complex cyclic phosphines that resemble alkaloids through replacement of nitrogen by phosphorus are being synthesized. This little-explored area may well develop further in the future, and it will be of great interest if oxidation-resistant alkaloid analogs can be prepared that will allow biological evaluation. Some examples of alkaloid mimics are shown as structures **7**–**12**, with the related alkaloid noted. An additional structure **13** has the framework of the mesembrine alkaloids, but





(13)

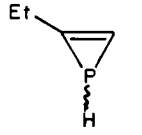
possesses the phosphine oxide structure[12]. This should be easily convertible to the phosphine, however (see Section III. D).

A review of the restricted size necessary for this chapter cannot be complete as the field is far too large. A considerable body of literature has been examined in order to present the scope of cyclic phosphine chemistry, both in historical perspective and in up-to-the moment advances. Many excellent pieces of research could not be mentioned. However, the authors hope that the review will be of value to those regularly involved in phosphorus chemistry and to those studying the field but not yet active in it.

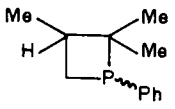
II. SOME SPECIAL PROPERTIES OF PHOSPHORUS IN CYCLIC PHOSPHINES

A. Geometrical Isomerism

A fundamental point that needs to be appreciated in understanding the chemistry of cyclic phosphines is that the pyramidal stability of tricovalent phosphorus can lead to the existence of separable stereoisomers. Not only are optically active phosphines known, but also many examples of stable geometrical isomers (*cis*, *trans* in monocyclics or *syn*, *anti* in bridged phosphines) have been encountered. As a general rule, the barrier to pyramidal inversion ($\Delta G^{\ddagger}$) in tertiary phosphines is about 35 kcal mol^{-1}, which endows them with half-lives at 135 °C of about 3–4 h[13]. This insures that cyclic tertiary phosphines with one or more C substituents will possess geometrical isomers of sufficient stability to allow separation techniques to be applied. There have been many reports where this has been accomplished, using such techniques as gas chromatography, fractional distillation or



(14)[14]



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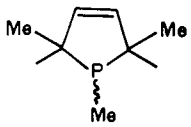
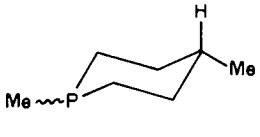
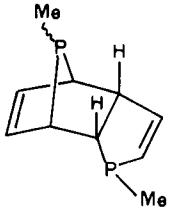


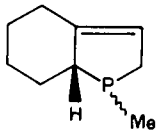
(16)[16]



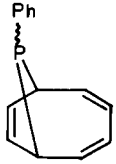
(17)[17]



(18)[18]



(19)[19]

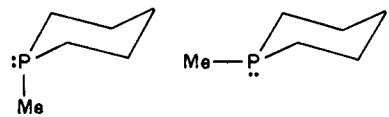


(20)[20]

crystallization. Tertiary phosphine oxide diastereoisomers are also readily separated and, as will be discussed in Section III.D, can easily be reduced to the phosphines without loss of stereochemical integrity. Some representative types of cyclic phosphines for which diastereoisomeric forms have been isolated are shown (**14**–**20**).

B. Ring Conformational Effects

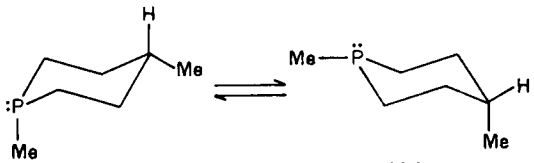
Cyclic phosphines in general adopt the ring shapes commonly found for carbocyclic counterparts. The longer C—P bond (about 1.84 Å) and smaller C—P—C bond angle (around 100° in tertiary phosphines) than are associated with carbon in cyclic systems introduce some modification of the ring shape. In the six-membered ring (phosphorinane), the chair shape is readily recognized in the structures determined from X-ray crystallographic investigations[21]. Five-membered phosphines probably adopt the envelope shape known for cyclopentanes (not necessarily with P at the 'flap'), but data on free phosphines, which are usually liquids, seem to be lacking. However, some X-ray crystallographic work on the solid metal coordination complexes of five-membered cyclic phospholenes has shown the envelope shape to be present[22]. One remarkable characteristic of cyclic phosphines is their markedly reduced tendency for the substituent on P to adopt the equatorial position. In 1-methylphosphorinane (**21**), the equilibrium between the conformers with equatorial and axial methyl is only slightly on the side of the equatorial form at $-140\,^{\circ}C$ ($K = 2.03$)[21]. An entropy effect causes a shift in the position of the equilibrium as the temperature increases, so that at room temperature there is a slight (2:1) preference for the axial form[23].



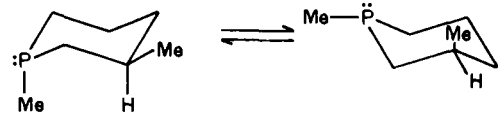
(**21**)

Even larger groups, such as phenyl ($K = 2.33$), still are found to exert little conformational preference in phosphorinanes, and in the 4-keto derivatives the axial–equatorial ratio in chloroform is 4:1[24]. The energy of activation for the phosphorinane ring inversion is close to that for cyclohexane[23]. When C substituents are present, the position of the conformational equilibria is usually controlled by the preference of that group to occupy the equatorial position. Thus, in 1,4-dimethylphosphorinane (**22**), NMR spectral evidence shows that the *cis* isomer has a strong preference for conformation **22a**, and only a negligible contribution from **22b** is present. This is true also in 1,3-dimethylphosphorinane (**23**), where the *trans* isomer shows a preference for conformation **23a** over **23b**[25].

These apparently weak preferences for one of the two sites at the phosphorus atom may arise from the failure of strong destabilizing non-bonded 1,3-interactions to develop, as they do so strongly in axial groups in cyclohexanes. A mechanism exists for the relief of these interactions in phosphines. In the first place, the interactions may be weaker because

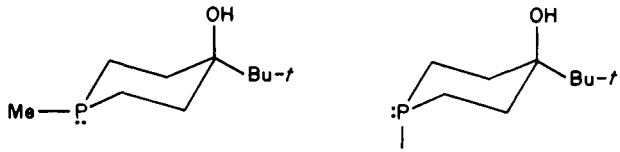


(**22a**) (**22b**)



(23a) (23b)

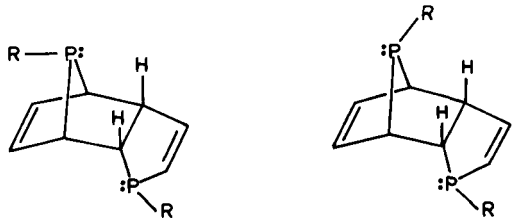
the longer C—P bonds in the ring and in the exocyclic group place the P substituent at a greater distance from the axial hydrogens. The special mechanism open to phosphorus is that the pyramidal shape may become flattened, thus further increasing the distance of an axial P substituent from the axial hydrogens. This flattening at phosphorus has been observed in several cyclic phosphines that have been studied by X-ray crystallography. Thus, in uncrowded phosphine **24a**[26] the dihedral angle at the $C_{(6)}$—P—$C_{(2)}$—$C_{(3)}$ site is 57°, but in isomer **24b**, where crowding could be present, the flattening reduces the dihedral angle to 46°.



(24a) (24b)

The lack of an expressed preference by a P substituent for a particular orientation allows even small groups on carbon to adopt the equatorial position, even if this means forcing the P substituent into the axial position. Thus, in *trans*-1,4-phosphorinanol, the OH group is predominantly equatorial and the *P*-methyl is axial[27]. As expected, hydrogen on phosphorus adopts the axial position[28]. In confirmation of the weak conformational effect as being special to phosphines, the corresponding oxides and sulfides, where the firm tetrahedral geometry prevents the easy flattening at phosphorus, have been found to have different conformational tendencies; the larger *P*-alkyl or *P*-aryl substituent clearly prefers the equatorial position, and O or S adopt the axial position.

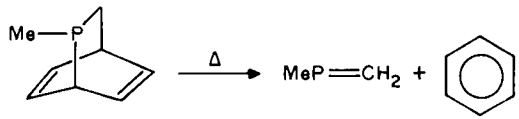
In bridged bicyclic phosphines, *syn*, *anti* isomers are possible, and several examples are known. Thus, 7-phosphabicyclo[2.2.1]heptenes (7-phosphanorbornenes) are known in both *syn* (**25**) and *anti* (**26**) form. The structures are easily assigned by NMR spectral effects[18], but there is no firm evidence to suggest which is the more stable form. Thermal equilibration attempts have been hampered by the ease with which the P-bridge is lost from these molecules[29]. The *syn* isomer rearranges to the *anti* isomer, however, in solutions containing alcohols or water[30], and at least in these media a conformational preference is expressed.



(25) (26)

C. Reactivity

The chemical reactions of cyclic phosphines in general do not differ from those of non-cyclic phosphines. However, there is some sensitivity to ring opening in special cases. Thus, the three-membered phosphiranes are thermally unstable and decompose with C—P bond opening. The four-membered phosphetanes are stable thermally and to most reaction conditions so far reported. Some bridged unsaturated phosphines have a mechanism available to them that allows an apparent retrocycloaddition reaction to occur. An example is provided by the recently synthesized 2-phosphabicyclo[2.2.2]octa-5,7-diene system[31]. Both *P*-methyl and *P*-phenyl derivatives of molecules having this ring system are known, but they decompose when heated in toluene solution at 35–40 °C with ejection of the P—C bridge as a phosphaalkene, as shown for **27** (equation 1)[32]. The 7-phosphanorbornenes (e.g. **25**, R = Me) undergo a more complicated decomposition, but the net effect is the ejection of the P-bridge.

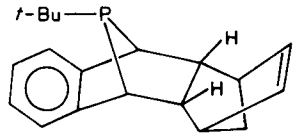


(27) (1)

Most reactions of phosphines proceed with a high degree of retention of configuration at phosphorus, and the well established stereospecificity in such reactions as oxidation (by a variety of reagents), sulfuration, quaternization, imination with azides, etc., are extremely valuable in synthetic operations. This avoids the formation of mixtures of isomers from a single phosphine starting material, and gives a product with a known stereostructure (assuming knowledge of the structure of the phosphine).

D. NMR Spectral Properties

NMR is the major tool in use for the study of the structure of cyclic phosphines in solution. The ^{31}P NMR chemical shift range is much wider in cyclic phosphines (about 350 ppm) than in non-cyclic phosphines (about 120 ppm), and is very sensitive to structural effects. A recent review[33] summarizes much of the data on cyclic phosphines, and makes it clear that accounting for the differences between structural types is not straightforward. The three-membered rings give shifts far upfield of all others, and this may be related to the high degree of s character in the lone pair on phosphorus. Phosphines with the bicyclic 7-phosphanorbornene framework have their ^{31}P NMR shifts at very far downfield positions; indeed, those with the *syn* configuration have the most downfield values ever recorded for any tertiary phosphine. Thus, the bridging P in **25** (R = Me) has a shift of δ +96.5[18]; the extreme so far reached is +152.5 in **28**[34].

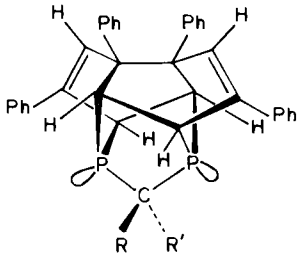


(28)

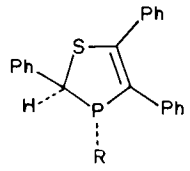
It is of importance that saturation of the double bonds in **25** (R = Me) removes the effect, and normal values are then seen. An explanation for the effect, which is also seen

for a number of other nuclei when at the 7-position, rests on the existence of an overlap of the C—P σ orbital with a π^* orbital of the double bond, which has diminished electron density at the 7-position and thus causes deshielding. Extending the bridge by one carbon in the 2-phosphabicyclo[2.2.2.]oct-5-ene system completely removes the effect, and normal values are seen[31]. Remarkably strong deshielding has recently been seen in two other types of cyclic phosphines where the hyperconjugative argument would not apply. Thus, phosphine **29**[35] (R = R^1 = H) has shifts of δ +80.8 and +91.7, and phosphine **30**[26] a shift of δ +80.0. As other types of phosphines are discovered that have the far downfield ^{31}P signals, the effect may become better understood and the structural origin defined.

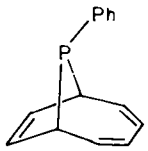
Abnormal upfield shifts are also common among unsaturated bicyclic phosphines. There is no immediately obvious explanation for a shift of δ −79 in a *P*-phenylphosphine such as **31**[20], but even more remarkable is the value of δ −145 reported[37] for the heterosubstituted phosphine **32**.



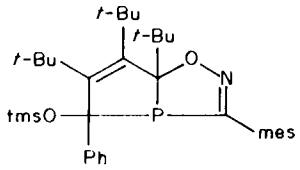
(29)



(30)



(31)



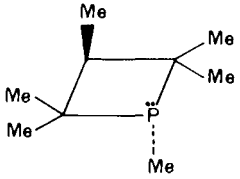
(32)

The nature of the P substituent in cyclic phosphines has a significant, but predictable, influence on the chemical shift. Thus, *P*-methyl cyclic phosphines invariably have chemical shifts that are about 18 ppm at higher field than found for the *P*-phenyl counterparts[21]. *Cis*, *trans* isomers differ significantly in their ^{31}P shifts, but not in a uniform way, so caution is required in using this parameter as the sole indicator of configuration at phosphorus. Thus, in *P*-methylphosphorinanes the isomer with an axial methyl is about 5 ppm at higher field than that with an equatorial methyl[23]; this is consistent with the effect known in cyclohexanes for methyl substituents, and is attributed to the γ-shielding effect that acts on an axial substituent. However, in some *P*-phenylphosphorinanes, the opposite relationship is seen[38]. The *syn*, *anti* isomers **25** and **26** differ by as much as 66 ppm, with the former more downfield[18]. Certainly, the ^{31}P NMR difference in a pair of isomeric phosphines is of value in other regards as well, such as in analyzing mixtures, in following the course of reactions or mixture separations and in establishing purity.

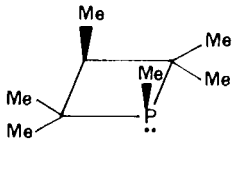
Carbon-13 NMR spectra are frequently more valuable than ^{31}P NMR in establishing

stereostructure in cyclic phosphines. A useful and reliable effect arises from γ-steric interactions on the exocyclic carbon attached directly to phosphorus. In many ring systems[39], an axial (or pseudoaxial) carbon is known to have an upfield shift of several ppm relative to the value for an equatorial (or pseudoequatorial) carbon, and this can be used to assign steric structure when both forms are available.

Another ^{13}C NMR effect that is of great importance is the $^{13}C-^{31}P$ coupling constant. For both $^{2}J_{PC}$ and $^{3}J_{PC}$, stereospecific effects are known that are empirically related to the orientation of the lone pair orbital on phosphorus[40]. The general rule for the two-bond coupling is that the value is a maximum when the lone-pair orbital has a dihedral angle relation of 0° (e.g. is 'eclipsed' or *syn*) with a carbon β to phosphorus, and diminishes to a negligible size when in an *anti* orientation. The first example reported[41] of this effect amply illustrates its magnitude and importance; in **33**, where the angle is close to 0°, the $^{2}J_{PC}$ value for the 2,4-dimethyls *cis* to 3-Me is 30.5 Hz, whereas in **34**, with a large angle, the coupling is 4.3 Hz. Many examples have been published subsequently (numerous examples, are cited in ref. 40a and a theoretical analysis of the lone pair effect is presented in ref. 40b).

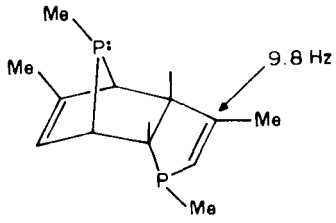


(33)

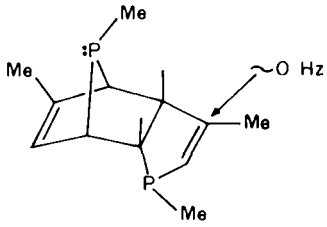


(34)

Three-bond P–C coupling in phosphines shows a strong dependence both on lone pair orientation and on the dihedral relation of the coupled nuclei, in a manner similar to the well known Karplus relation for H—H coupling. In freely rotating phosphines[42], $^{3}J_{PC}$ follows a Karplus-like relation and has a maximum when phosphorus and carbon have dihedral angles of 0° and 180°. The minimum value occurs at 105–110°. However, in cyclic phosphines the orientation of the lone pair is fixed and this clearly has an influence on $^{3}J_{PC}$ that can overcome the Karplus control. Thus, if the lone pair is remote from the coupled carbon, the coupling constant will be small even if the dihedral angle is favorable for strong coupling. The effect is illustrated in the 7-phosphanorbornene derivatives **35** and **36**[18]. This effect also holds for three-bond coupling between two ^{31}P nuclei (e.g. for **35**, 22.0 Hz; for **36**, 4.9 Hz).

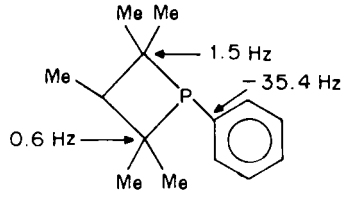


(35)



(36)

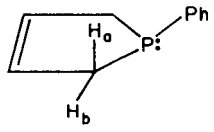
Even the one-bond $^{13}C-^{31}P$ coupling constant can be an indicator of structure at phosphorus; this parameter is sensitive to hybridization (and hence bond angle) at phosphorus, and in general is large and negative when the degree of s character is large.



(37)

The effect is dramatically illustrated in small rings, as in **37**[43]. The contraction of the internal C—P—C angle diminishes the s character in the ring C—P bond and diverts it to the external C—P bond.

Proton NMR spectra of cyclic phosphines are also useful in deducing stereostructure where clearly resolved spectra can be obtained. This is not always easy, however, and more use is being made of ^{13}C NMR spectra, which generally are better resolved. One valuable parameter is two-bond $^{31}P-^{1}H$ coupling. Just as for $^{2}J_{PC}$ as in **38** (and indeed recognized earlier[44]), this value depends on the proximity of the lone pair to the coupled proton. A number of cases of this phenomenon have been encountered.



$^{2}J_{PH_a} = -6$ Hz

$^{2}J_{PH_b} = +25$ Hz

(38)

III. REACTIONS THAT FORM CYCLIC PHOSPHINES

A. Ring Closure at Difunctional Phosphorus

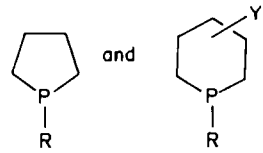
Phosphonous dihalides (RPX_2) are useful building blocks for cyclic phosphines and were used in the first recorded synthesis of such compounds in 1915[1]. The method remains of value[17,45], since numerous phosphonous dihalides are known. These compounds are highly reactive to most nucleophiles, and this property can be used to advantage if the nucleophilic species is a dicarbanion (or carbanion-like). Many cyclic phosphines, with rings from three to seven members, have been prepared by this approach. Selected examples are shown in Scheme 1.

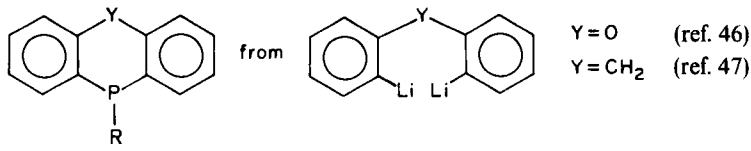
Primary phosphines and derivatives with removable masking groups (such as Me_3Si and CH_2OH), in addition to metallic phosphides, are also widely used in one-step cyclizations. These species are highly nucleophilic and react readily with electrophilic substances such as alkyl halides and acyl derivatives (Scheme 2). So far, the method has found most use in the synthesis of phosphiranes and some benzo-fused systems.

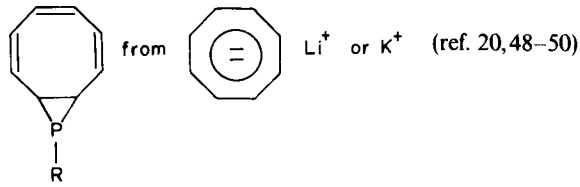
A valuable variant is the use of a dilithio derivative of a bis-secondary phosphine, which leads to rings with two phosphine groups (Scheme 3)[59].

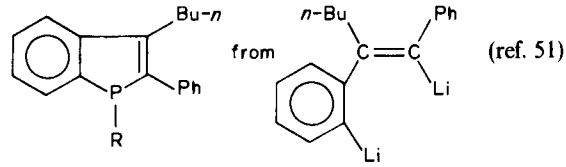
Another variant, which provides access to a cyclic system where there is a double bond to phosphorus, involves the use of tris(trimethylsilyl)phosphine as the source of phosphorus (equation 2)[60].

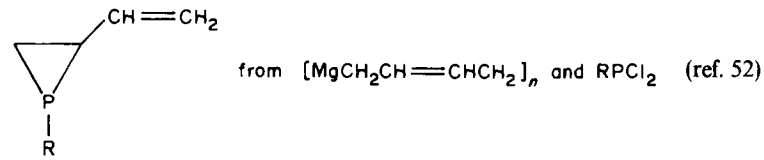
Phosphines and masked derivatives also participate in Michael additions to α,β-unsaturated systems, and this property has been exploited to great advantage to provide entry to keto-phosphines with six-membered rings (phosphorinanones) (Scheme 4). Both


and
Y
P
R
from di-Grignards (refs 1, 45)

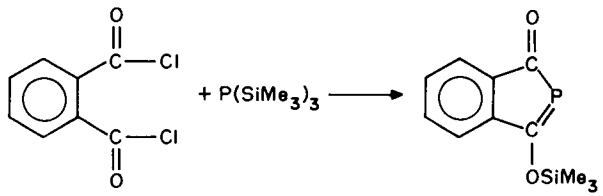

Y
P
R
from
Y
Li Li
Y = O (ref. 46)
Y = CH2 (ref. 47)


P
R
from
Li+ or K+ (ref. 20, 48–50)

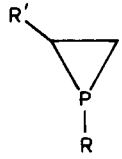

Bu-n
Ph
P
R
from
n-Bu
Ph
C
C
Li
Li
(ref. 51)


CH=CH2
P
R
from [MgCH2CH=CHCH2]n and RPCl2 (ref. 52)

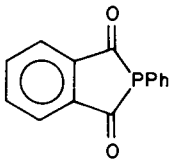
SCHEME 1

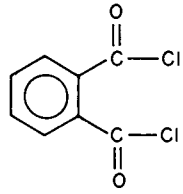

O
C
Cl
C
Cl
O
+ P(SiMe3)3
O
C
P
C
OSiMe3

(2)

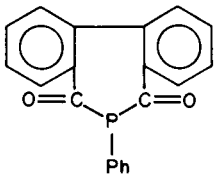


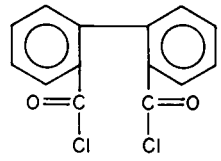
from $ClCH_2CHRCl$ and $NaPH_2$ or NaPHR (refs 14.53, 54)



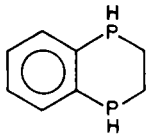
from 

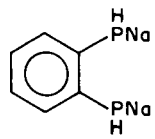
and $PhP(SiMe_3)_2$ (ref. 55) or $PhPH_2$ (ref. 56)



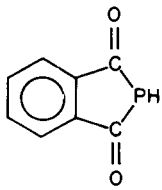
from 

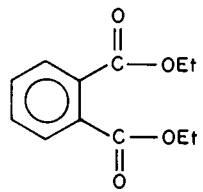
and $PhP(SiMe_3)_2$ (ref. 56)



from 

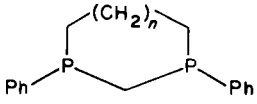
and $Cl(CH_2)_2Cl$ (ref. 57)



from 

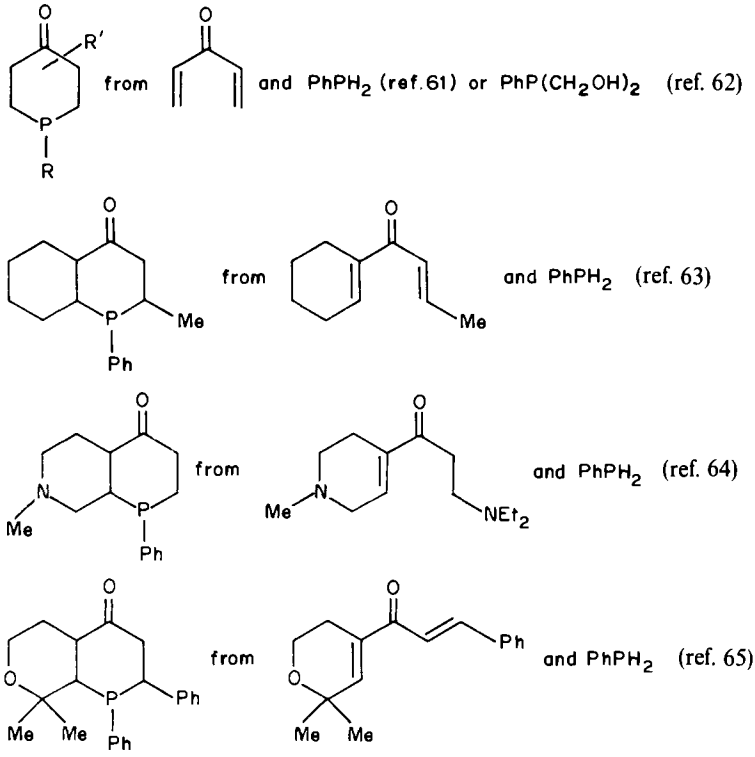
and KPH_2 with 18-crown-6 (ref. 58)

SCHEME 2



from $PhPCH_2PPh$ (Li, Li) and $X(CH_2)_nX$, $n = 2$, 3 or 4

SCHEME 3

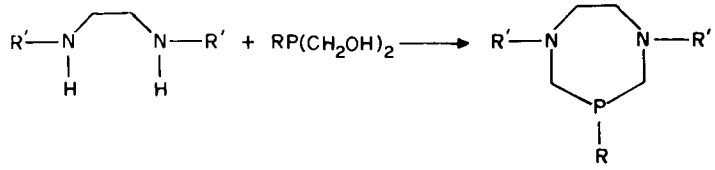


SCHEME 4

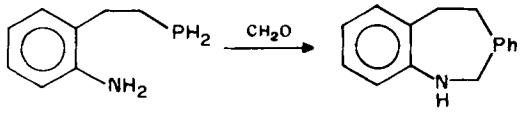
dienones and aminoenones, which can be considered as masked dienones, have been used in this cyclization process.

Acetylenes and olefins (requiring radical-generating conditions, frequently by incorporating aibn in the reaction mixture) also add phosphines, and as the examples in Scheme 5 show, this property has provided some especially interesting phosphines with unsaturation or with other heteroatoms in the ring.

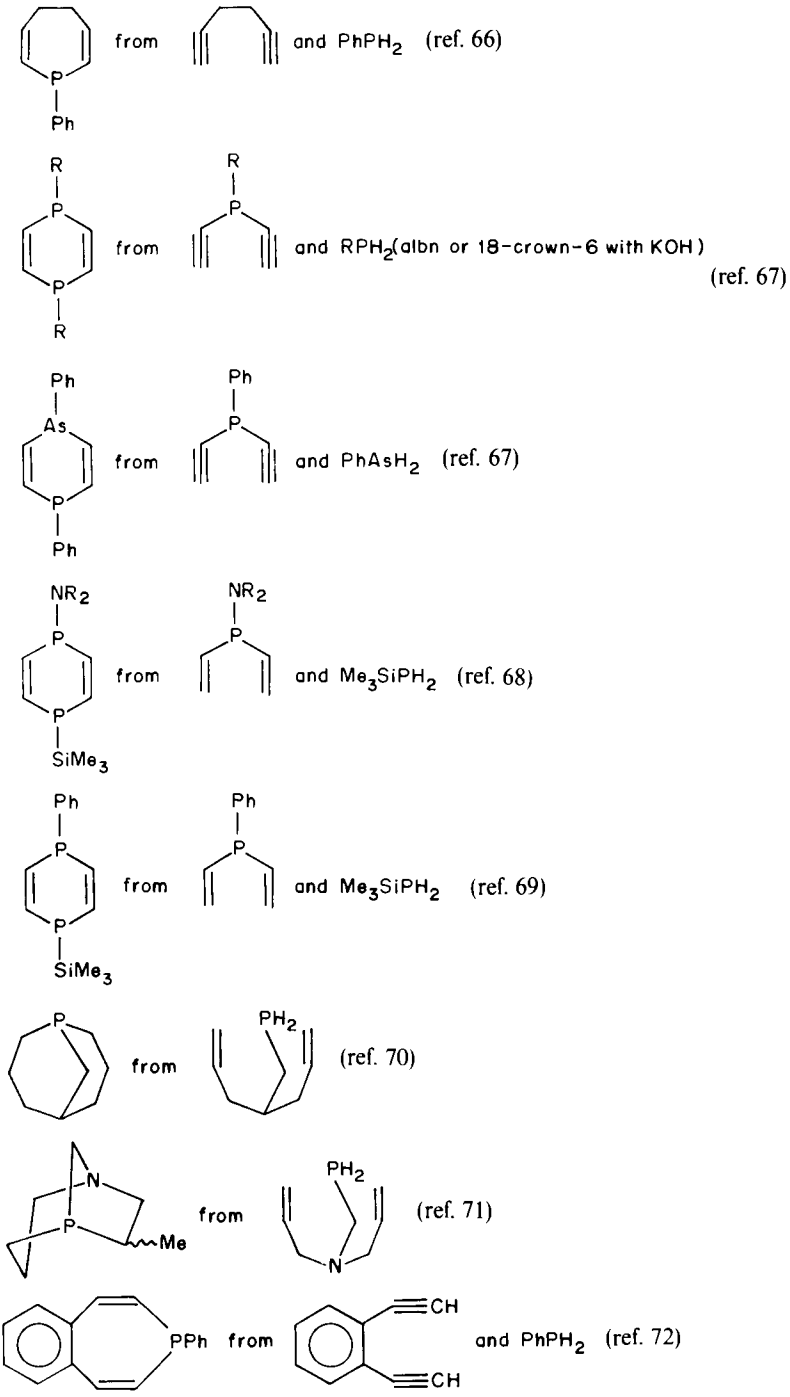
Nitrogen-containing phosphines have been prepared by the reaction of diamines with bis-(hydroxymethyl)phosphines (equation 3)[73] and by cyclization of aminophosphines with various carbonyl compounds (equation 4)[74].



(3)

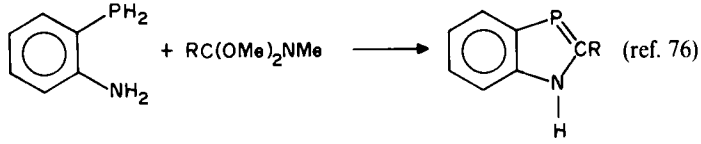


(4)

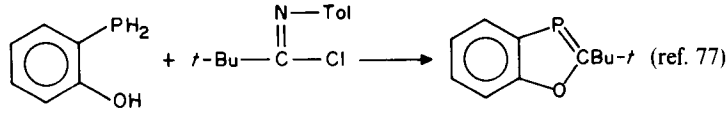

from
and PhPH2 (ref. 66)
Ph
R
from
and RPH2(aibn or 18-crown-6 with KOH)
(ref. 67)
As
from
and PhAsH2 (ref. 67)
NR2
from
and Me3SiPH2 (ref. 68)
SiMe3
from
and Me3SiPH2 (ref. 69)
PH2
from
(ref. 70)
N
Me
from
(ref. 71)
PPh
from
CH
and PhPH2 (ref. 72)

SCHEME 5

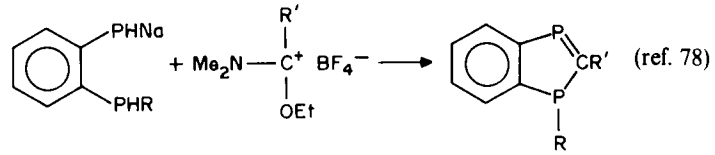
Major advances have recently been made in the synthesis of five-membered heterocyclic systems that contain phosphorus double-bonded to carbon. This work, which has recently been reviewed[75], is of interest in the area of aromatic phosphorus chemistry (see Section IV). The general approach is to employ a phenylphosphine derivative bearing an *ortho* OH, NH_2, SH or PH_2 substituent in a condensation with a carboxylic acid derivative. A rich new aspect of cyclic phosphine chemistry is developing from these methods and compounds, and some selected examples are shown in equations 5–7.



(ref. 76) (5)



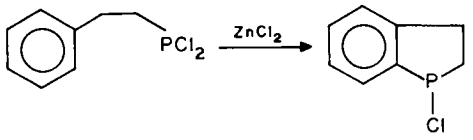
(ref. 77) (6)



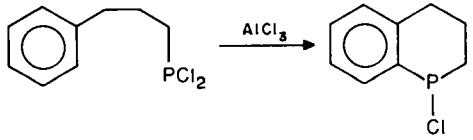
(ref. 78) (7)

B. Ring Closure by Intramolecular Reactions at Phosphorus Functions

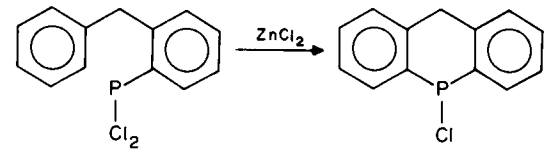
Phosphorus halides of both the type RPX_2 and the less familiar R_2PX (phosphinous halides), and also secondary phosphines, that also contain olefinic or aromatic unsaturation in accessible locations can be caused to undergo intramolecular cyclization. The cyclization into aromatic rings requires conventional Friedel–Crafts catalysts such as $AlCl_3$ or $ZnCl_2$ (equations 8–10).



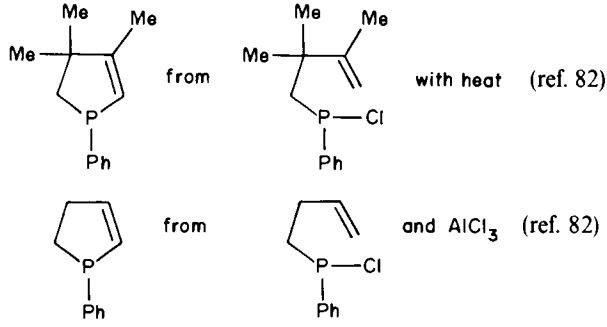
(ref. 79) (8)



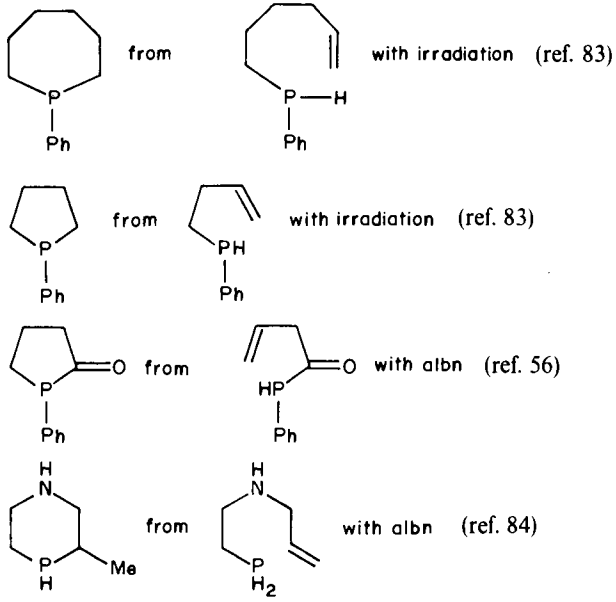
(ref. 80) (9)



(ref. 81) (10)



SCHEME 6



SCHEME 7

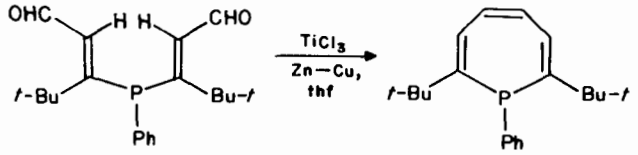
Lewis acids also may be used in cyclizations with olefinic groups (Scheme 6), although thermal or radical conditions also may be effective.

Phosphine additions to double bonds are conducted under radical conditions (Scheme 7).

C. Ring Closure by Intramolecular Condensations Remote from Phosphorus

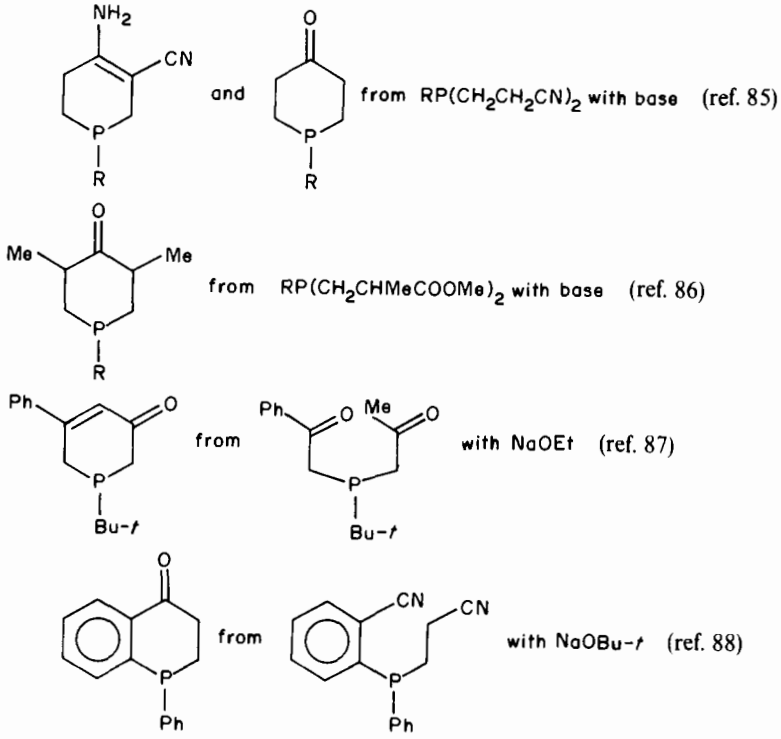
Such condensations as the Thorpe, Dieckmann and aldol types, which have been so valuable in cyclic compound syntheses of many sorts, also have been effective in generating cyclic phosphines, usually those with six ring members (Scheme 8). A valuable feature of these processes is that they provide phosphines with functionality at one or more ring carbons that can be exploited in the development of more complicated structures.

The recently introduced McMurry reaction has also been applied to the synthesis of the particularly fragile phosphepine system[89]. By placing *tert* butyl groups on the ring, kinetic stabilization is provided to the ring system, preventing intermolecular reactions (equation 11).

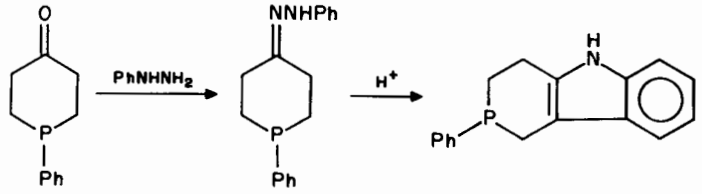


(11)

Some syntheses of multicyclic phosphines also containing nitrogen are based on further ring closures of the 4-phosphorinanones resulting from methods described above (equations 12–17).

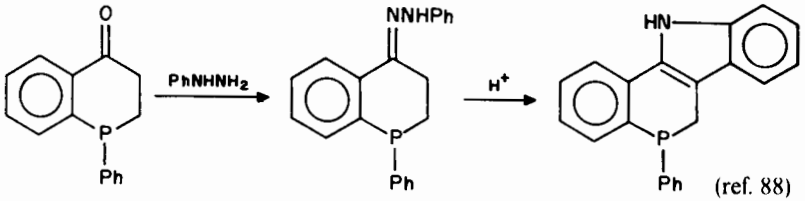


SCHEME 8



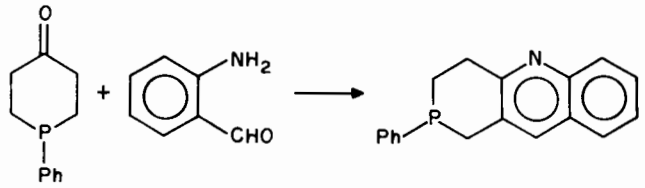
(12)

(ref. 90)



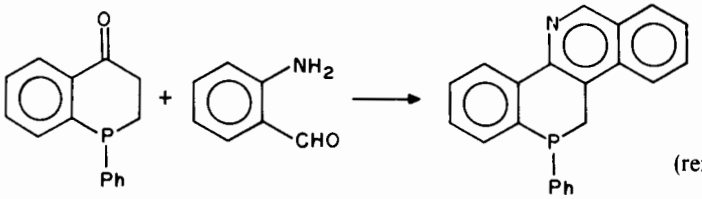
(13)

(ref. 88)



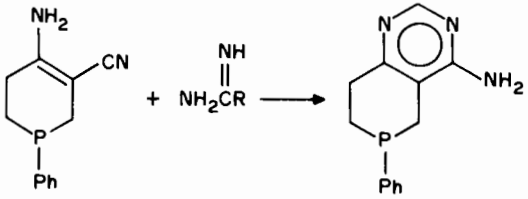
(14)

(ref. 90)



(15)

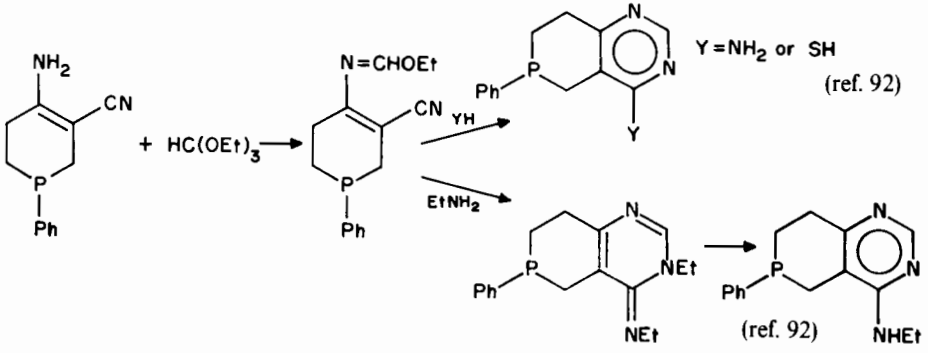
(ref. 88)



R = NH_2 or H

(16)

(ref. 91)



Y = NH_2 or SH

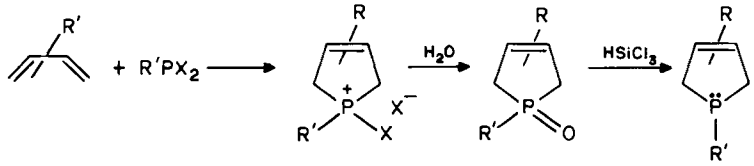
(ref. 92)

(ref. 92)

(17)

D. Conversion of Cyclic Phosphorus Compounds with Various *P*-Functions to Phosphines

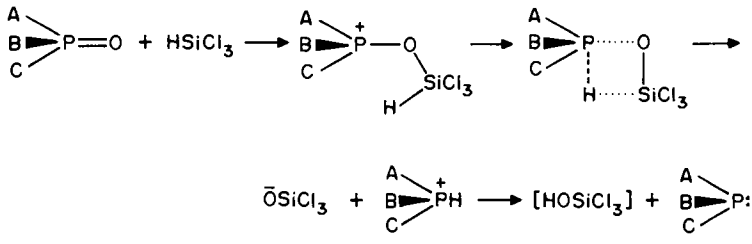
In Sections III.A–C, the presentation has centered exclusively on processes that result immediately in cyclic phosphines. Many cases are known, however, where cyclizations have been carried out on compounds with phosphorus in a higher coordination or oxidation state, or with displaceable P substituents present, and these products are then converted to phosphines. The importance of this approach is considerable, since valuable methods do exist for the generation of phosphines from other *P*-functions. There are, in fact, many cyclic phosphorus compounds (especially tertiary phosphine oxides) known in the literature that are awaiting conversion to phosphines. Indeed, in a sense, one could consider phosphine oxides as pro-phosphines, since it is rare (but documented, see below) for a phosphine oxide *not* to be convertible to the corresponding phosphine when this is desired. It is frequently more expeditious to design a phosphine oxide synthesis and then deoxygenate to the phosphine than to approach the phosphine directly. A case in point is the synthesis of the 3-phospholene system; there is no versatile way to construct this system with phosphorus in the phosphine state, but the ring is easily constructed by the McCormack reaction[93], giving oxides that are then reducible to the phosphines (equation 18).



(18)

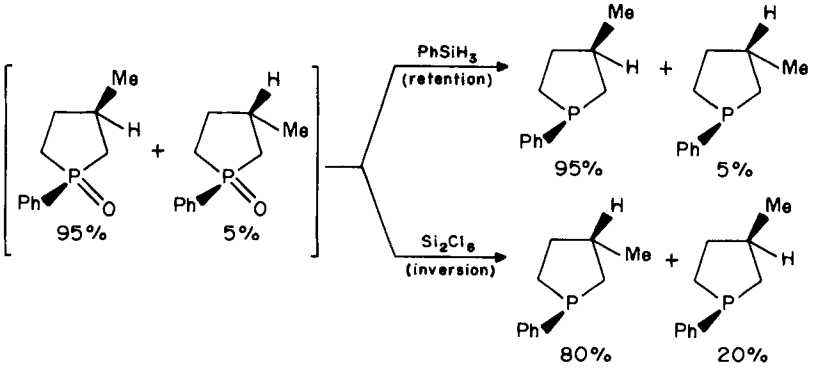
By far the most important process for the reduction of phosphoryl compounds of various types (but especially phosphine oxides) rests on the action of silicon hydrides[94]. This technique was introduced in 1964, and was immediately recognized as a major advance in synthetic methodology in organophosphorus chemistry. Prior to that time, and to the present, the otherwise highly versatile lithium aluminum hydride and related agents had only rarely given satisfactory results when used with phosphine oxides. Some exceptional cases do exist, however, as in a recent synthesis of a 2-phosphaadamantane by removal of oxygen from the corresponding oxide[95]. The most widely used silicon hydrides are trichlorosilane (a cheap, commercially available reagent), phenylsilane and diphenylsilane.

In most silane reductions, a four-center mechanism may be involved and with rare exceptions leads to phosphines having the same configuration at phosphorus as in the oxides (equation 19). This is of great importance in cyclic phosphine chemistry, where diastereoisomerism is frequently present and serious uncertainties or product mixtures could result from a non-specific reduction.



(19)

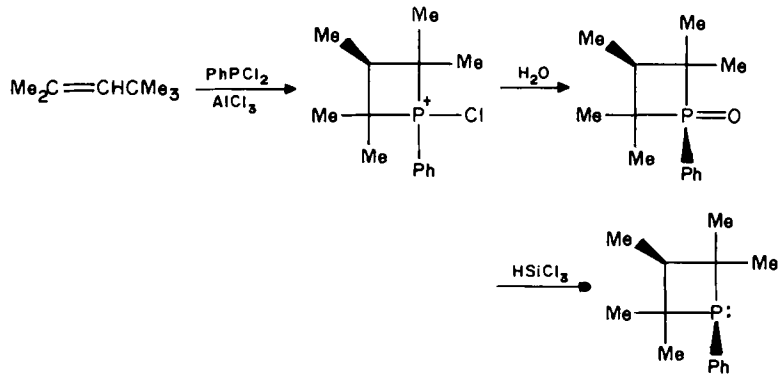
When racemization is encountered in phosphine oxide reductions with $HSiCl_3$ (and probably others), it can be attributed to isomerization (pseudorotation or turnstile rotation) of a pentacovalent adduct with trigonal bipyramidal geometry before its collapse. This adduct seems not to be formd, or to be rapidly deprotonated, when the complex of $HSiCl_3$ with weakly basic amines, notably pyridine, is used rather than $HSiCl_3$ alone. This matter has been discussed at length elsewhere in connection with the deoxygenation of bridged phosphine oxides[18]. A change in stereochemistry (to inversion) can sometimes be effected when a stronger amine (especially triethylamine) is present[96], and inversion generally occurs when the reducing agent is Si_2Cl_6, which may in fact be involved in the $HSiCl_3$–Et_3N reaction[97]. Knowledge of the reducing system selected can be of vital importance when diastereoisomeric phosphines can exist, and can be exploited to prepare specimens of isomers of known structure, as in the example in equation 20[98].



(20)

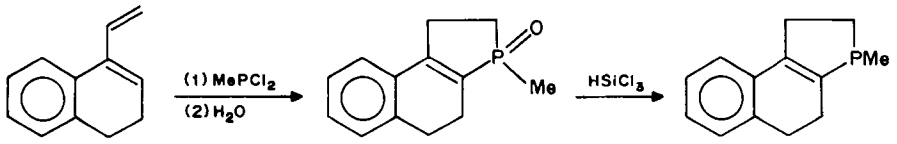
As noted above, the concept of phosphine synthesis following construction of rings where phosphorus is in the oxide state is of very broad utility, and has led to many compounds not accessible by any known direct cyclic phosphine synthesis. Since phosphine oxides frequently can be synthesized by applications of common organic chemical methods, the matter of phosphine synthesis then becomes less specialized, except that proper techniques to avoid accidental air oxidation back to the oxide are generally required. Some selected examples of such phosphine oxide syntheses, and conditions for their deoxygenation, are given in equations 21–28.

1. Phosphetanes[99].



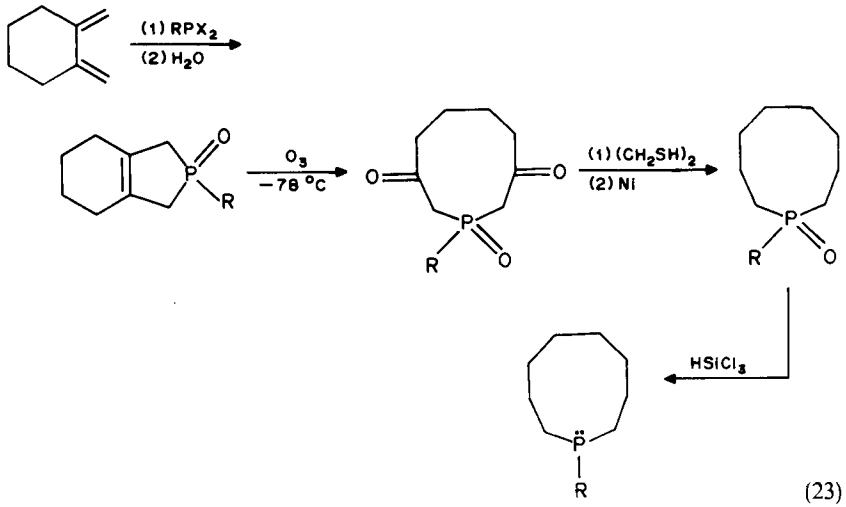
(21)

2. Phospholene oxides; many examples are known using the basic McCormack process outlined in Section II.D. An application resulting in a multicyclic phosphine is selected[100].



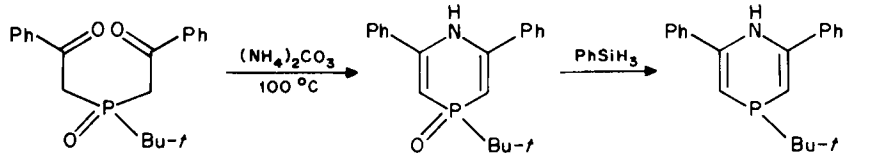
(22)

3. Large-ring phosphines[101].



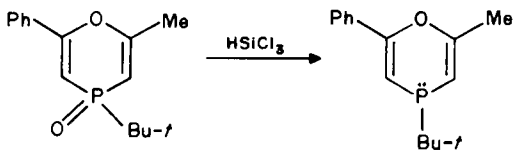
(23)

4. 1,4-Azaphosphorinanes[102].



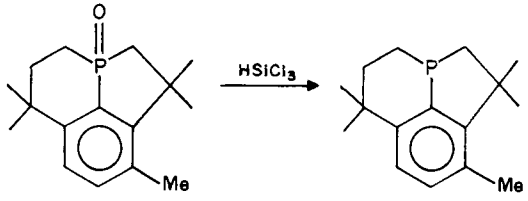
(24)

5. 1,4-Oxaphosphorinanes[103].



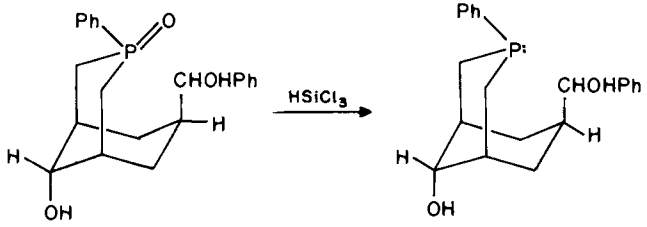
(25)

6. Phosphajulolidine derivatives[9,104].



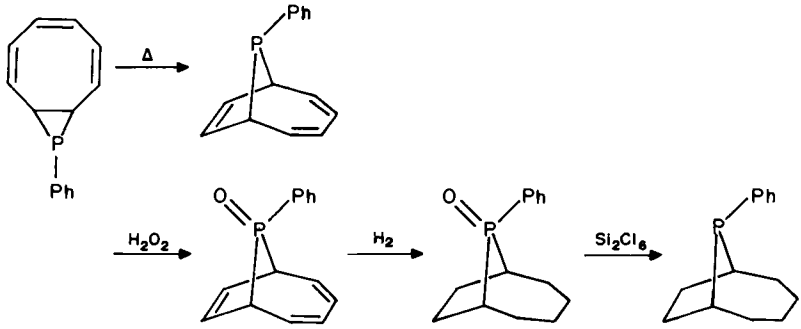
(26)

7. A phosphaadamantane precursor[105].



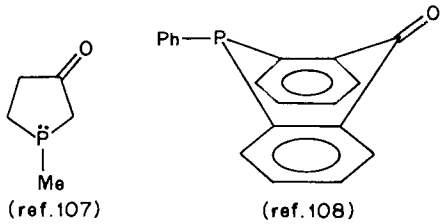
(27)

8. A bridged phosphine[106].



(28)

The silane reducing agents may also be applied to phosphine oxides where *C*-functional groups are present. Keto groups have been found to survive the usual conditions of silane reductions, allowing phosphines such as those shown below to be prepared, whereas with α,β-unsaturated ketones, reduction did take place at the carbonyl group (equation 29)[109].

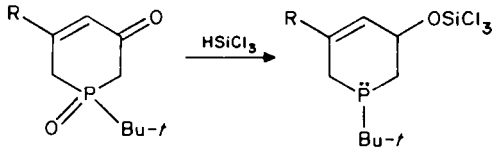


(ref.107) (ref.108)

Alcoholic groups are converted to silyl esters with trichlorosilane, but may be easily regenerated by hydrolysis (equation 30)[107]. Carboxylate functions survive with no difficulty (equation 31)[110].

Silance reductions are not without difficulties, however. It has been reported[111] that the oxide **39** failed to undergo reduction with silanes, whereas an enamine phosphine (**40**) was simultaneously reduced at the carbon—carbon double bond (equation 32)[112].

More serious problems have arisen when the basic reduction procedure is applied to some multicyclic or bridged structures, as summarized in equations 33 and 34.



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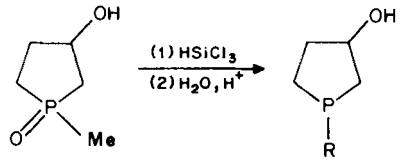

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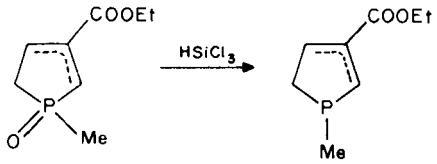

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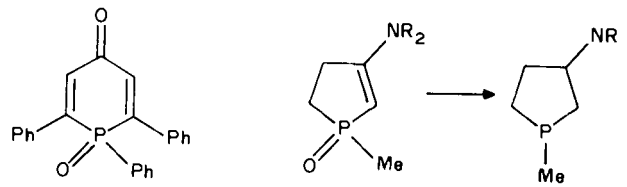
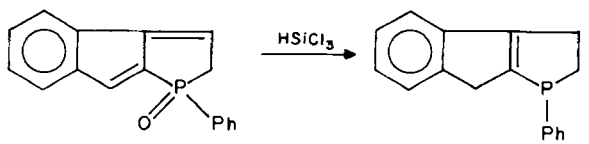
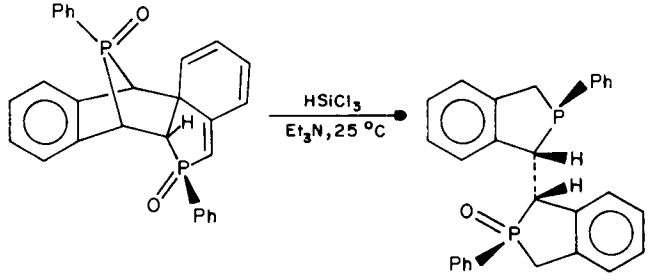


(32)



(33)

(ref. 114)



(34)

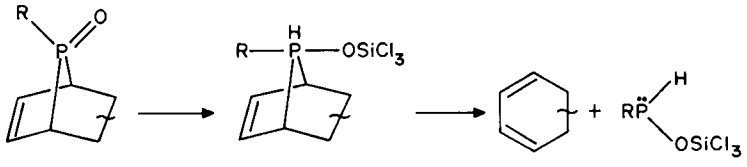
(ref. 115)

Oxides in the 7-phosphanorbornene series can undergo loss of the P-bridge with trichlorosilane[18,113]. The complication in the latter reaction appears to occur because a pentacovalent intermediate is developed at the 7-phosphanorbornene moiety, which then undergoes fragmentation by an apparent retro-cycloaddition (equation 35). This complication can be avoided by use of the $HSiCl_3$-pyridine complex[18], and the valuable phosphines retaining the bridged framework can be readily prepared.

Other phosphoryl functions are also sensitive to the silane reducing agents (equations 36 and 37), and generally undergo replacement of a P substituent by hydrogen in addition to the deoxygenation[116]. The process has been of relatively little importance for the generation of cyclic secondary phosphines, but could find value if interest in such phosphines develops in the future.

Secondary phosphines can also be prepared by lithium aluminum hydride reduction of *P*-chlorides (equations 38 and 39).

A different reduction technique recently introduced makes use of organometallic compounds as the reducing agent for phosphine sulfides. In this procedure (equation 40), the phosphine sulfide is reacted with $[NiCp_2]$ (nickelocene) and allyl iodide to give a nickel complex [NiCpL(I)] of the corresponding phosphine; this is decomplexed with trimethyl phosphite[121], cyanide ion[121] or *N*-methylimidazole[122]. The conditions are mild for both steps, and optically active phosphine sulfides are reduced with complete retention by this method. A phospholene has been produced in 90% yield by this procedure[121].



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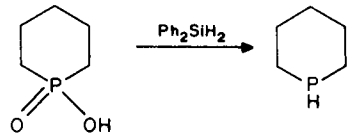
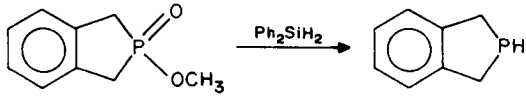
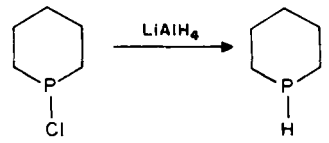


(ref. 117) (36)



(ref. 118) (37)



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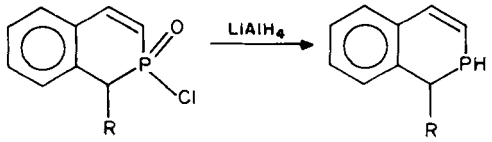

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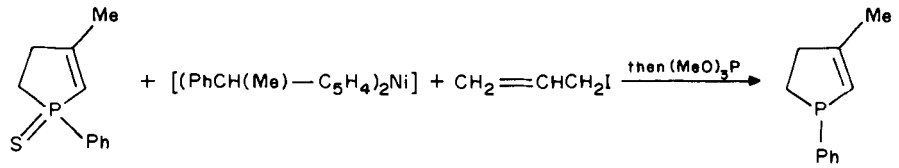
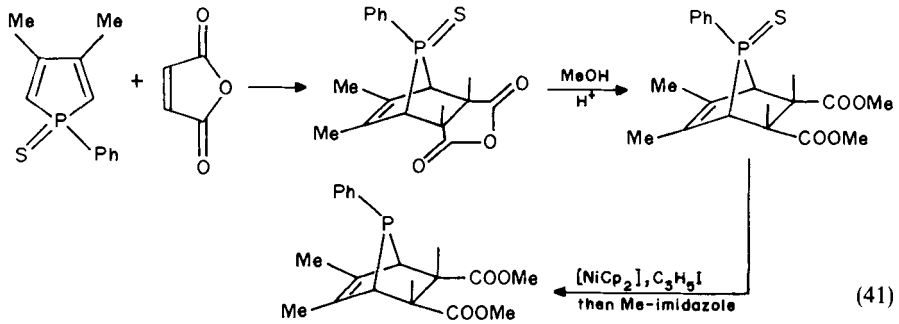


(40)

The metallic compound was optically active but did not induce optical activity in the phosphine product. An important application was in the production of a 7-phosphanorbornene (equation 41).

The complex $MgCp_2TiCl_2$ in boiling thf also reduces phosphine oxides[123].

Phosphonium salts have also been end-products of syntheses just as phosphine oxides have, and techniques exist for the removal of either *P*-ethyl or *P*-phenyl groups that then lead to the tertiary phosphines. Ethyl is removed by thermal treatment as ethylene, whereas phenyl has been cleaved from salts with lithium aluminum hydride or sodium (equations 42–44).



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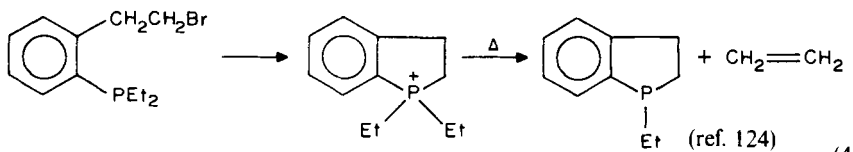

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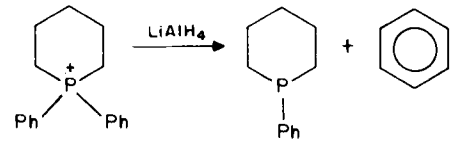
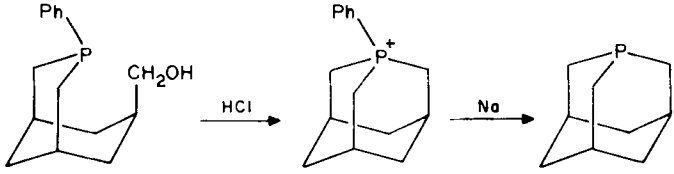


(ref. 125) (43)

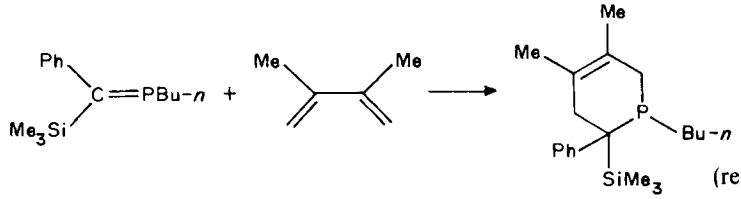


(44)
(ref. 126)

E. Cycloadditions and Other Reactions with C—P Multiple Bonds

A major recent advance in organophosphorus chemistry is the recognition that multiple bonds to phosphorus can be a reality. Normally, compounds with such bonds are not stable unless the bonding site is sterically protected from polymerization by attachment of very large groups, or they are thermodynamically stabilized by electronic (usually delocalization) effects. It is becoming increasingly evident that the phosphaalkenes ($RP{=}CR_2$) and phosphaalkynes ($P{\equiv}CR$), even when lacking stabilization effects and generated as transient species, can be useful as participants in cycloaddition reactions, and thus serve as precursors to cyclic phosphines. Action as a dienophile in Diels–Alder processes, and as a dipolarophile to 1,3-dipoles, are now well documented. These and other reactions are providing some valuable new structures, and are making an important addition to the methods of forming phosphorus heterocycles.

Some examples of phosphaalkenes that undergo cycloadditions with dienes are $ClP{=}CPh(tms)$[127], $ClP{=}C(tms)_2$[128,129], $ClP{=}C(tms)\ COOR$[130], $Ph(tms)C{=}POR$[131], n-$BuP{=}CPh(tms)$[132], $PhP{=}CHNMe_2$[133], $RC{\equiv}CP{=}CR^1(tms)$[134], $CF_3P{=}CF_2$[135,136], $CF_3P{=}CHF$[137] and $C_2F_5P{=}CF(CF_3)$[138]. With simple dienes, dihydrophosphinines are produced (equation 45).

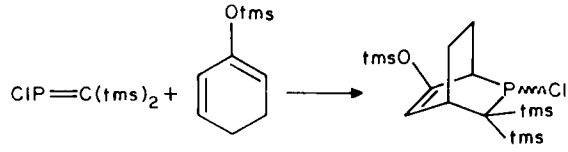


(45)
(ref. 132)

When cyclic dienes are used, bridged cyclic phosphines can be formed, and this represents a very valuable approach to such compounds (equations 46–48).

The adducts from the *P*-chloro dienophiles still possess a P—Cl bond, and can be viewed as immediate precursors of tertiary phosphines through the application of organometallic reagents to displace the chlorine. The *P*-chlorotetrahydrophosphinines are also valuable precursors of λ^3-phosphinines, especially those with functional groups (see Section V).

The phosphaethenes $MeP{=}CH_2$ and $PhP{=}CH_2$, which lack any stabilizing effects, have recently been generated as transient intermediates by thermal fragmentation of



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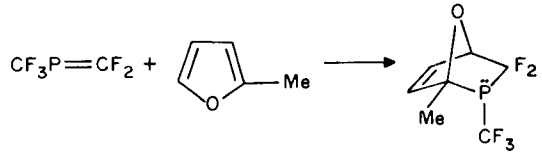

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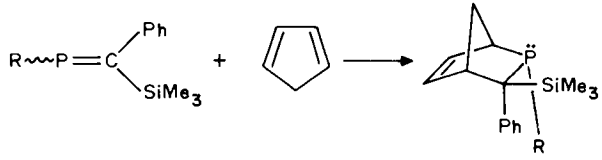
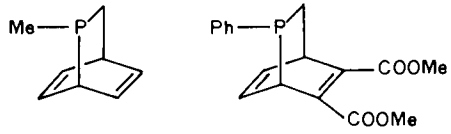
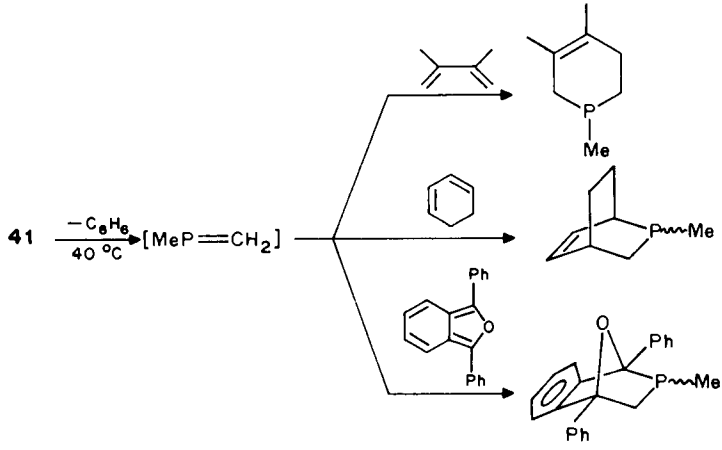


(ref. 139) (48)



(41) (42)



(49)

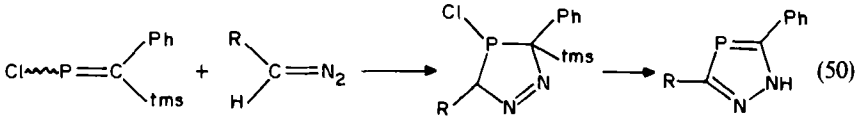
phosphines in the 2-phosphabicyclo[2.2.2]octa-5,7-diene system[32]. They are formed at temperatures below 40 °C from phosphines **41** and **42**, respectively. The processes are clean, and when dienes are included in the reaction medium, these transient species are trapped very effectively. Some products formed and isolated from $MeP{=}CH_2$ reactions are shown in equation 49.

Examples of 1,3-dipolar cycloadditions with phosphaalkenes are illustrated below. Frequently, the initial cycloadduct is not stable under the reaction conditions; elimination reactions are common and indeed of great value in that they generate cyclic phosphines with C—P double bonds, as in the reaction with diazoalkanes (equation 50)[140].

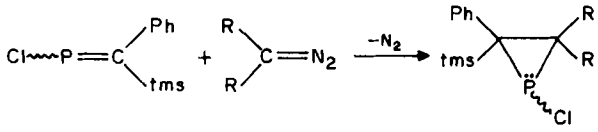
Valuable 1-chlorophosphiranes also may be generated in the reaction with diazo compounds, provided that the C atom bears two substituents so that the elimination reaction to form the 1,2,4-diazaphosphole ring is blocked (equation 51)[141]. *P*-Alkylphosphaethenes also give phosphiranes (equation 52).

Cyclic 1,3-dipoles such as munchnones[142] and dithiolate[36] also react with the phosphaalkenes, forming intermediates (e.g. **43**) that undergo secondary eliminations (equations 53 and 54).

Conjugatively unsaturated phosphaalkenes can act as dienes toward alkynes in cycloaddition reactions. The multiple bond system in the λ^3-phosphinines behaves in



(50)



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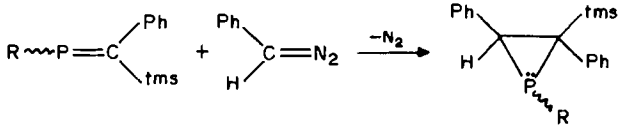
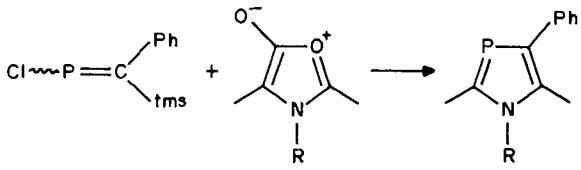


(52)



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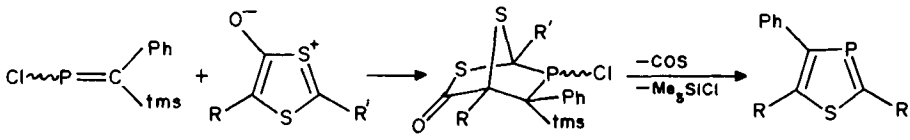
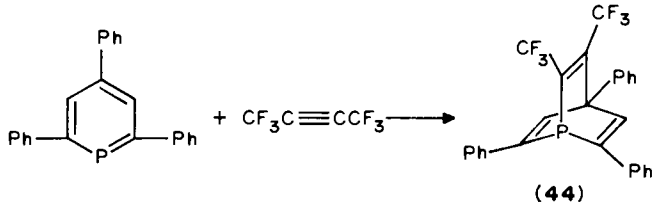


(43)

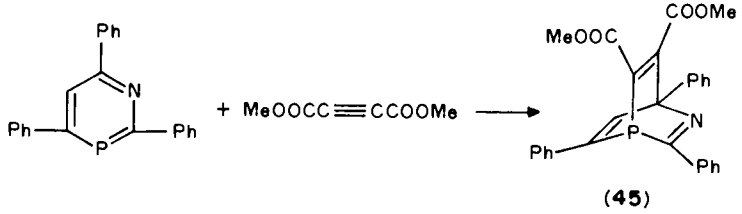
(54)

this fashion, and this has been exploited to prepare phosphabarrelenes (equation 55)[143]. 1,3-Azaphosphinines behave similarly and provide azaphosphabarrelenes (**45**)[144], which decompose under the reaction conditions to form λ^3-phosphinines (equation 56).

A recently reported reaction of λ^3-phosphinines with diazomethane has been found to follow an unexpected and intricate pathway, resulting in the entirely new cyclic phosphine framework **29**, mentioned before, that has been given the name 'chiropteradiene'[35]. This unusual framework has been confirmed by X-ray crystallographic analysis. Some other examples of reactions with phosphinines are given in Section V.



(44) (55)



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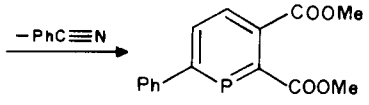

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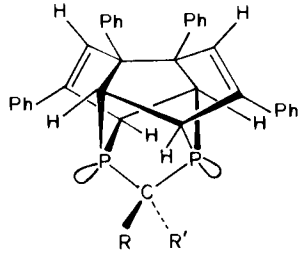
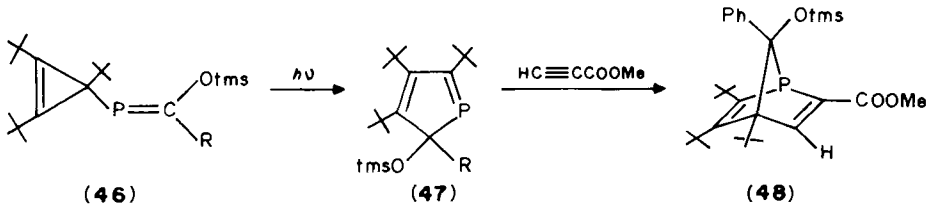


(29)

Other reactions of C—P double bonds are proving to be of synthetic value. The construction[37] of a kinetically stabilized[145] 2*H*-phosphole derivative (**47**) is made possible by a rearrangement of a (cyclopropenyl)phosphaalkene (equation 57) (**46**). This rare type of phosphole is itself of interest as a precursor of a novel bridged phosphine system (**48**) from a Diels–Alder reaction. The P—C double bond of the 2*H*-phosphole **47** acts as a dipolarophilic center towards a nitrile oxide, giving a new bicyclic phosphine **49**.



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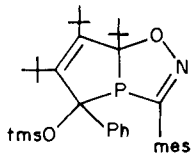
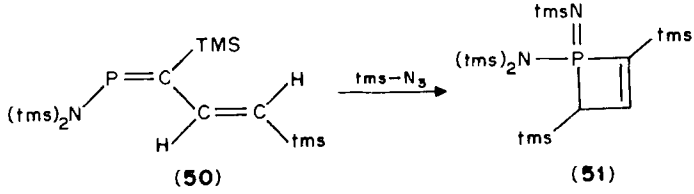


(49)

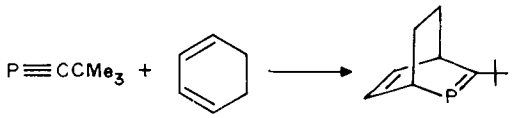
The 1-phosphadiene system may prove of value also in the synthesis of cyclic phosphines. An example of the construction of the phosphetene ring system in an oxidative process from the 1-phosphadiene **50** (equation 58) has been reported[146], and although the product **51** is strictly not a phosphine, it or related structures could well function as precursors of this rare ring system.

Valuable new synthetic approaches to cyclic phosphines are emerging from the expanding studies of the recently developed family of triply bonded phosphorus derivatives. This is an exciting new area, and more examples of rare cyclic phosphine synthesis can be anticipated. Some recently reported reactions, all giving new types of ring systems, are shown in equations 59–61.

The Diels–Alder reaction with phosphaalkynes[3,147], shown here with cyclic dienes, may not be as straightforward with non-cyclic dienes; such dienes may give cyclic adducts as intermediates, but the final product has a P—P bond in a bridged framework[149].



(58)



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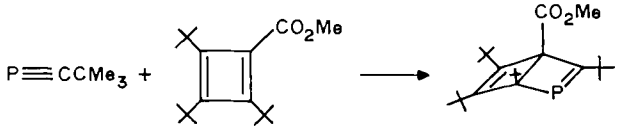

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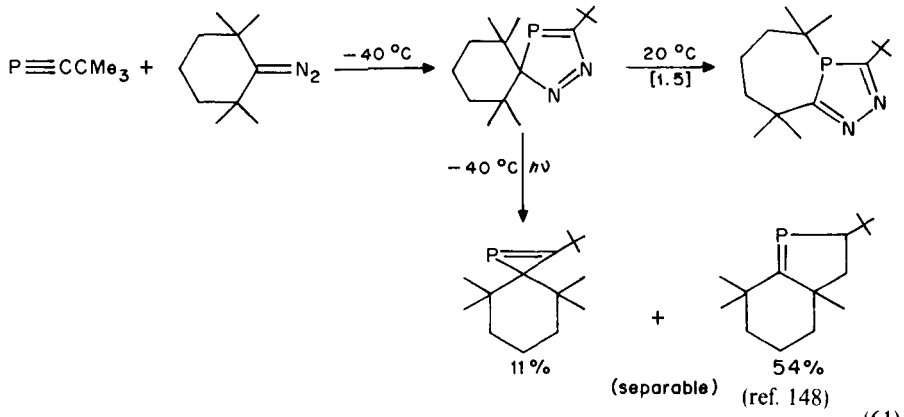
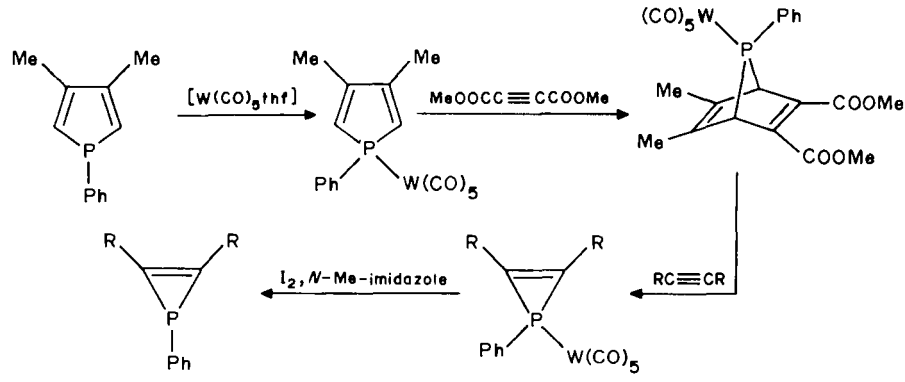


(61)

F. Cyclic Phosphine Syntheses in the Coordination Sphere of Transition Metal Complexes

A new concept in phosphine chemistry that is proving to be highly valuable for the synthesis of some rare species is to conduct transformations on phosphines while coordinated to metallic atoms. The new species produced remains coordinated to the metal and derives stabilization therefrom. The products can generally be de-complexed to allow isolation of the free phosphine. An excellent example is provided by the first synthesis of phosphirenes (equation 62)[5,150]. Here a 7-phosphanorbornadiene is created in a complex form (a process also made possible by an initial modification of the chemistry of phospholes, allowing a facile Diels–Alder reaction to occur) and used as a precursor of a terminal phosphinidene complex, which then acts to transfer the phosphinidene moiety to an alkyne substrate. The free phosphine is then liberated by breaking the complex through addition of iodine and then *N*-methylimidazole[6]. The phosphirenes proved to be remarkably stable; their chemistry is discussed in a recent review[151]. No other synthetic method has yet been employed to created the phosphorus(III) phosphirenes, which illustrates the power of this new approach.

When an alkene replaces the alkyne in this process, a phosphirane in complexed form is



(62)

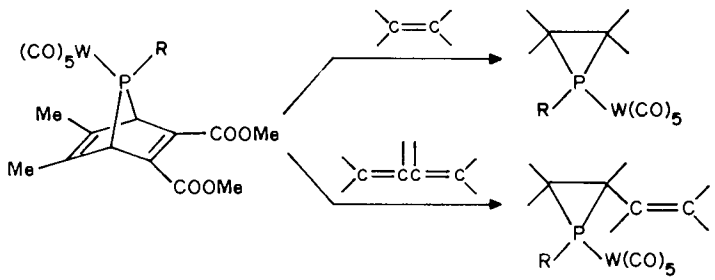
created (equation 63). This is a valuable new method for forming this ring system[152,153], first synthesized in 1967[53]. Especially valuable is the reaction with dienes; this results in the synthesis of the vinylphosphirane structure.

A phosphirane is also formed in the reaction of the complex with diphenylthiirane; with an oxirane, a 1,3,2-dioxaphospholane was formd as a byproduct with the phosphirane[154]. A recent innovation in phosphirane synthesis by the metallic complex approach is to employ a non-cyclic aminophosphine complex as the source of an aminophosphinidene for transfer to an alkyne[155]. This has provided the first examples of 1-aminophosphirenes (equation 64).

The complexed phosphirenes, after generation as above[5,150], are themselves valuable as precursors of another novel family of phosphorus heterocycles, the 2-keto-1,2-dihydrophosphetes[156]. This is accomplished by an insertion reaction of CO into a C—P bond (equation 65). These new ring compounds have not yet been isolated as the free phosphines, however.

Insertion of a monosubstituted alkyne into a C—P bond of a complexed phosphirane has been found to occur in the presence of $[Pd(PPh_3)_4]$, giving complexed phospholes with new *C*-substitution patterns[157].

Phosphole complexes have proved of value in other regards. When a mixture of 3,4-dimethyl-1-phenylphosphole and a metal carbonyl is irradiated, a dimeric form (**53**) of the phosphole is created, with complexation of both phosphine sites to a single metal atom (equation 66)[158]. The unique feature of this dimeric product is that the ring fusion is the opposite of that formed when the dimeric structure is created from other phosphole derivatives, such as oxides, sulfides and salts. The fusion in the $W(CO)_5$ complex is *exo* rather than the conventional *endo*, and this is thought to occur from the effect of the metal in holding two phosphine centers in close proximity, or in another description



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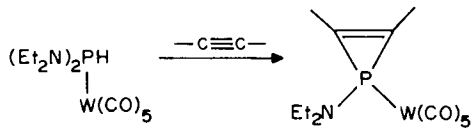

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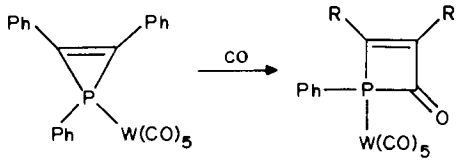
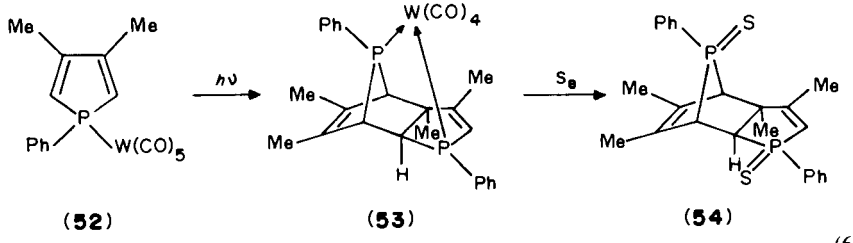


(65)

acting as a template. Decomplexation with sulfur then provided the first example (**54**) of a phosphole dimer derivative with the *exo* fusion (equation 66).

When the simple complex **52** of 3,4-dimethyl-1-phenylphosphole bearing $W(CO)_5$ or $Cr(CO)_5$ was exposed to solar radiation, a remarkable bridged phosphine (**55**) was created[159]. The structure was solved by X-ray crystallographic analysis. The free phosphine remains to be released from the complex.

Metal complexes of λ^3-phosphinines also are proving of value in the synthesis of novel phosphines. Some examples are shown in equation 67[160]. These products remain in the complexed form. Some related reactions were performed in another laboratory[161], and here the free phosphines were liberated by a process involving CO and triphenylphosphine (equation 68).



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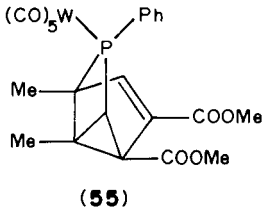
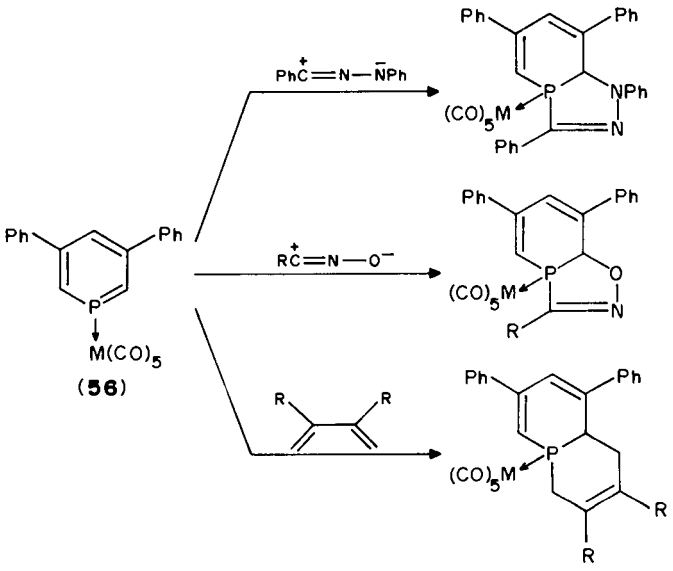
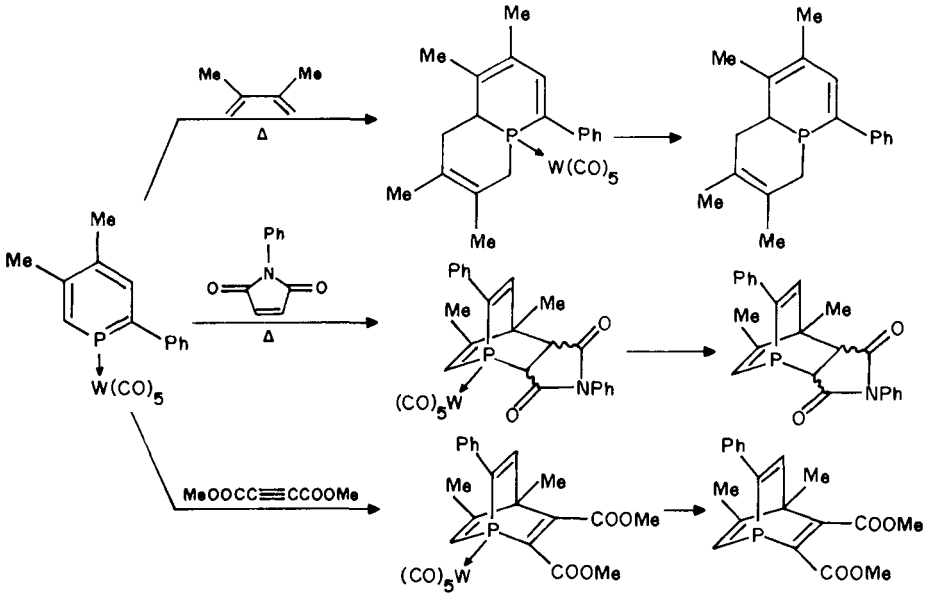
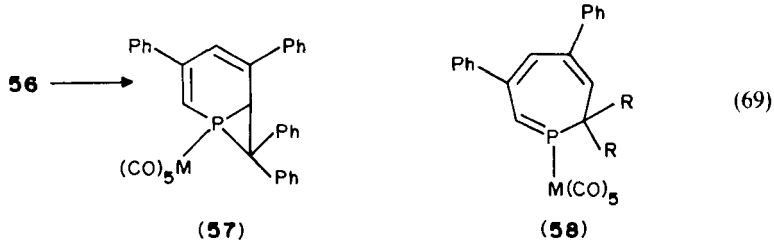






(68)

The phosphine complex **56** also undergoes an important reaction with diphenyldiazomethane, which results in the formation of a phosphanorcaradiene complex (**57**)[162]. This type of structure appears to be formed also with dialkyldiazomethanes, but an equilibrium is established with an undetectable amount of the 2*H*-phosphepine derivative **58**, as suggested by other reactions of the product. The non-complexed phosphine corresponding to **57** is formed when the parent phosphine is reacted with diphenyldiazomethane[35].

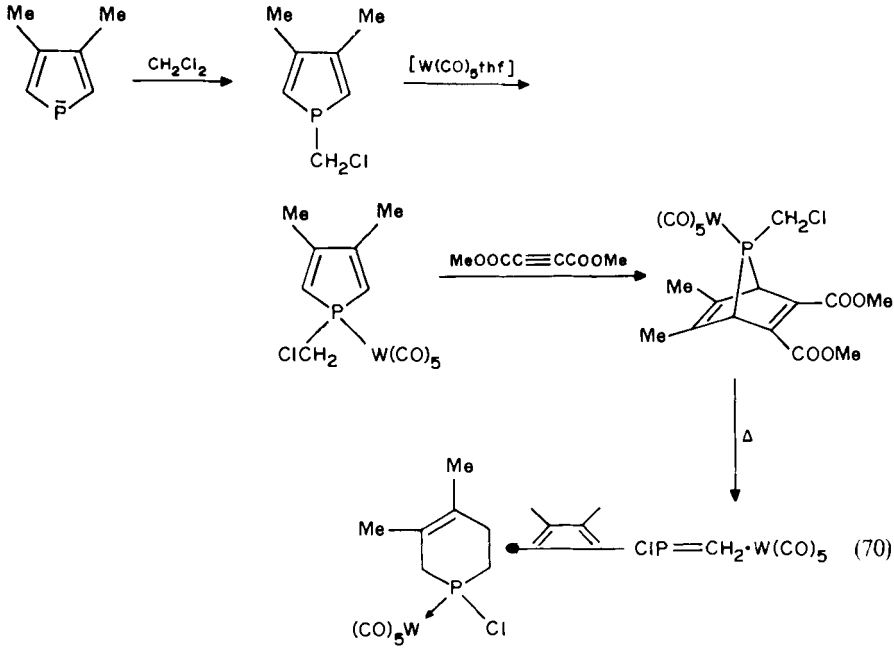


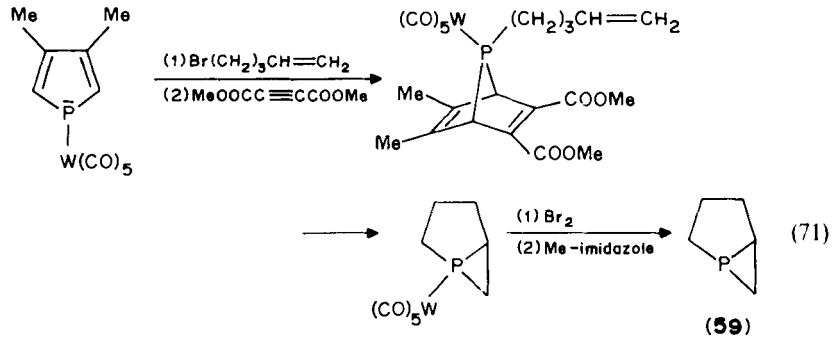
(69)

(**57**) (**58**)

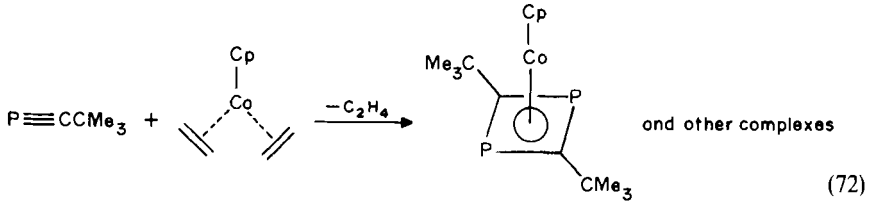
A source of the phosphinidene complex $[(ClP{=}CH_2){\cdot}W(CO)_5]$ involving an apparent rearrangement of $[ClCH_2P{=}W(CO)_5]$ has been developed from a 7-phosphanorbornadiene derivative[163]; reaction with dienes then leads to a [4 + 2] cycloadduct (equation 70).

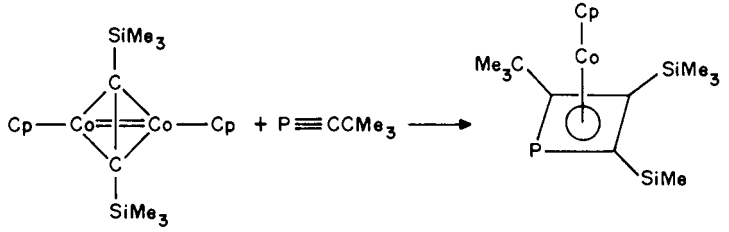
The phosphinidene complex $[Ph(EtO)C{=}P(Ph)W(CO)_5]$ also gave a tetrahydrophosphinine from the [4 + 2] reaction[164]. In another related process[165], the phospholyl anion is complexed with $W(CO)_5$ and then alkylated with an alkenyl halide. The complex is then reacted with an alkyne to give a norbornadiene complex, which at 110 °C is quantitatively converted to a new type of fused phosphirane (**59**) by an intramolecular phosphinidene insertion (equation 71).





A cobalt complex has found use in the dimerization of phosphaalkynes, thereby producing the first diphosphacyclobutadiene derivatives (equation 72)[166]. The phosphine has not yet been produced in free form. A phosphacyclobutadiene also in complexed form has been obtained with the aid of the complex **60** (equation 73)[167].

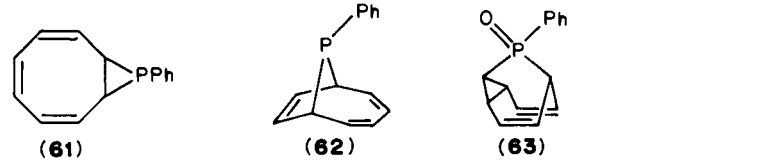




(60) (73)

G. Thermal and Photochemical Reorganizations of Phosphines

Reorganization of the carbon skeleton of phosphines has been accomplished in several instances, and generally leads to unusual compounds not attainable by the general methods described already in this section. Bridged or cage structures have resulted from such reorganizations, an excellent example being provided by reactions based on the availability of bicyclic phosphirane **61**. As noted previously, this compound is formed readily by reacting the dianion of cyclooctatetraene with phenylphosphonous dichloride[20]. Thermal treatment produces the bridged phosphine **62**[20], and UV irradiation[168] leads to the tricyclic phosphine **63**. The oxide of **62** can be converted by irradiation to **64** or to **65**, as determined by the photochemical conditions[168]; oxide **65a** can also be formed by irradiation of **64**. Treatment of **65a** with silver fluoroborate causes rearrangement to **66**, which was reduced with Si_2Cl_6 to the phosphine **67**. Oxide **65a** was also reduced to the phosphine **65b**[169].



(61) (62) (63) (64) (65) (66) (67)

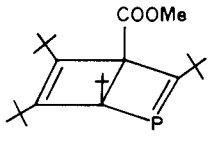
(a) X = O

(b) X = lone pair

Remarkable transformations have been observed among valence isomers of phosphinines[170]. For example, the Dewar-phosphinine **68**, formed from cycloaddition of a phosphaalkyne with a cyclobutadiene, gives on irradiation an isolatable prismane structure (**69**); on continued irradiation, a benzvalene analogue (**70**) is formed. Other transformations of a similar nature have also been discovered.

A benzvalene framework with two phosphorus atoms has been created from a 1,4-diphosphinine on irradiation (equation 74)[171].

A novel cage structure (**72**) was formed when the 1,4-diphosphine derivative **71** was irradiated (equation 75)[172].



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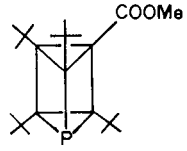

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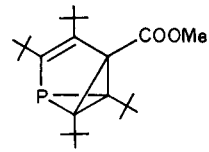

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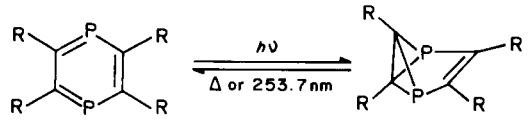

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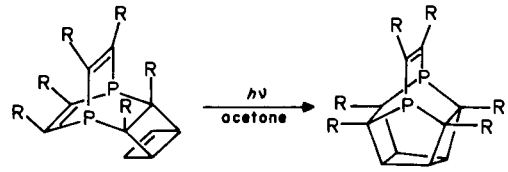
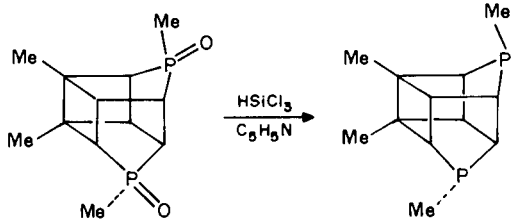


(71) (72)

(75)

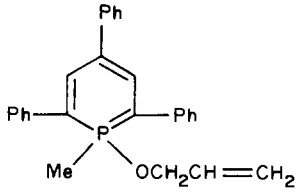
A cage phosphine oxide (**73**) was synthesized when the dimer of 1-phenylphosphole was irradiated,[173] and this oxide was later converted to the cage phosphine **74** with trichlorosilane–pyridine (equation 76)[18].



(76)

(73) (74)

An intramolecular thermal rearrangement of the λ^5-phosphinine **75**, proceeding through a dihydrophosphinine **76**, gave the unusual tricyclic phosphine oxide **77**[174]. Deoxygenation should result in the corresponding tricyclic phosphine, but this reaction has not yet been performed.



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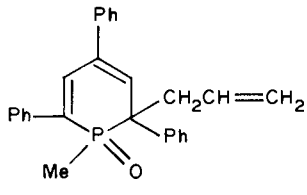

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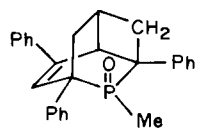


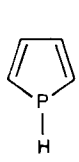
(77)

The newer phosphine syntheses, made possible by discoveries based on low-coordination phosphine chemistry and on metal coordination compounds, can be expected to provide further examples of unsaturated cyclic phosphines in the future, and these in turn should be a source of complicated frameworks from thermal or photochemical treatment.

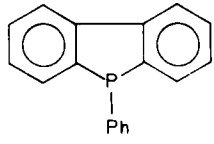
IV. SYNTHESES OF FULLY UNSATURATED PHOSPHACYCLOPENTADIENE DERIVATIVES: 1*H*- AND 2*H*-PHOSPHOLES, FUSED-RING PHOSPHOLES, PHOSPHOLYL ANIONS AND PHOSPHOLES CONTAINING ADDITIONAL HETEROATOMS

A. 1*H*-Phospholes and Fused-ring Derivatives

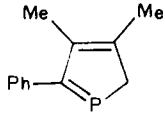
Although much of the basic chemistry of the common heterocyclopentadienes furan, pyrrole and thiophene was established by the early part of this century, no mention of the related 1*H*-phosphole system (**78**) appeared in the literature until 1953, when a synthesis of the fused-ring derivative **79** by four routes was reported[175]. An additional route was developed[176] shortly thereafter. 1*H*-Phospholes without additional fused rings were first reported in 1959[177,178] and reliable general syntheses of these were developed in the 1960s and 1970s[179–182]. The first functionally substituted 1*H*-phospholes (with the functionality being either on a ring carbon atom or the P atom) were also synthesized in the 1970s[110,183,184], but not until 1983 was a synthesis of the parent phosphole **78** itself reported[185], and this compound was not synthesized in pure form and fully characterized until 1987[186]. 2*H*-λ^3-Phospholes (e.g. **80**) are an even more recent development, with the first example being reported in 1981[187]. This systematic development of synthetic methods paralleled the increasing realization that phospholes (both 1*H*- and 2*H*-) do not merely represent a synthetic challenge but are molecules of considerable theoretical and practical interest. As a consequence of this increasing interest, reviews of phosphole chemistry in general have appeared fairly frequently[188–192].



(**78**)



(**79**)



(**80**)

*1. General syntheses of simple 1*H*-phospholes*

Four synthetic approaches to simple 1*H*-phospholes having some general applicability have been reported. Two of these employ 3-phospholene derivatives as starting materials, and these are readily obtained directly or indirectly from the well known McCormack cycloaddition (see Section III.D). The more versatile of these two approaches was developed by Mathey[180] and involves the dehydrohalogenation of McCormack diene–phosphonous dihalide cycloadducts to give the corresponding phospholes in one step (equation 77).

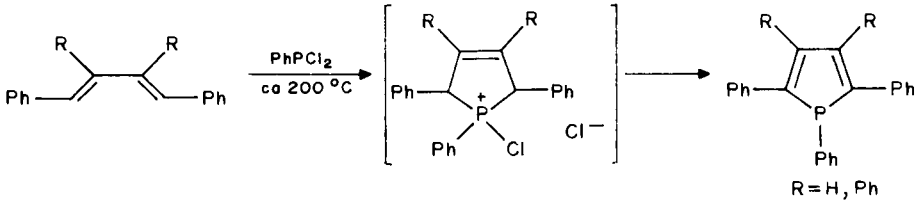
While the initially reported procedure[180] was satisfactory for the preparation of moderate amounts of simply substituted phospholes, the yields were sometimes low and the phospholes obtained frequently contained significant amounts of impurities. Two important modifications have been made to this procedure. In the first[181], the solvent

(77)

X=Cl or (more usually) Br

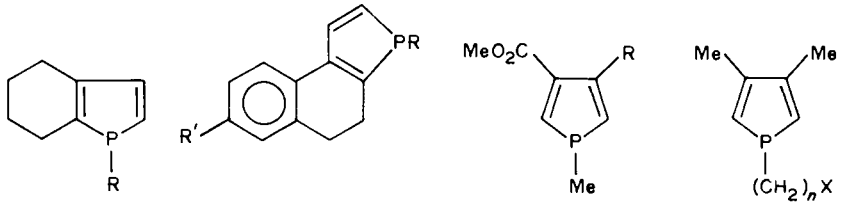
was changed from benzene under reflux to a hydrocarbon–dichloromethane mixture, which allows the reaction to be carried out at room temperature or below. In the second modification[182], the dehydrohalogenating nitrogen base was changed from dbu to other heterocyclic amines such as 2-picoline. The procedure is now such that yields of up to 80% are not uncommon and large-scale syntheses of certain phospholes are possible[193].

In a few instances, in reactions reported before the general procedure noted above was established, addition of a dehydrohalogenating base is unnecessary and the reaction can be driven to completion (ca 10 h) by the application of heat[194] (equation 78). The yields are generally good but may be further improved[195] if an excess of phenylphosphonous dichloride is used, under reflux, as a solvent. This direct dehydrohalogenation is limited to the systems shown in equation 78. Attempts[194,196,197] to extend the scope of this reaction by using other dienes or other phosphonous dihalides have been unsuccessful.

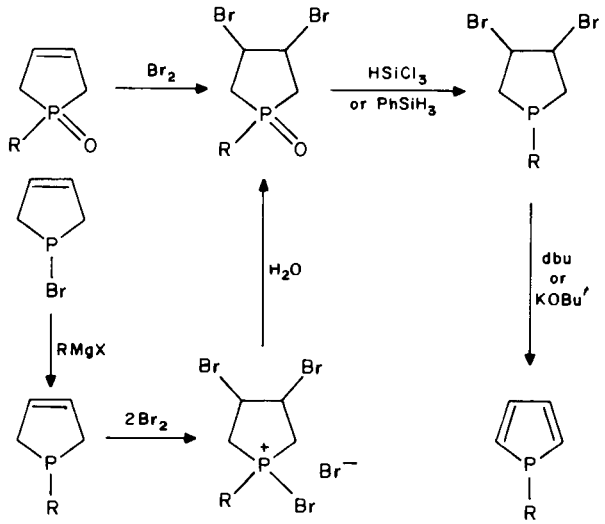


(78)

Mathey's more general procedure, described above, has also been used for the synthesis of the bicyclic and tricyclic phospholes **81** and **82**[198] and, as the final stage of a long synthetic sequence, the functionally substituted phosphole **83**[111]. Phospholes functionally substituted on the phosphorus atom (e.g. **84**) are also obtainable by this route[199].

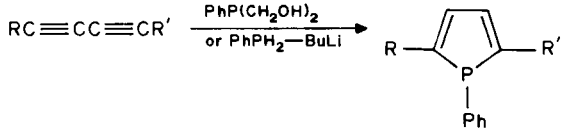


The second of the procedures, which use 3-phospholene derivatives as starting materials, employs 3-phospholene oxides rather than phospholenium salts[110,200,201]. The procedure, of which two variants are illustrated in equation 79, is lengthy but is particularly useful for the synthesis of *C*-unsubstituted phospholes.

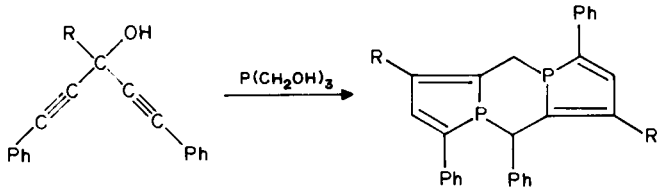


(79)

The third reasonably general synthesis, illustrated in equation 80, was developed by Märkl and Potthast[202]. The main limitation of this approach is that only 1,2,5-trisubstituted phospholes may be synthesized and it is, therefore, little used. Braye *et al.*[183] later showed that, in the addition of phenylphosphine to 1,3-diynes, butyllithium may be replaced with potassium hydroxide or copper(I) or mercury salts. Certain other catalysts may also be used. Related cycloadditions of phosphine derivatives to unsaturated systems are discussed in Section III. A. One interesting variation on this procedure is the reaction of tris(hydroxymethyl)phosphine (which acts as a reactive source of PH_3) with 1,4-diyn-3-ols[203]. This gives heavily substituted tricyclic systems containing two phosphole rings (equation 81). The yields are low and, as will be seen below, there are more convenient approaches to systems containing two or more phosphole rings.

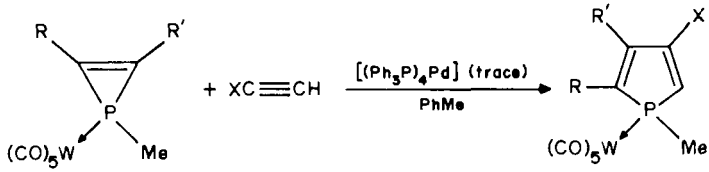


(80)



(81)

The most recent approach[157] to phosphole synthesis (equation 82) which shows some general potential (see also Section III. E) is entirely different from those described so far in that it does not require the construction of the four-carbon skeleton prior to cyclo-attachment of the phosphorus atom.

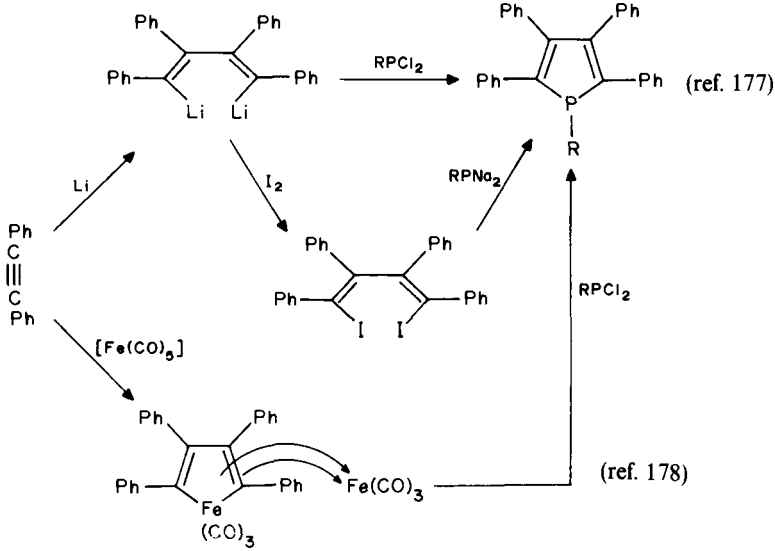


(82)

Eight phosphole complexes have been prepared by this route in yields of 31–85% and, while the phospholes prepared by this method are obtained in complexed form, reliable methods for the generation of the free phospholes from related complexes have been developed[6]. The most significant aspect of this approach is that R, R′ and/or X may be functional groups such as OEt or CO_2Et and *C*-functionalized phospholes with a variety of substitution patterns are therefore now fairly readily available. Previously reported approaches to *C*-functionalized phospholes[110,184,204,205], two of which will be discussed below, are of limited application. Only terminal alkynes may be used for this reaction and the substituent X is always attached to the 4-position in the product.

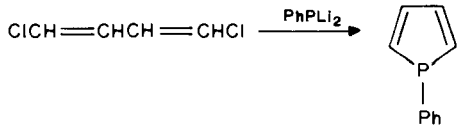
2. Limited-scope syntheses of the 1H-phosphole ring

There are several syntheses of this type, including the first reported syntheses (equation 83) of phospholes without additional fused rings[177,178].



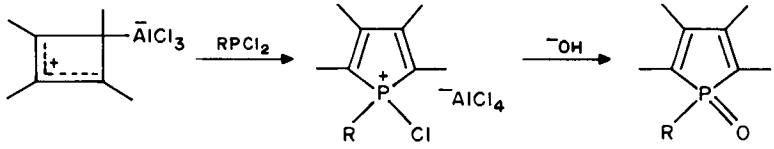
(83)

Related to the first of these is a much more recent synthesis[206] (equations 84) which leads, in low yield, to ring-unsubstituted phospholes. However, these are also readily available in moderate to good yield using either the Mathey[180–182] or Quin[110,200] approaches.

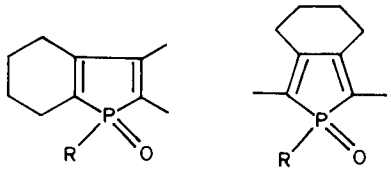


(84)

Another recent approach[207] which, like the first two syntheses mentioned above, leads to pentasubstituted phosphole derivatives, employs reactions between synthetically versatile aluminum halide–cyclobutadiene σ complexes and phosphonous dichlorides (equation 85). While the heavy substitution is normally undesirable, the method does have the advantage that bicyclic systems such as **85** and **86** are readily prepared. The fact that phosphole oxides rather than phospholes are produced is of little significance since such oxides are readily reduced by silane derivatives (Section III. D).

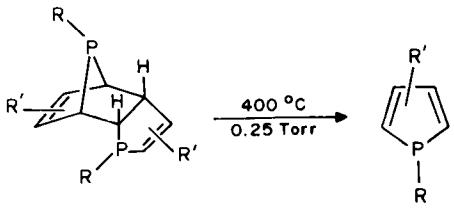


(85)

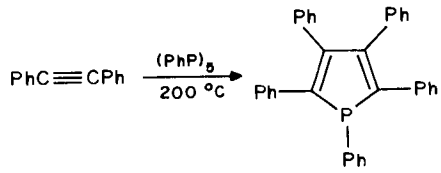


(**85**) (**86**)

Other phosphole and phosphole oxide syntheses of very limited utility have been reported. These include the thermally induced retro-Diels–Alder reactions (equation 86, moderate yield) of phosphole dimers[29,208], the reaction of pentaphenylcyclopentaphosphine with diphenylacetylene[209] (equation 87, very low yield) and a variety of reactions in which the phosphole ring is assembled (usually as an oxide or phospholium salt) with the aid of cobalt[210, 211] or manganese[212] complexes. The reactions, although chemically interesting, have little value as synthetic procedures.



(86)



(87)

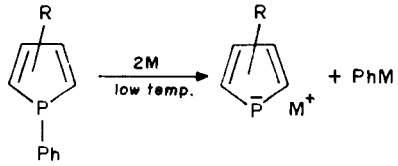
3. Syntheses of phospholes from other phosphole derivatives

A rich chemistry has developed around simple 1*H*-phosphole derivatives. Some of the more important aspects are discussed in Section VI, but one aspect, the transformations of

simple phospholes into other phosphole derivatives, now includes several reactions that lead to the synthesis (frequently in good yield) of other phospholes which are not easily accessible by the more conventional methods already described. These tranformations can mostly be grouped into the three categories of ligand exchange at the phosphorus atom, substitution at the carbon atoms of the phosphole ring and thermally induced transformations.

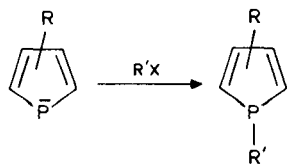
a. Ligand-exchange reactions. These may be grouped into two subcategories, namely those reactions which involve the intermediacy of a phospholyl anion (of which many examples are known) and those in which the three-coordinate phosphorus atom of a simple phosphole acts as an electrophile.

Phospholyl anions have been known since 1971[183]. They are generated in high yield by treating 1-phenylphospholes with lithium, sodium or potassium metal (equation 88). In the free ion, the negative charge is delocalized around the ring[213]. However, all reactions so far studied in which phospholyl anions act as nucleophiles occur at the phosphorus atom. The other product of the reaction, the phenyl anion, is also a highly nucleophilic species and its presence can interfere with subsequent reactions of the phospholyl anion. Several techniques have been developed to suppress the effect of Ph^-. These include treatment of the mixture with *tert*-butyl chloride (not very satisfactory)[183] and addition to the reaction mixtures of salts of metals which are less electropositive than alkali metals [214-216]. Aluminum trichloride is particularly useful in this respect[216] and the yields of subsequent reactions of the phospholyl anions are usually very good.



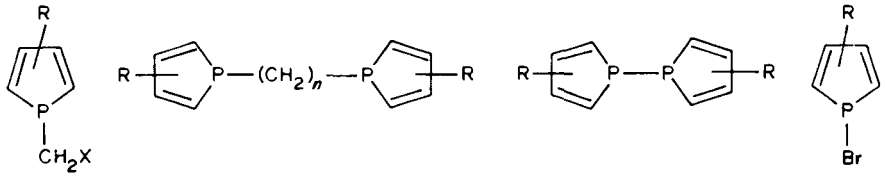
(88)

Phospholyl ions can be readily alkylated by treatment with alkyl halides (equation 89) and there are numerous examples in the literature, e.g. refs. 183, 216, 217. *P*-functionalized phospholes of the type **87** may also be produced by treating the phospholyl anion with an excess of species such as α,ω-dihalogenoalkanes[164,183,218,219], ethyl bromoacetate[183], ethylene oxide[213] and a variety of other ω-functionalized α-halogenoalkanes[214]. Under different conditions, phospholyl anions react with α,ω-dihalogenoalkanes to give [183,186,220] α,ω-diphospholylalkanes of type **88**. These are of particular significance for two reasons. First, **88** ($n = 2$) can also be cleaved by an alkali metal[186,220] to give two equivalents of the corresponding phospholyl ion but, in this reaction, the $-CH_2CH_2-$ unit is eliminated as ethylene and pure phospholyl anions uncontaminated with phenyl- or alkyl-lithium compounds are obtained. Second, for the case of **88** (R = H, $n = 2$), the unsubstituted phospholyl anion is produced and this may be protonated[186] with CF_3CO_2H at $-90\,^{\circ}C$ in thf to give the parent phosphole **78**, previously obtained[185] in impure form by protonation of the phosphole anion produced by more conventional P—C cleavage reactions. Several other protonations have been carried out[183,185,221], but extreme care must be taken to maintain low temperatures during the reaction or 1,5-



(89)

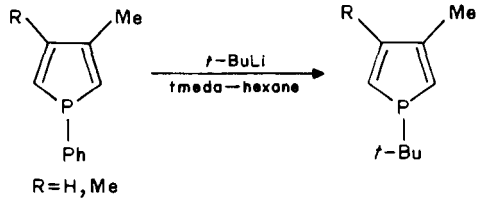
sigmatropic migrations of the hydrogen atom attached to phosphorus occurs to give a 2*H*-phosphole derivative of type **80**. More will be said about this later.



(87) **(88)** **(89)** **(90)**

Another synthetically useful reaction of these phospholyl anions is with iodine or $COCl_2$ to give 1,1′-biphospholyls of type **89**[222,223]. These are also of some synthetic value since they too may be cleaved[185] by an alkali metal to give phospholyl anions uncontaminated with other organic species. They may also be cleaved[222] with bromine to give *P*-bromophospholes (**90**). These, in turn, will react with alcohols[222] to give *P*-alkoxyphospholes.

One last ligand-exchange reaction at the phosphorus atom of *P*-phenylphospholes, which appears not to involve a phospholyl anion intermediate, should be noted. In this reaction, the *P*-phenyl group is displaced[224,225] directly by a *tert*-butyl group on treatment of the phosphole with *tert*-butyllithium in the presence of tmeda (equation 90). The mechanism of this reaction is uncertain.

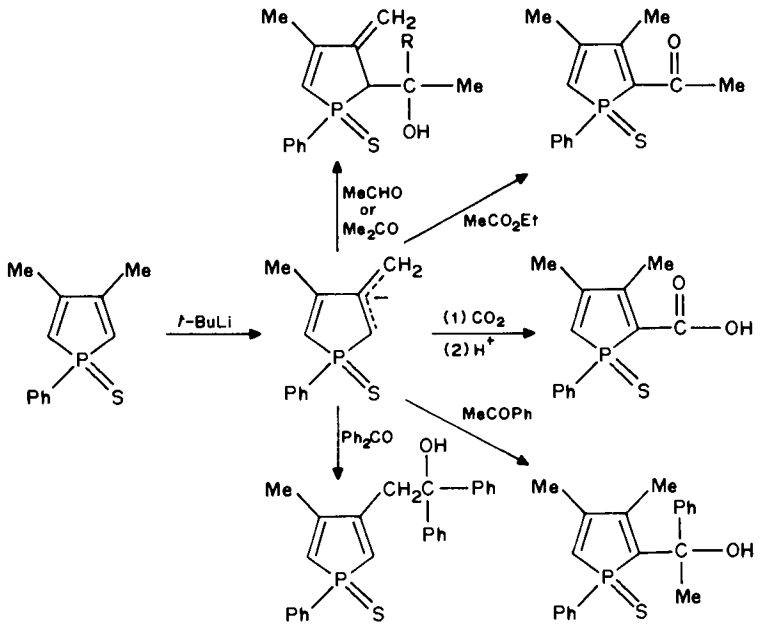


R=H, Me (90)

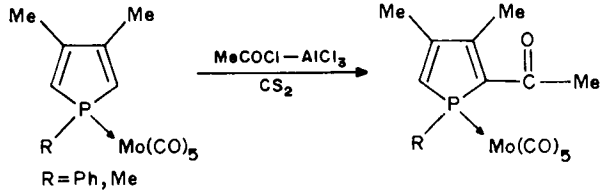
Finally, it should be noted that an extensive coordination chemistry has been developed around phospholyl anions. The subject is outside the scope of this survey but it has been reviewed, together with the coordination chemistry of 1*H*-phospholes, fairly recently[226].

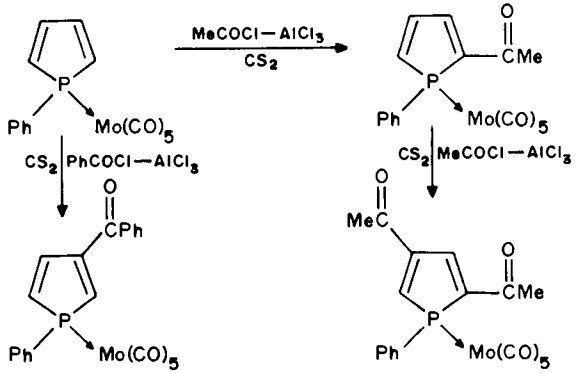
b. Substitutions at the ring carbon atoms of phosphole derivatives. As mentioned earlier in this section, functionally substituted phospholes with the functionality on a ring carbon atom are difficult to obtain. Two approaches (one leading to **83** and the other summarized in equation 82) have already been discussed. However, there are two other routes which use phosphole derivatives as starting materials. The first of these[184,204] is outlined in equation 91 but, although a wide variety of functionally substituted phosphole sulfides are produced, there are severe limitations on the scope of this reaction. Thus, a 3-methyl group is required for the generation of this anionic intermediate and, unless the phosphole sulfide has additional substitution, a Diels–Alder type of dimerization of the system occurs[227]. The fact that phosphole sulfides rather than phospholes result from these reactions is of little consequence since the sulfides are readily desulfurized by dimethylphenylphosphine[228].

The remaining route involves[205] direct Friedel–Crafts acylation of [(phosphole)Mo$(CO)_5$] complexes and the synthesis is summarized in equations 92 and 93. Other metal carbonyl complexes were tried[205] but the reaction appears to be specific for molybdenum complexes. Certain steric effects were noted. For example, if phenyl is replaced with



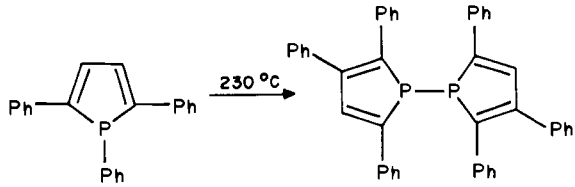
bulkier groups on the phosphole, no acetylation occurs in the 3,4-dimethyl-substituted system and it is directed to the 3-position in the *C*-unsubstituted system. Benzoylation never occurs in the 2-position. The substituted phospholes may be regenerated[205] from the complexes by heating them in a CO atmosphere under pressure.





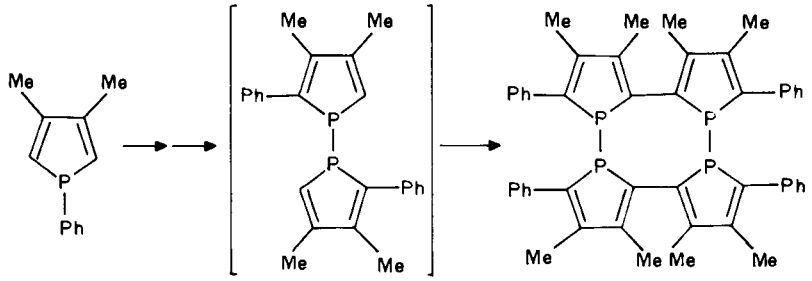
This method and the method developed earlier by the same group[157] (already discussed) are probably the most useful approaches to *C*-functionally substituted phospholes.

c. Thermally induced transformations of 1H-phospholes into more complex 1H-phospholes. There are only two reports of reactions of this type[229,230]. If 1,2,5-triphenylphosphole is subjected to prolonged heating (10 days) at 230 °C, it is slowly transformed[229] in good yield into an unsymmetrically substituted 1,1′-biphospholyl (equation 94). The reaction is thought[229] to involve several, unisolated, 2*H*- and 1*H*-phosphole intermediates, at least one of which has been trapped[229]. More will be said about intermediates of this type later.

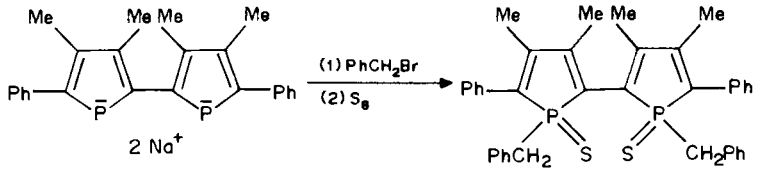


(94)

In the second thermally induced transformation[230], 3,4-dimethyl-1-phenylphosphole yields, in 60 h at 170 °C, a red tetramer. Again, a 1,1′-biphospholyl intermediate is thought[230] to be involved (equation 95) and some evidence was presented to support this. As with the 1,1′-biphospholyls discussed earlier[185], the P—P bonds of the tetramer may be cleaved[230], this time with sodium naphthalide, to give the corresponding 2,2′-biphospholyl dianion, which can be alkylated to give a 2,2′-biphospholyl, isolated as a disulfide (equation 96), in good yield.



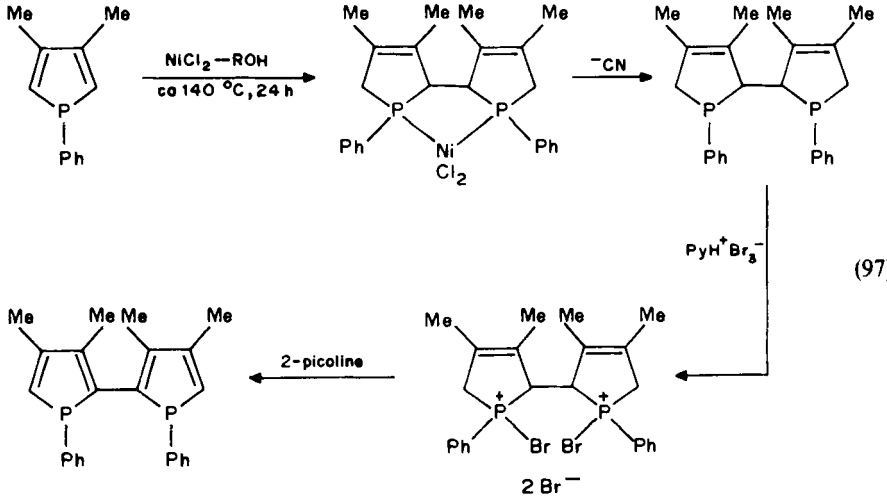
(95)



(96)

An alternative route to less heavily substituted 2,2′-biphospholyls has been reported recently[231] and this too uses simple 1*H*-phospholes as starting materials (equation 97). These 1*H*-phospholes undergo[232] a reductive dimerization with alcohols in the presence of nickel(II) chloride and the resulting product, after decomplexation, is subjected[231] to the normal Mathey approach[180–182] to phosphole synthesis from 3-phospholenium

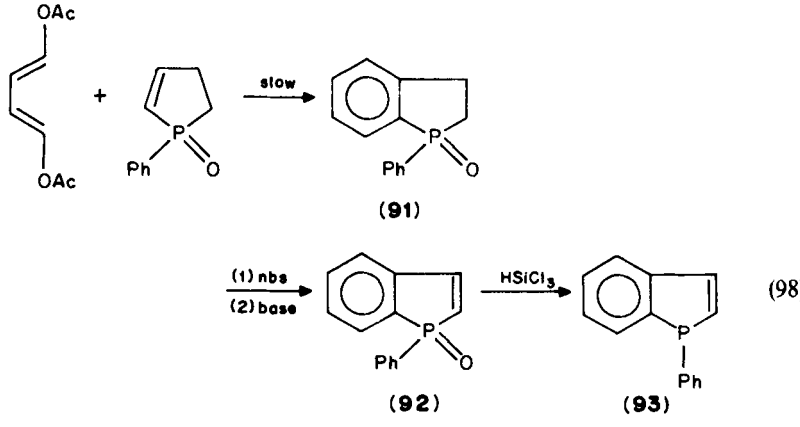
salts already described. An extensive coordination chemistry has been established[231] for these 2,2′-biphospholyls.



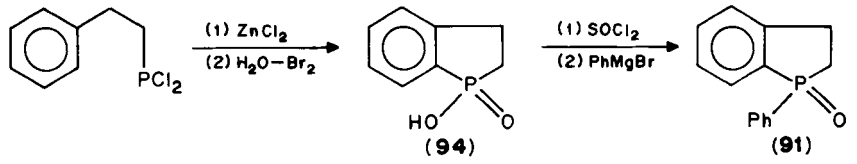
(97)

4. Syntheses of fused-ring phospholes: phosphindoles and dibenzophospholes

a. Phosphindoles. Although several syntheses of phosphindoles (phosphorus analogs of indoles) have now been reported, only two of these show any potential as general syntheses. There are two versions of the first of these. In the original version[233], the bicyclic system is constructed by a Diels–Alder reaction and this is followed by conventional bromination, dehydrobromination and P=O reduction steps (equation 98). However, the cycloaddition is slow and, in a more recent version[234], the phosphindoline oxide intermediate **91** was first synthesized by the method of Swan and his group[79] (equation 99) and the phosphinic acid so obtained (**94**) was converted first into the acid chloride and then the *P*-phenyl oxide (**91**). The later steps in the synthesis of the 1-phenylphosphindole (**93**) remain the same. This route has also been used[235] to synthesize 1-benzylphosphindole.

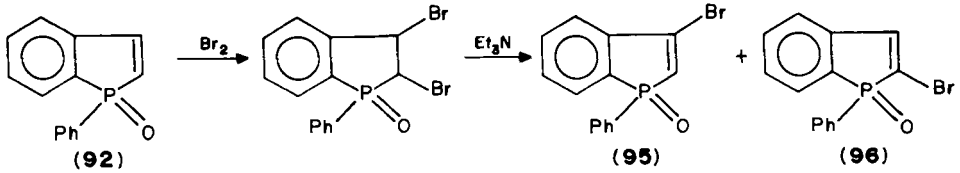


(98)



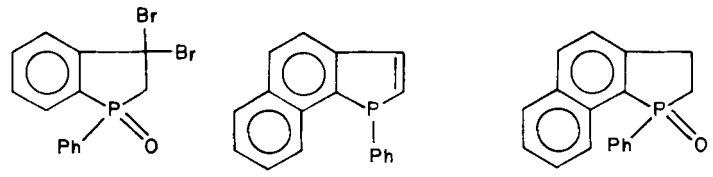
(99)

Mathey's group has further modified this synthesis[234] in two important respects. First, the phosphindoline oxide **92** will undergo bromine addition followed by dehydrobromination to give (equation 100) a mixture (5:1, separable by chromatography) of the bromophosphindole oxides **95** and **96**. In a second modification, **91** is allowed to react with an excess of nbs and the reaction mixture (which almost certainly contains the dibromo compound **97**) gives, after dehydrobromination in the normal manner, a mixture (again easily separable) of **92** and **95**. Clearly, these modifications, together with the ease[233,234] with which phosphindole oxides are reduced to the corresponding phosphindoles, open up a relatively straightforward route to functionally substituted phosphindoles.



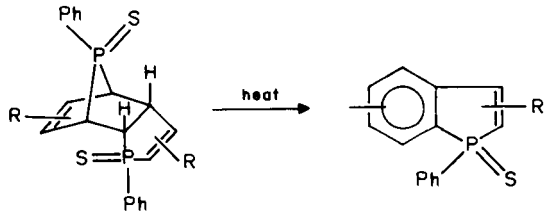
(100)

Quin *et al.*[198] used similar bromination–dehydrobromination–P=O reduction techniques to prepare the benzophosphindole **98** from the known[101] benzophosphindoline derivative **99**.

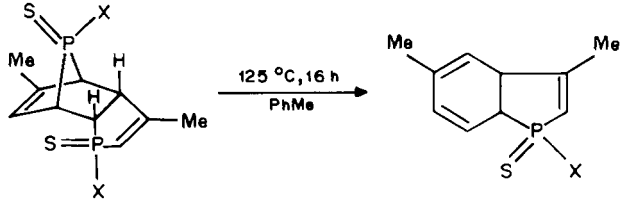


The only other synthesis of phosphindoles which is potentially fairly general is the thermolysis of phosphole sulfide dimers. Again, there are two variants[158,227] of this approach. In the first of these[227], certain phosphole sulfide *endo* dimers (readily obtainable[227] by treatment of the appropriate monomeric phosphole with sulfur) are heated strongly under reduced pressure. Elimination of both the phosphorus bridge and two atoms of hydrogen occur to give, in low yield, a phosphindole sulfide (equation 101). However, although the procedure is very simple and the resulting sulfides should be readily reducible[228] to the phosphindoles, the yields are low. In similar reactions where the stereochemistry about the bridging phosphorus atom is reversed, thermolysis at lower temperatures in solution leads smoothyl[236] to the formation of dihydrophosphindole sulfides (equation 102).

In another reaction which is probably closely related to that shown in equation 101 in its final step, **100** can be synthesized[158] in good yield by heating the molybdenum complex

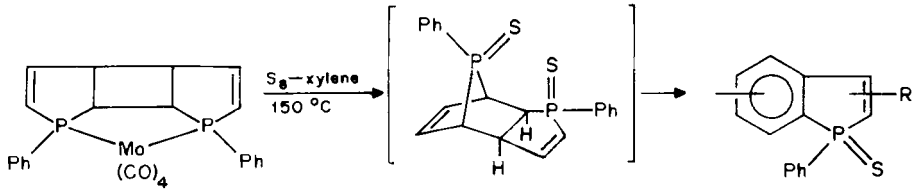


(100) (101)



X=OR, NR_2 (102)

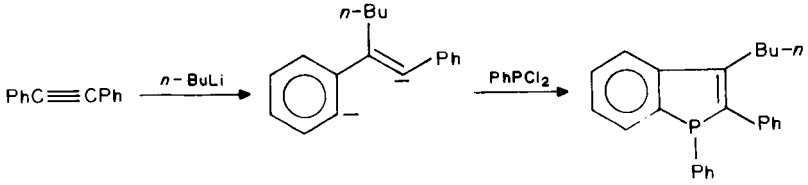
101 (formed[158] from 1-phenylphosphole by treatment with $[Mo(CO)_6]$ under UV irradiation) with sulfur in xylene at 150 °C. It is probable[158] that the *exo*-phosphole sulfide dimer **102** is an intermediate (equation 103) and that this is formed from an intermediate molybdenum complex of the *exo*-phosphole dimer.



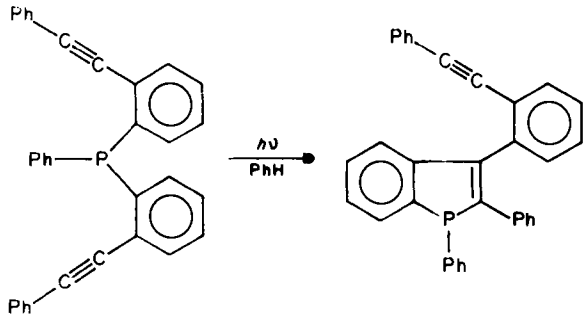
(101) (102) R=H (100)

(103)

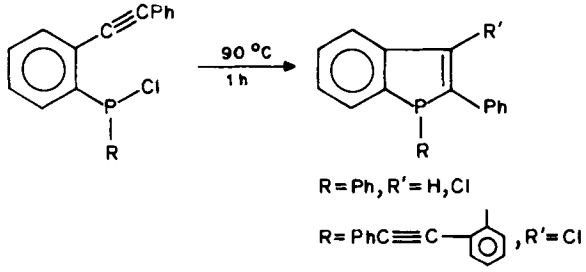
The remaining syntheses are very specialized and lead to heavily substituted phosphindole derivatives. Thus, if diphenylacetylene is treated with butyllithium followed by $PhPCl_2$, a phosphindole is obtained[50] (equation 104; see also Section III. A). An even more heavily substituted phosphindole is obtained[237] by the route outlined in equation 105 and similar structures have recently been obtained[238] by thermally induced cyclizations of some complex chlorophosphines (equation 106).



(104)

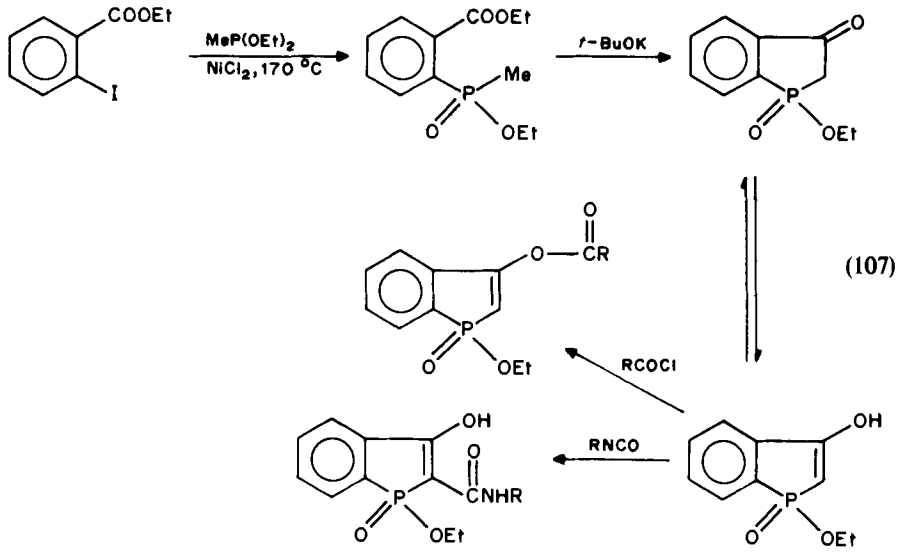


(105)



(106)

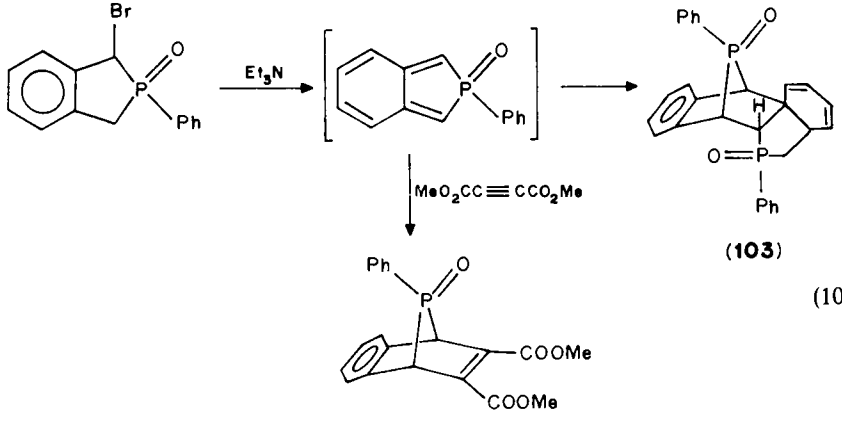
The last synthetic route reported[239], which also leads to heavily substituted (but functionalized) phosphindole derivatives, is summarized in equation 107. Although this route does not, as it stands, lead to the formation of phosphindoles in which phosphorus is bound to three carbon atoms, there is clearly some potential for the procedure to be modified so as to allow this.



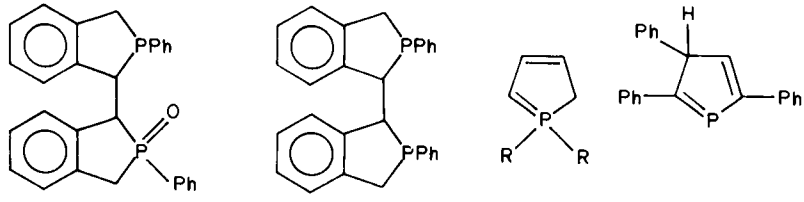
(107)

As with simple 1*H*-phospholes, it is possible with phosphindoles to exchange the exocyclic group attached to phosphorus, either via a phosphindolyl anion route or directly. Both types of reaction have been carried out successfully[217,234].

Before considering dibenzophospholes, brief mention should be made of the isophosphindole system. This system has been made[240] (equation 108) as a transient species which dimerizes rapidly but which may be trapped[240] as a Diels–Alder adduct with dimethyl acetylenedicarboxylate. Attempts have been made[115] to deoxygenate the dimer **103** with trichlorosilane to give the corresponding phosphine, with a view to dedimerizing it to give the corresponding isophosphindole. However, a reductive cleavage of a C—C bond of **103** occurred to give, under mild conditions, the monoxide **104** and, under more severe conditions, the bisphosphine **105**. In view of the success enjoyed by Matheys' group[231] in the synthesis of 2,2'-biphospholyls from partially unsaturated precursors (equation 97), it is possible that **105** could be transformed into a 2,2'-bisisophosphindolyl.



(103) (108)

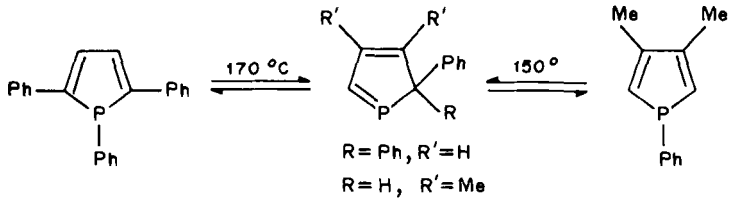


(104) (105) (106) (107)

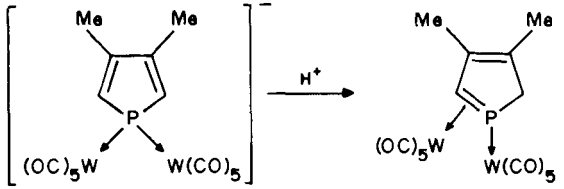
b. Dibenzophospholes. There have been relatively few developments in the synthesis of 5*H*-dibenzophospholes of type **79** in recent years. The early syntheses have been thoroughly reviewed[188] and no further comment will be made here. Only two significant developments in the synthesis of compounds of type **79** have occurred since then. First, it has been shown[217] that, as with simple 1*H*-phospholes and phosphindoles the exocyclic P—C bond may be cleaved with alkali metals to give a dibenzophospholyl anion, which will react with alkyl halides in the normal manner. Thus, ligand exchange at the phosphorus atom can be effected. The second development has been that Cornforth and coworkers[241–244] have reported several syntheses, involving mainly *m*-quaterphenyl intermediates, of heavily-substituted 5*H*-dibenzophosphole derivatives. Details of these syntheses are not within the scope of this chapter.

B. 2*H*-λ^3-Phospholes and Phosphaazulenes

Whereas 2*H*-λ^5-phospholes of type **106** have been known for some time (for a review of many of the systems, see ref. 245), 2*H*-λ^3-phospholes are a comparatively recent discovery. The first report[187] came in 1981 when it was shown that, at elevated temperatures, 1,2,5-triphenylphosphole and 3,4-dimethyl-1-phenylphosphole undergo reversible [1,5] sigmatropic rearrangements of the phenyl group (equation 109). In each case, the equilibrium lies on the side of the *P*-phenyl isomer. More recently, it has been shown[185,221] that for 1*H*-phospholes bearing a hydrogen atom on the phosphorus, a similar [1,5] shift of hydrogen occurs spontaneously at or below room temperature. Most of these monocyclic 2*H*-phospholes are highly reactive systems which have only been characterized indirectly by trapping experiments (about which more will be said later since they are of value in the synthesis of other phosphorus heterocycles). However, it has been possible in one instance[246] to isolate and characterize (X-ray) a tungsten carbonyl complex of a 2*H*-λ^3-phosphole by protonating a tungsten carbonyl complex of a phospholyl anion (equation 110). The only other relatively stable 2*H*-λ^3-phosphole derivatives so far reported (apart from **47**, discussed in Section III. E) are the phosphaazulenes (discussed below) and certain 2*H*-λ^3-phospholes containing additional heteroatoms (both monocyclic and with additional fused rings), which will be discussed in Section IV.C.



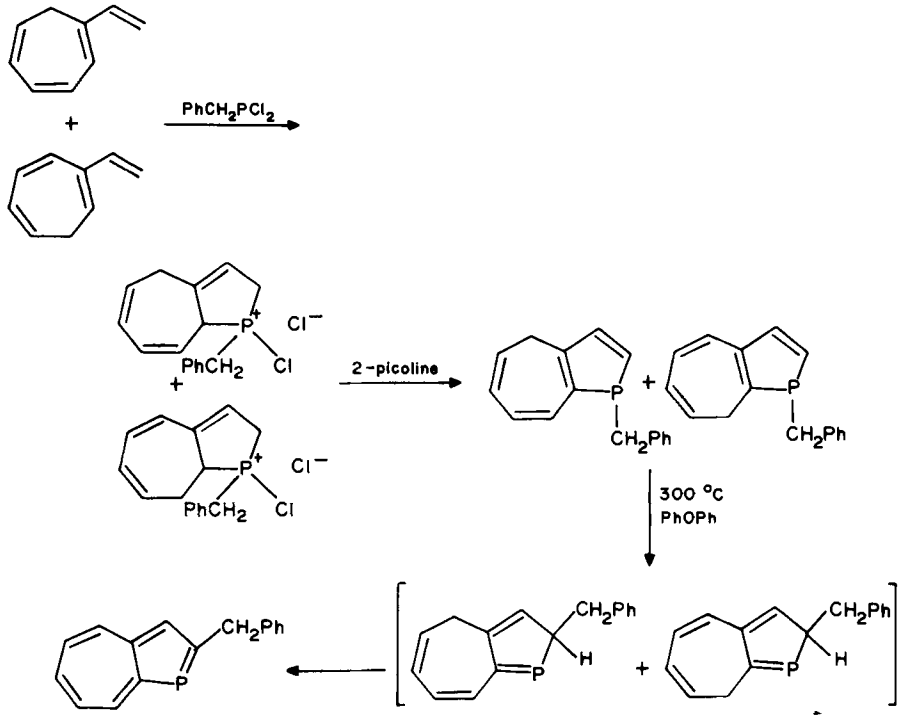
(109)



(110)

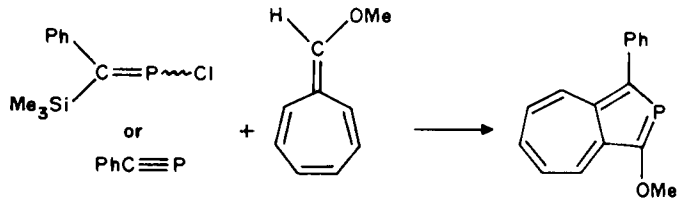
Before discussing these other systems, however, very brief mention of 3*H*-λ^3-phospholes should be made. Although no such systems have yet been characterized, it should be remembered that under prolonged heating, 1,2,5-triphenylphosphole is transformed[229] into an unsymmetrically substituted 1,1′-biphospholyl (equation 94). Bearing in mind the [1,5] shifts illustrated in equation 109, it is probable that in the reaction outlined in equation 94 two consecutive [1,5] phenyl shifts occur to give the transient 3*H*-λ^3-phosphole **107**, which reacts further to give the biphospholyl.

As mentioned above, 2*H*-λ^3-phospholes are, in general, short-lived and highly reactive species. However, shortly after the first 2*H*-λ^3-phosphole was reported, the syntheses of the much more stable 1-phosphaazulene[247] and 2-phosphaazulene[248] systems (which may be regarded as cycloheptatrieno-2*H*-λ^3-phospholes) were published. Like the simple 2*H*-λ^3-phospholes referred to above, 1-phosphaazulene has been synthesized, as the benzyl derivative **108**, from a 1*H*-phosphole precursor which, on heating, undergoes a [1,5] sigmatropic rearrangement followed by aromatization (elimination of hydrogen) as shown in equation 111. The product,a blue–green oil, is sufficiently stable for it to be purified by chromatography on silica gel and reduced-pressure distillation.



(108) (111)

The 2-phosphaazulene was synthesized as the substituted derivative **109** by an entirely different route (equation 112). Compound **109** is also a stable species which crystallizes as red platelets (which dissolve in chloroform to give a green solution) after chromatographic purification. The chemistry of these phosphaazulenes has yet to be investigated in detail.



(112)

(109)

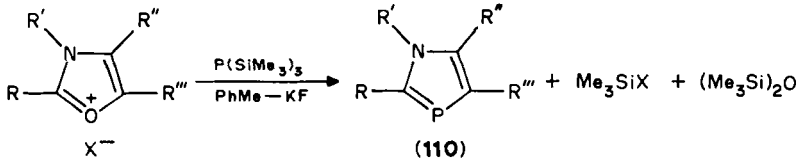
C. Phospholes Containing Additional Heteroatoms

Fully unsaturated, five-membered heterocycles containing two or more heteroatoms have long been known and many of them possess aromatic character. However, such systems in which phosphorus is one of the heteroatoms are comparative newcomers, with the first example being reported in the late 1960s. In most of these systems, the phosphorus is directly bonded to a heteroatom and structures of this type are outside the scope of this chapter. Some aspects of their synthesis[249], their NMR properties[250] and their reactivity

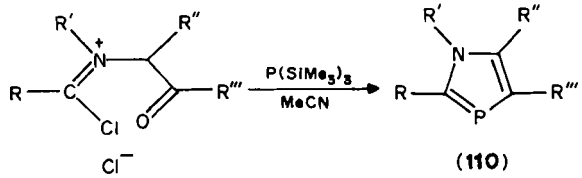
in cycloaddition reactions[251] have been reviewed. More recently, however, such systems in which the phosphorus atom is bonded only to carbon have been reported and developments in this area will be discussed here. In almost all cases, the phosphorus atoms are two-coordinate (unless a second phosphorus atom or benzannelation is also present) and the systems are, therefore, related to the 2*H*- and 3*H*-λ^3-phospholes discussed above. Examples in which there are either one or two additional heteroatoms are known and fused-ring derivatives have also been reported. Some of the more important synthetic routes to some of these systems which are of wider interest have been briefly mentioned in Section III. E but, since these phosphorus heterocycles are so novel and recent, a full treatment will be given here.

1. Systems containing one additional heteroatom

a. 1H-1,3λ³-Azaphospholes. Monocyclic systems of this type were first reported in 1986 by two groups and variations on four synthetic routes have so far been developed. In the first of these[142], oxazolium salts are treated with tris(trimethylsilyl)phosphine (equation 113). Variations on this general procedure allow[142] the formation of di-, tri- and tetra-substituted 1*H*-1,3λ^3-azaphospholes. Acyclic relatives of the oxazolium salts may also be used[142] as starting materials in reactions with $P(SiMe_3)_3$ (equation 114).



X⁻ (110) (113)

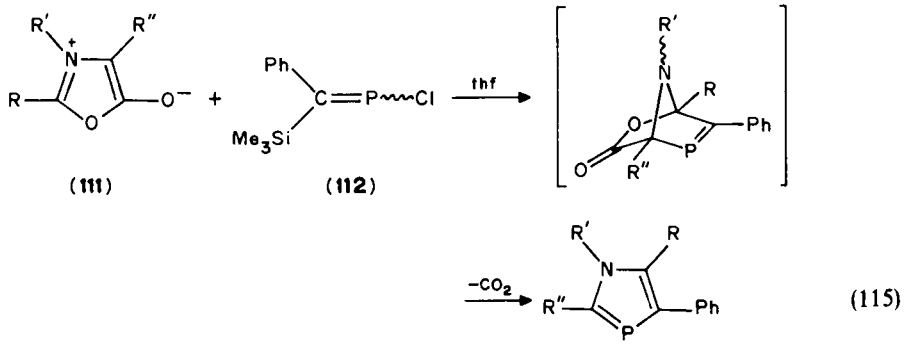


Cl⁻ (110) (114)

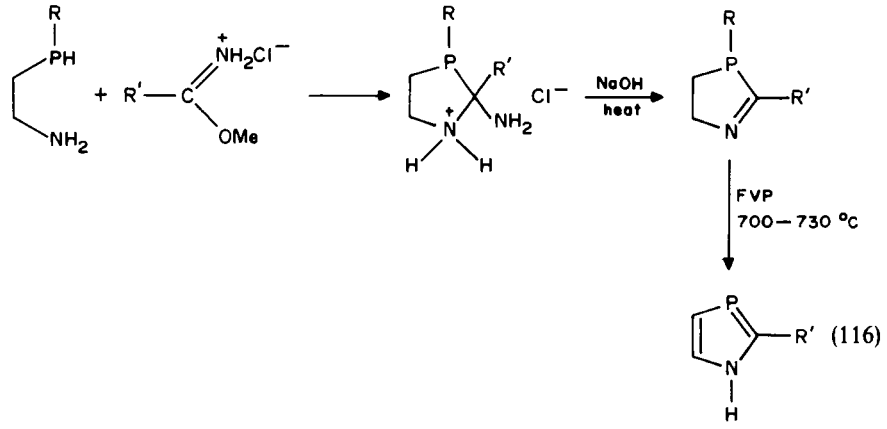
In a related approach, the same group has found[142] that 'munchnones' (**111**, 1,3-oxazolium-5-olates) act as dipolarophiles in [3 + 2] cycloadditions with the *P*-chlorophospha-alkene **112** to give, via an unisolated bridged bicyclic intermediate, 1*H*-1,3λ^3-azaphospholes in good yield (equation 115; see also Section III. E). In very similar reactions, Regitz and coworkers have replaced **112** with the phosphaalkynes HC≡P[252] and *t*-BuC≡P[253] with similar results.

An entirely different route, leading to *N*-unsubstituted 1*H*-1,3λ^3-azaphospholes and using flash vacuum pyrolysis (FVP) techniques (equation 116), has been reported by Heinicke[254]. Treatment of the azaphosphole product of the reactions with lda leads to lithiation and the lithiated system can be silylated (equation 117) at low temperature. Treatment of the lithiated compound with an alkyl halide at low temperature gives what is probably a short-lived 3*H*-1,3λ^3-azaphosphole which polymerizes rapidly. Yields are low to medium (19–58%) in these syntheses and NMR spectral data have been acquired for a variety of substitution patterns.

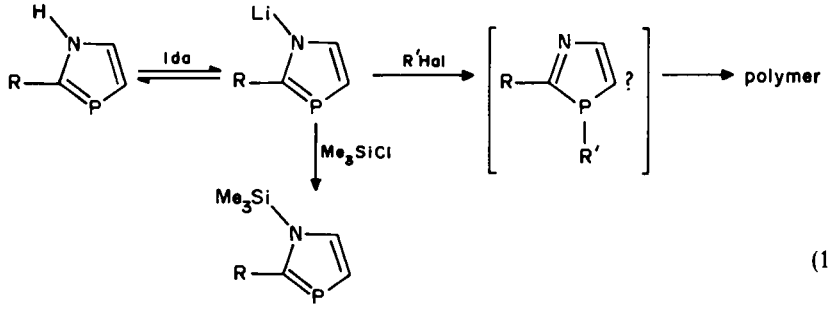
1*H*-1,3λ^3-Azaphospholes have also been synthesized[255] by reaction of 'munchnones' with $P(SiMe_3)_3$. The advantage of using $P(SiMe_3)_3$ rather than the *P*-chlorophosphaalkene **112** mentioned earlier is that azaphospholes functionally sub-



(115)



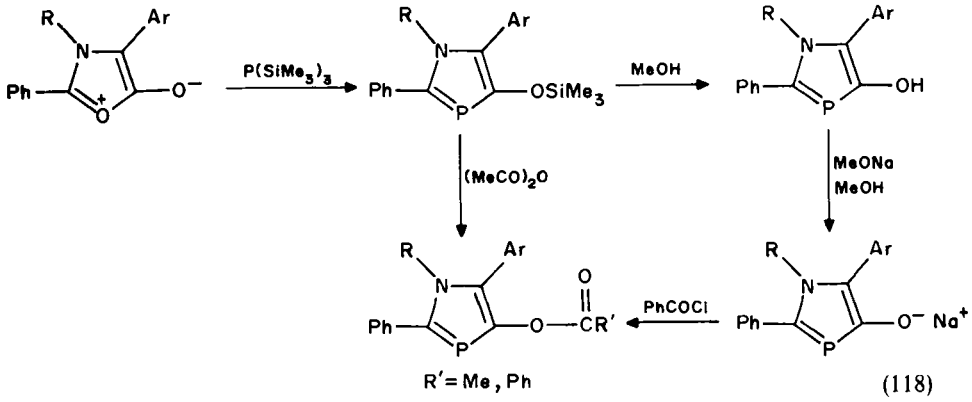
(116)



(117)

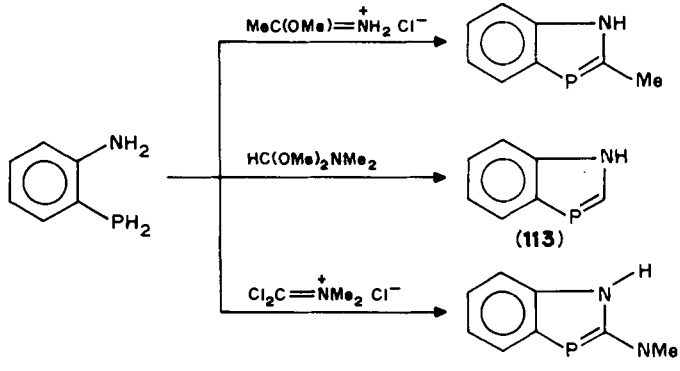
stituted on a ring carbon atom are formed (equation 118). The hydroxyazaphosphole is fairly stable and shows no tendency to tautomerize to the keto form.

Fused-ring derivatives of azaphospholes have been known longer than the monocyclic derivatives, with the first synthesis being reported in 1978[76] (see also Section III.A). Issleib *et al.*[76] have given details of several approaches to 1*H*-1,3,λ^3-benzazaphospholes. The first of these involves cyclization reactions of 2-aminophenylphosphine with a variety of reagents. Typical examples are shown in equation 119. Other reagents used were RCOCl,



(118)

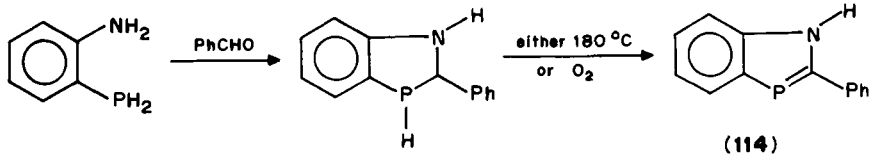
RCO_2Et, $HC(OEt)_3$ and, by suitable choice of cyclizing reagent, either hydrogen or substituent groups can be placed on the five membered ring carbon atom. In all instances, the nitrogen atom bears a hydrogen. Yields are in the range 11–85% depending on the nature of the reagent and the conditions used.



(113)

(119)

An alternative approach[76] is the reaction of 2-aminophenylphosphine with benzaldehyde followed by either thermal dehydrogenation of the intermediate benzazaphospholene or oxidation of that intermediate in a stream of air (equation 120). The X-ray crystal structure of the unsubstituted 1*H*-1,3λ^3-benzazaphosphole **113** has been determined[256].

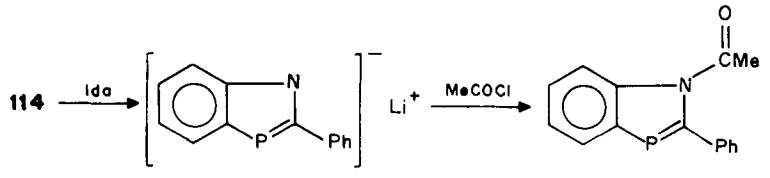


(114)

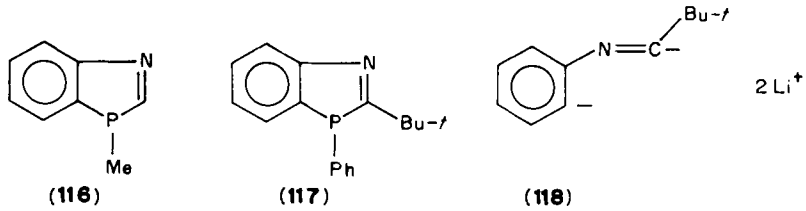
(120)

N-Substituted derivatives of the system have also been prepared by two methods. The first[257] is a simple modification of the method of Issleib *et al.*[76] using 2-(*N*-methylamino)phenylphosphine in the cyclization reactions and further discussion is unnecessary here. In the second method[76], **114** is treated with lithium diethylamide and

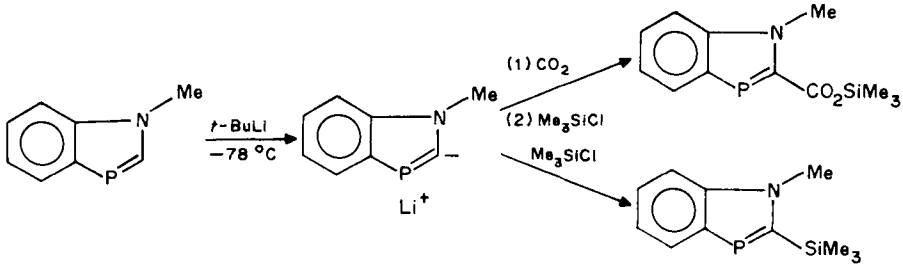
the resulting lithiated product (**115**) is further treated with acetyl chloride to give 1-acetyl-1,3,λ^3-benzazaphosphole (equation 121). If, however, **115** is treated with methyl iodide, the 3*H*-benzazaphosphole **116** is formed. The only other known example of this system is **117**, which is formed from **118** by treatment with phenylphosphonous dichloride[258].



(121)

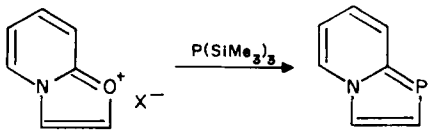


1*H*-1,3λ^3-Benzazaphospholes functionally substituted on the five-membered ring carbon atom have been prepared[257] by *C*-lithiation of 1-methyl-1,3λ^3-benzazaphosphole followed by treatment with either CO_2–Me_3SiCl or Me_3SiCl alone (equation 122).



(122)

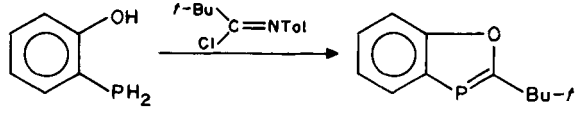
Recently, 1*H*-1,3λ^3-azaphospholes containing a fused heterocyclic ring have been prepared[259]. The method is very similar to that used[142] to prepare monocyclic azaphospholes from oxazolium salts (equation 113) and is shown in equation 123.



(123)

b. 1,3λ^3-Oxaphospholes. The 1,3λ^3-oxaphosphole system appears to be known only in the benzannelated form. The only reported[77,260] syntheses of the system are very similar to those employed by Issleib *et al.*[76] for the syntheses of benzazaphospholes (equation 119)

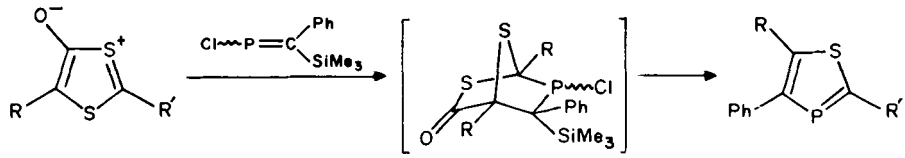
in that 2-hydroxyphenylphosphine (2-phosphinophenol) is condensed with suitable imino compounds as shown in equation 124.



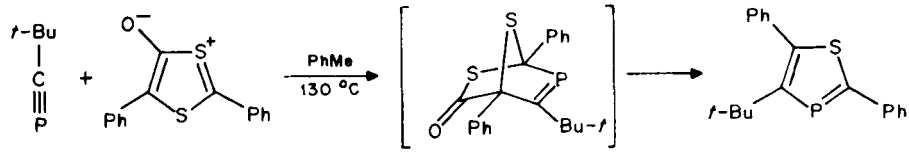
(124)

A crystal structure determination of the 2-(*p*-chlorophenyl) derivative has shown[260] that there is extensive delocalization in the five-membered ring. This ring system has otherwise been little studied except for its reactions with molecular oxygen[261], 1,3-dienes[262] and *o*-quinones[263].

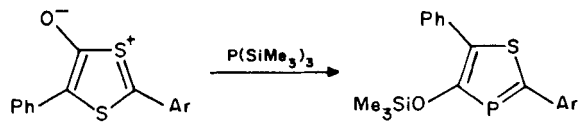
c. 1,3λ³-Thiaphospholes. Both monocyclic and benzannelated derivatives of this system are known. The monocyclic systems were prepared using methods similar to those used, and already described, for the synthesis of 1,3-azaphospholes and the three routes so far reported[36,253,255] (see also Section III. E) are summarized in equations 125–127.



(125)

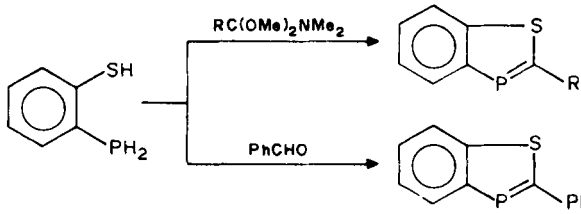


(126)



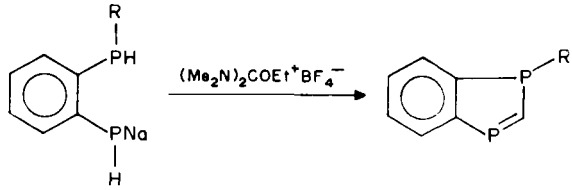
(127)

Similarly, the only routes to 1,3λ³-benzthiaphospholes so far reported[264] are closely related to syntheses (already discussed) of benzazaphospholes[76] (equations 119 and 120) and benzoxaphospholes[77] (equation 124). The routes are outlined in equation 128.



(128)

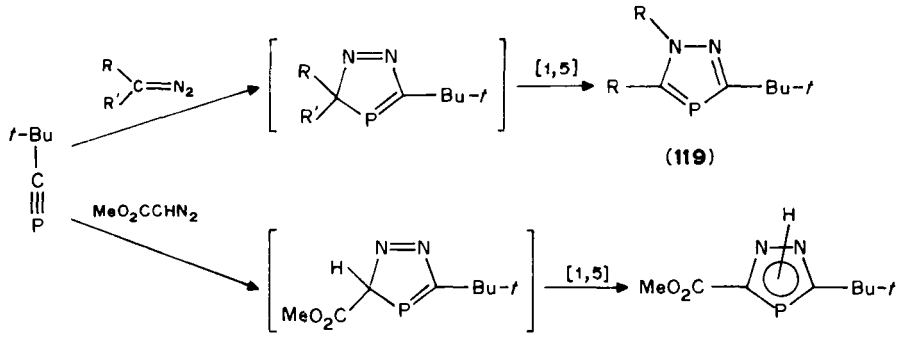
d. 1,3-Diphospholes. There is only one report[78] of this system and, again, only benzannelated derivatives are known. As with the approaches to benzaza-[76], benzoxa-[77] and benzthia-phospholes[264] already discussed, the synthesis uses cyclization reactions of suitably substituted phenylphosphines, in this case the alkali metal phosphides of 1,2-diphosphinobenzenes (equation 129).



(129)

2. *Systems containing two additional heteroatoms*

Most of these systems reported are 1*H*-1,2,4λ^3-diazaphospholes and the first synthetic routes were reported[4,128,140,265,266], almost simultaneously by four groups in 1984. Some of these syntheses have been considered briefly in Section III.E. Variation on three routes were reported. In the first, the stable (at room temperature) phospha-alkyne *t*-BuC≡P reacts smoothly[265,266] with diazo compounds in regiospecific [3 + 2] cycloaddition reactions in which the initially formed 3*H*-cycloadducts aromatize via a [1,5] sigmatropic rearrangement (equation 130). Similar reactions occur[252] with the transient phospha-alkyne HC≡P which is generated[253] from *t*-BuC≡P under flash thermolytic conditions.

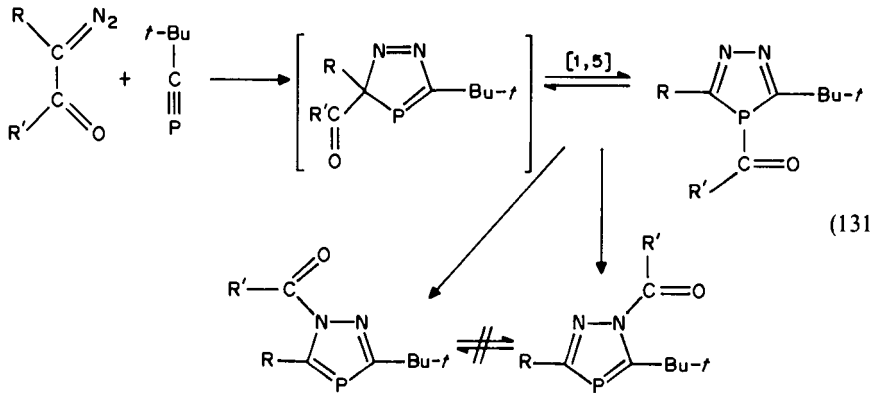


(130)

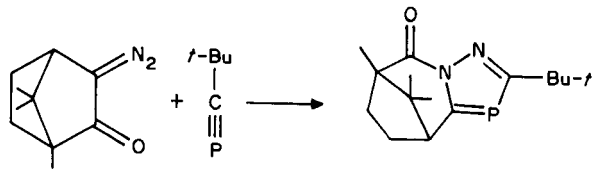
Regitz and co-workers[267] have extended the scope of this type of reaction in several ways. Thus, in addition to more detailed studies of the reaction of simple mono- and di-substituted diazoalkane derivatives with *t*-BuC≡P to give compounds of type **119**, reaction with diazoketones (e.g. equations 131–133) and diazophosphoryl compounds (e.g. equation 134) have been carried out with the formation of a wide variety of substituted and polycyclic 1*H*-1,2,4-diazaphospholes and, sometimes, their 4*H*-isomers.

In a further study of these reactions[148], as already mentioned briefly in Section III.E, the same group has shown that certain spiro-3*H*-1,2,4-diazaphospholes may be photolyzed at −40 °C to give another previously unknown phosphorus heterocyclic system, the 2*H*-phosphirenes (equation 135).

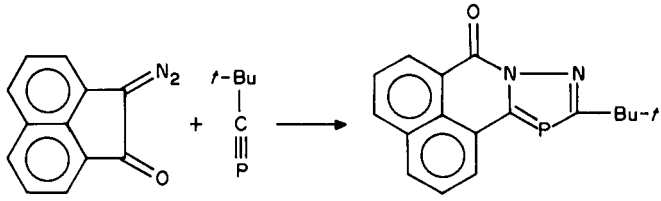
Clearly, phosphaalkynes can be expected to react with other 1,3-dipoles to give a variety of phospholes containing additional heteroatoms. This is indeed the case and such



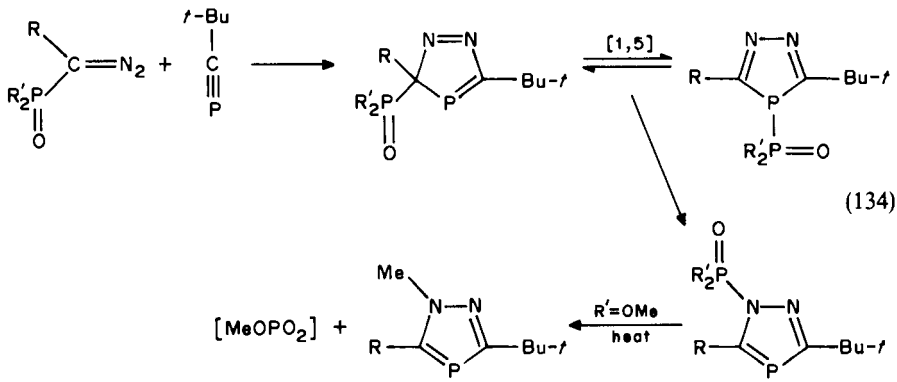
(131)



(132)

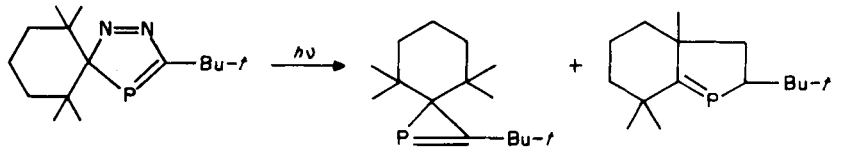


(133)



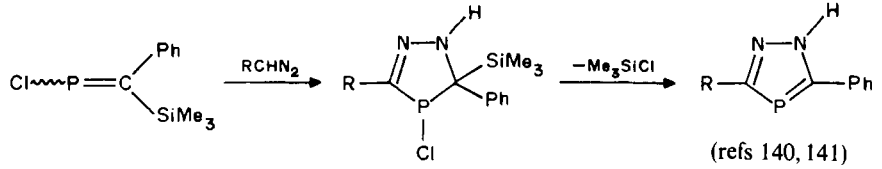
(134)

reactions will be explored shortly. However, other routes to 1,2,4-diazaphospholes will first be discussed. The second route to these systems is similar to that described above in that certain phosphaalkene derivatives undergo[128,140,141,268] [3 + 2] cycloaddition reactions with diazo compounds and the initially formed adduct undergoes an elimination



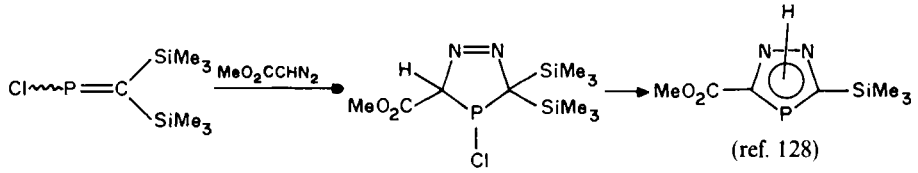
(135)

reaction to produce the fully unsaturated, aromatic, 1,2,4-diazaphosphole (equations 136 and 137) with a wide variety of substituents on the ring.



(refs 140, 141)

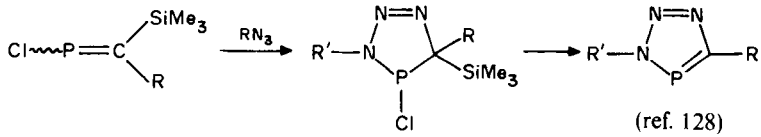
(136)



(ref. 128)

(137)

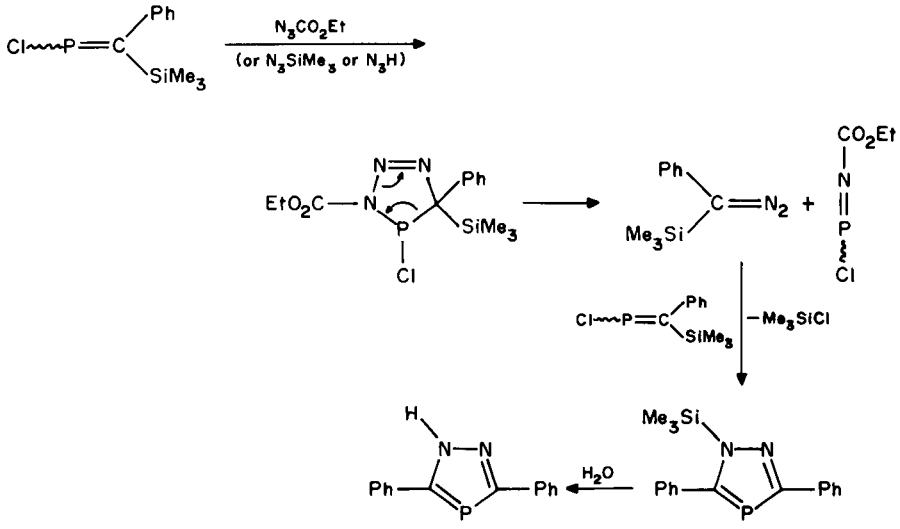
As mentioned for the phosphaalkyne reactions discussed above, suitably substituted phospha-alkenes will react with other 1,3-dipoles to give products which will mostly be discussed later. However, one of these should be discussed here since, although in the general case the products are outside the scope of this survey, under certain circumstances a further reaction occurs which can lead to 1,2,4-diazaphospholes. Thus, certain *P*-chlorophospha-alkenes react[128,252,269] with azides to give, ultimately, triazaphospholes (as do also phospha-alkynes[252,265,266,270]) as shown in equation 138. In certain circumstances, however, the initially formed cycloadduct undergoes[269] a retro-cycloaddition to give a diazoalkane derivative which reacts with more of the chlorophospha-alkene to give a 1,2,4-diazaphosphole (equation 139).



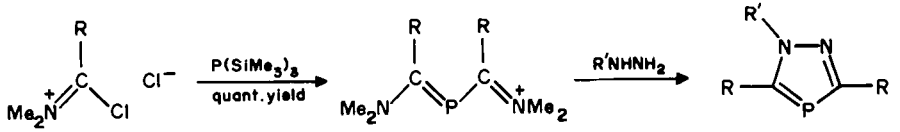
(ref. 128) (138)

The third route, reported in 1984[4], was the room-temperature to 100 °C condensation of 1,3-bis(dimethylamino)-2-phospha-allyl chlorides with hydrazines (equation 140). Again, several 1,2,4-diazaphospholes were prepared by this route.

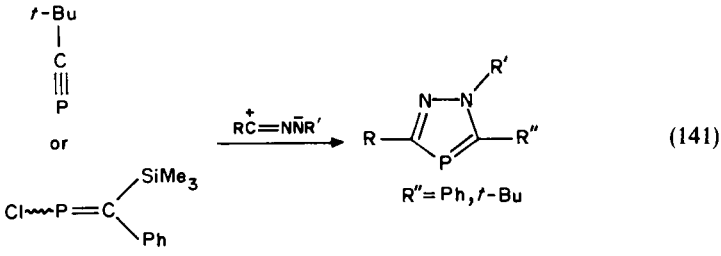
Since these early reports, other routes to 1,2,4-diazaphospholes have been developed. These are similar in many respects to reactions discussed in Section IV.C.1.a for the synthesis of 1,3-azaphospholes. They include the reactions of phospha-alkynes[265] or certain phospha-alkenes[268] with nitrile imines (equation 141), $P(SiMe_3)_3$ with 1,3,4-



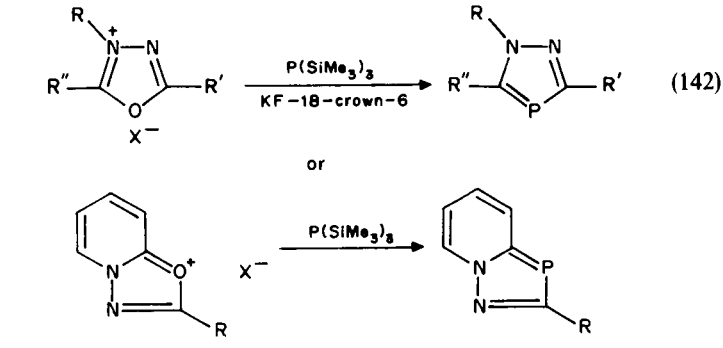
(139)



(140)

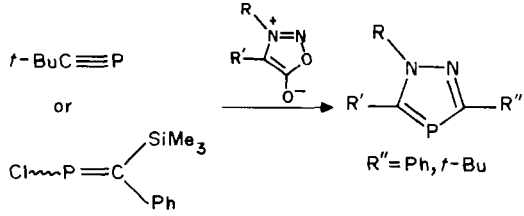


(141)



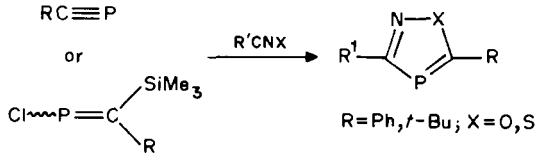
(142)

oxadiazolium salts[271] or oxadiazolopyridinium salts[259] (equation 142), or phospha-alkynes[253] and some phosphaalkenes[271] with 'sydnones' (equation 143).

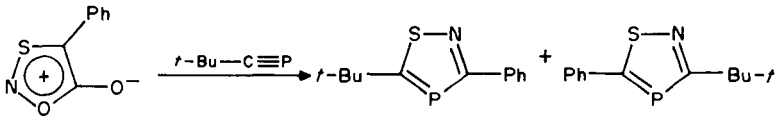


(143)

Other phospholes containing two additional heteroatoms have been prepared by routes similar to those outlined above. These include 1,2,4-oxazaphospholes, prepared[128,252,265,269] by [3 + 2] cycloadditions of phospha-alkynes or phospha-alkene derivatives with nitrile oxides (equation 144) and 1,2,4-thiazaphospholes prepared either by treatment of phospha-alkynes with nitrile sulfides (equation 144) or 1,3,2-oxathiazolium-5-olates (equation 145)[253].



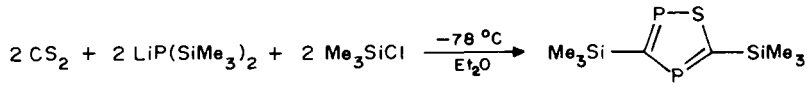
(144)



(145)

It is interesting that it has been reported very briefly that nitrile ylids also react with the *P*-chlorophosphaalkenes discussed above to give 1,3-azaphospholes[269].

The only other report of a phosphole containing two other heteroatoms not bonded to the phosphorus concerns a 1,2,4-thiadiphosphole which is prepared[272] (equation 146) by a route entirely different to those outlined above.



(146)

Continued rapid development in this area of phosphorus heterocyclic chemistry is to be expected as, indeed, is the development of syntheses of compounds containing two-coordinate phosphorus in general.

V. SYNTHESIS OF FULLY UNSATURATED SIX-MEMBERED HETEROCYCLES OF PHOSPHORUS: λ^3-PHOSPHININES, FUSED-RING λ^3-PHOSPHININES AND λ^3-PHOSPHININES CONTAINING ADDITIONAL HETEROATOMS

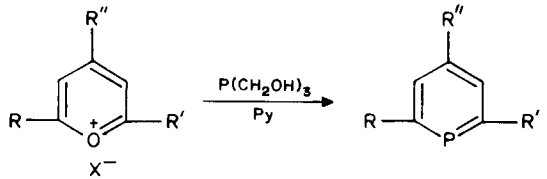
A. λ^3-Phosphinines and Fused-ring Derivatives

λ^3-Phosphinines of the type **120**, previously known[273] as λ^3-phosphorins, are even more recent additions to the range of known phosphorus heterocycles than are the simple

phospholes discussed in Section IV.A. The first report[2] of the synthesis of the system (as the heavily substituted derivative **1**) came in 1966, 3 years after the λ^5-phosphinine **121** had been reported[274]. The λ^5-phosphinines are largely outside the scope of this chapter although, as will be seen shortly, they may sometimes be converted into or derived from λ^3-phosphinines. The chemistry of λ^5-phosphinines has been reviewed[275,276]. This first reported synthesis of a λ^3-phosphinine constituted much more than just the announcement of a previously unknown phosphorus heterocycle. Indeed, it was a landmark in the development of organophosphorus chemistry in general since it was the first piece of evidence that phosphorus can enter into pπ bonding to give stable compounds containing two-coordinate phosphorus. Since then, many routes to λ^3-phosphinines have been developed. The chemistry of these systems was last reviewed systematically in 1982[277,278].

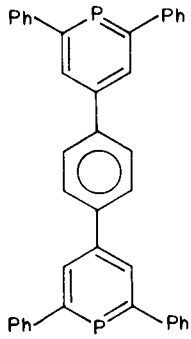
(120) **(121)**

The first published approach[2] leads to heavily substituted λ^3-phosphinines, although the procedure itself is simple. Thus, pyrylium salts are treated with tris(hydroxymethyl)phosphine in pyridine with the elimination of formaldehyde and water (equation 147).

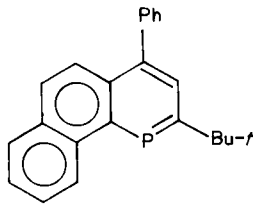


(147)

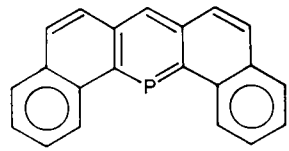
In all instances, the 2- and 6-positions are substituted in the product and, generally, the 4-position is also substituted. Other substitution patterns have been reported. A variety of monocyclic λ^3-phosphinines have been prepared[279,280] by this route, as have the *p*-terphenyl-related system **122**[62] and the fused-ring derivatives **123**[281] and **124**[282]. Yields range from 4 to 29% in these syntheses.



(122)



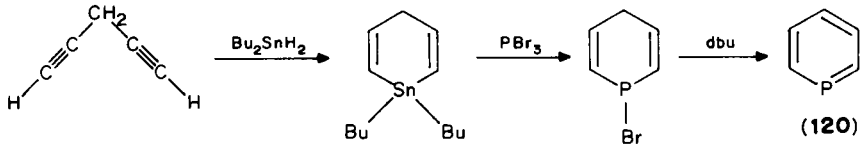
(123)



(124)

Two variations on this synthesis were published shortly after the initial report. In the first[283] tris(hydroxymethyl)phosphine is replaced with tris(trimethylsilyl)phosphine in acetonitrile and in the second[284], it is replaced with phosphine in the presence of mineral acid. The phosphine is usually generated from phosphonium iodide. Yields as high as 62% were obtained using the silylphosphine and in the range 15–81% with phosphine itself.

The next significant development came[285] with the synthesis of the parent λ^3-phosphinine **120**. The reaction, outlined in equation 148, utilizes a novel (at that time) phosphorus for tin replacement reaction to construct the ring and the remaining unsaturation is introduced by a dehydrohalogenation reaction. In this synthesis, final purification was achieved by preparative gas-liquid chromatography.

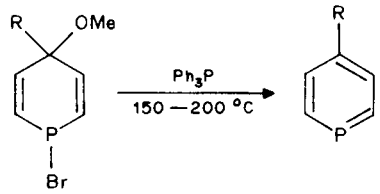


(120)

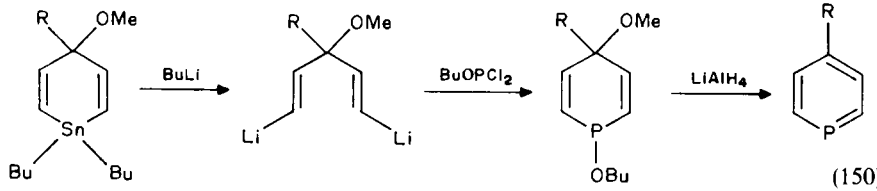
(148)

The reaction has been extended[286] to the synthesis of both 2-substituted and 2,6-disubstituted λ^3-phosphinines, which are obtainable in yields of up to 45%.

Clearly, the route outlined in equation 148 has the potential to be used for the synthesis also of 4-substituted λ^3-phosphinines. This has indeed been achieved by suitable modification of the procedure. Two such modifications are outlined in equations 149[287,288] and 150[289]. The first of these gives the product in yields of 19–42% whereas the second can give yields as high as 83%.

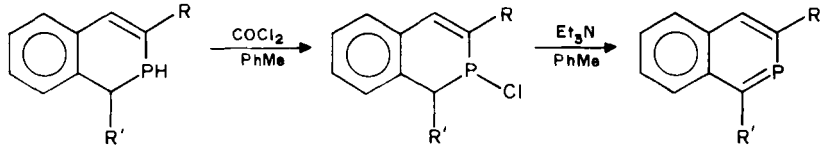


(149)

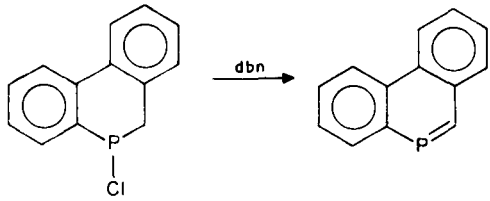


(150)

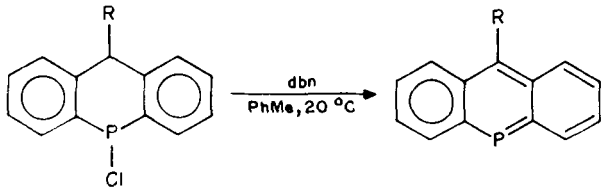
The elimination of hydrogen halide from *P*-halogenated phosphorus heterocycles, as occurs in the final step of equation 148, has also proved useful in the synthesis of fused-ring λ^3-phosphinines although, generally, the *P*-chloro compounds are formed by conventional cyclization reactions rather than the phosphorus for tin exchange reaction shown in equation 148. The method is sufficiently versatile to allow the formation of benzo[*c*]-λ^3-phosphinines[290] (equation 151), dibenzo[*b,d*]-λ^3-phosphinines[291] (equation 152) and dibenzo[*b,e*]-λ^3-phosphinines[291] (equation 153). Whereas the tricyclic systems are of limited stability, the bicyclic systems are stable and isolable in yields of up to 64%.



(151)



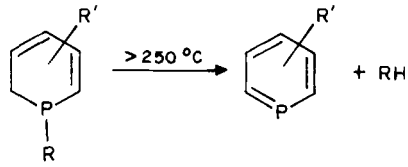
(152)



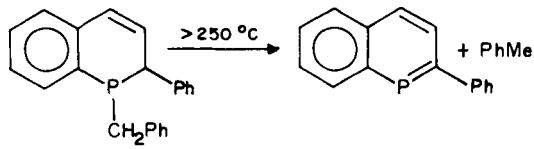
(153)

Other elimination reactions of suitably substituted 6-membered phosphorus heterocycles can be made to occur thermally. These fall into two broad classes, viz. thermal elimination from 1,2- or 1,4-dihydro-λ^3-phosphinines or thermally induced reversions of λ^5-phosphinines to λ^3-phosphinines by elimination of the two exocyclic substituents on the phosphorus atom. Considering the first of these processes, suitable 1,2-dihydro-λ^3-phosphinines (which may be prepared by a variety of routes as reported below) are those in which the phosphorus bears a good leaving group and the sp^3 carbon adjacent to the phosphorus bears a hydrogen atom.

The basic reaction is illustrated in equation 154 and, for this procedure, yields in the range 53–75% have been obtained[62,292,293], depending on the substitution pattern of the dihydrophosphinine and the nature of the leaving group on P. The method has also proved to be useful in the synthesis of fused-ring λ^3-phosphinines (equation 155)[294].

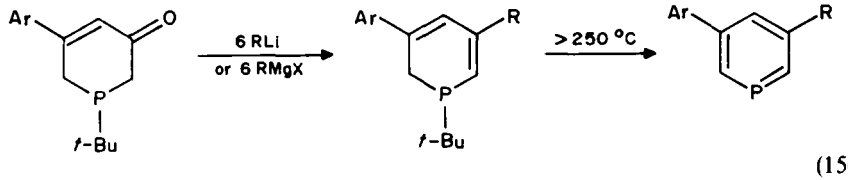


(154)

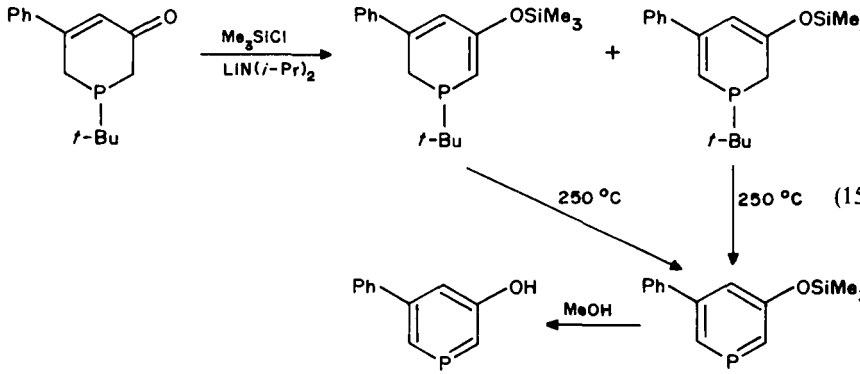


(155)

Two other examples of λ^3-phosphinine syntheses, in which the final step is the kind of elimination outlined above, will be specifically noted here. The reason for this is that the starting material (a 5-oxo-1,2,5,6-tetrahydro-λ^3-phosphinine derivative; see Section III.B and ref. 87) is very useful in that it may also be used as a starting material for other λ^3-phosphinine syntheses (discussed below) which follow entirely different reaction pathways and sometimes lead to functionally substituted products. The two reactions are shown in equations 156,[87,295] and 157[103]. The second of these syntheses led to the first known functionally substituted λ^3-phosphinine.

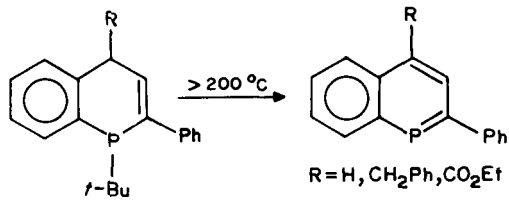


(156)



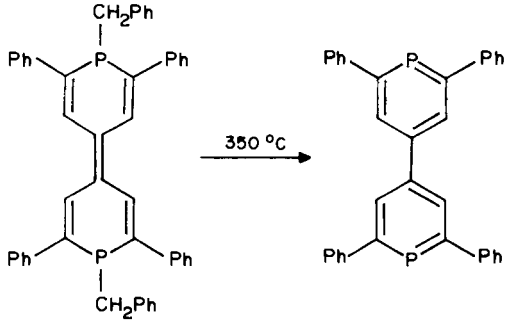
(157)

Thermally induced 1,4-eliminations are also known but, apparently, only for bicyclic systems as yet (equation 158)[296]. A related elimination is that shown in equation 159[62].



(158)

The other major thermal elimination route to λ^3-phosphinines is, as already mentioned, elimination of the two exocyclic P substituents in λ^5-phosphinines. The general reaction is summarized in equation 160; elimination can be made to occur with a wide variety of substituents on the phosphorus atom. Systems which undergo this reaction include those in which $R' = R'' = CH_2Ph$[292], NAr_2[297], Cl (in the presence of triphenylphosphine)[298], Br[278,298], SR[278,298]; $R' = CH_2Ph$, $R'' = CPh_3$[292]; and $R' = OMe$, $R'' = t$-Bu[299]. In the last example cited, the product is a fused-ring derivative of λ^3-phosphinine.



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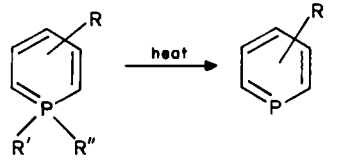
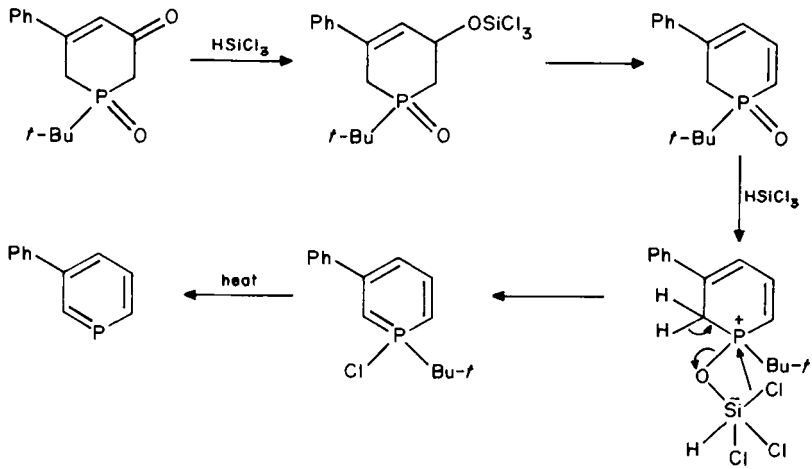


(160)

Although the above reactions are interesting, they were, at the time of their discovery, somewhat self-defeating in terms of their value as synthetic routes for λ^3-phosphinines since most known λ^5-phosphinines were themselves prepared from λ^3-phosphinines[276]. Very few routes to λ^5-phosphinines which did not involve λ^3-phosphinine intermediates were known[274,300]. However, more recently, it has been found that 5-oxo-1,2,5,6-tetrahydro-λ^3-phosphinine derivatives are extremely useful as precursors to λ^5-phosphinines and, ultimately, λ^3-phosphinines. Indeed, it is sometimes not necessary to isolate the λ^5-phosphinine as an intermediate. In the first paper on this topic[301], in addition to reporting in detail on the synthesis of the starting materials for these reactions, Märkl *et al.* established the reaction pathway outlined in equation 161. In a subsequent paper[302], the syntheses of both 3,4- and 3,5-disubstituted λ^3-phosphinines by a modification of the route outlined above were reported. The results of this investigation are summarized in a condensed form in equation 162.



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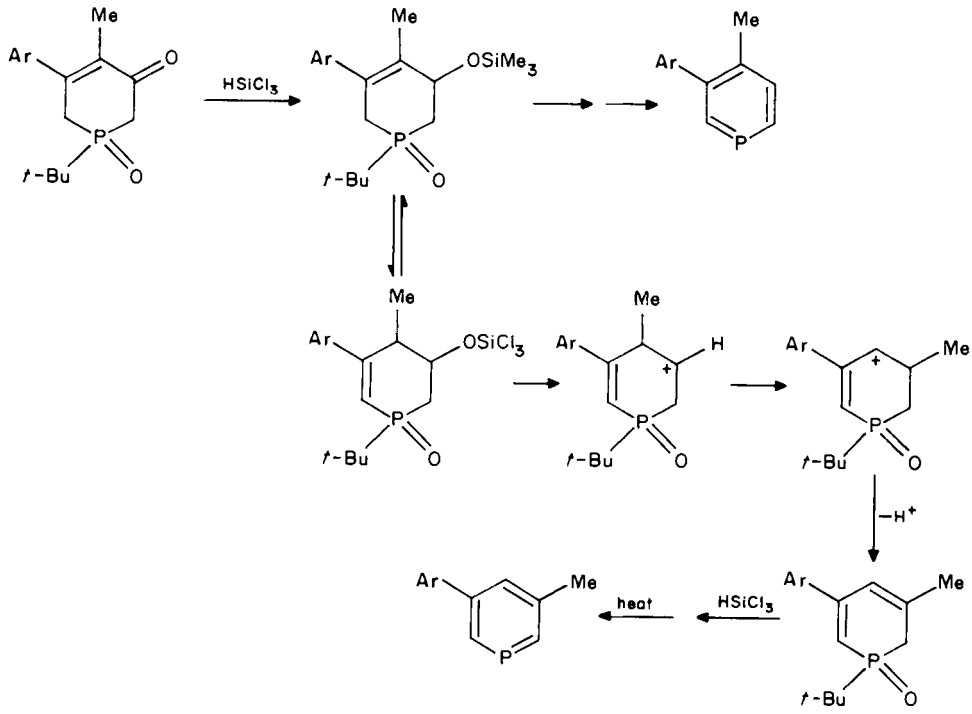
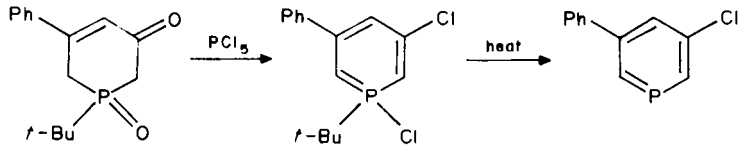


(162)

Two extensions of the scope of this type of reaction have also been published. In the first[303], it was found that $HSiCl_3$ may be replaced by PCl_5 with similar results except that ring chlorination also occurs (equation 163).

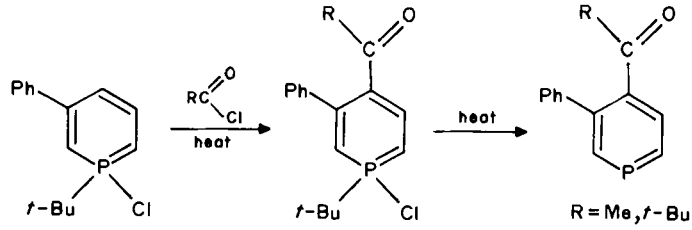


(163)

The analogous bromo-λ^3-phosphinine may also prepared[303] by replacing PCl_5 by PBr_3. If a very large excess of PCl_5 is used, complex mixtures of tri- and tetra-chloro λ^5- and λ^3-phosphinines are obtained and some dichloro-λ^3-phosphinines have also been isolated by suitable modifications of the procedure.

In the second of these extensions of the basic process, Märkl and Hock[304] found that the *P*-chloro-λ^5-phosphinines obtained as intermediates in the reactions of 5-oxo-1,2,5,6-tetrahydro-λ^3-phosphinines with $HSiCl_3$ may be acylated with acid chlorides to give 4-acyl-λ^5-phosphinines, which can be converted by heating into the corresponding λ^3-phosphinines (equation 164).

Several other syntheses of λ^3-phosphinines are known. Among these are reactions in which the six-membered ring is first constructed by ring expansion of a phosphole derivative. This is followed by treatment of the product with either P_4S_{10} or Lawesson's reagent and, in turn, the product of this reaction is heated strongly with Raney nickel. An



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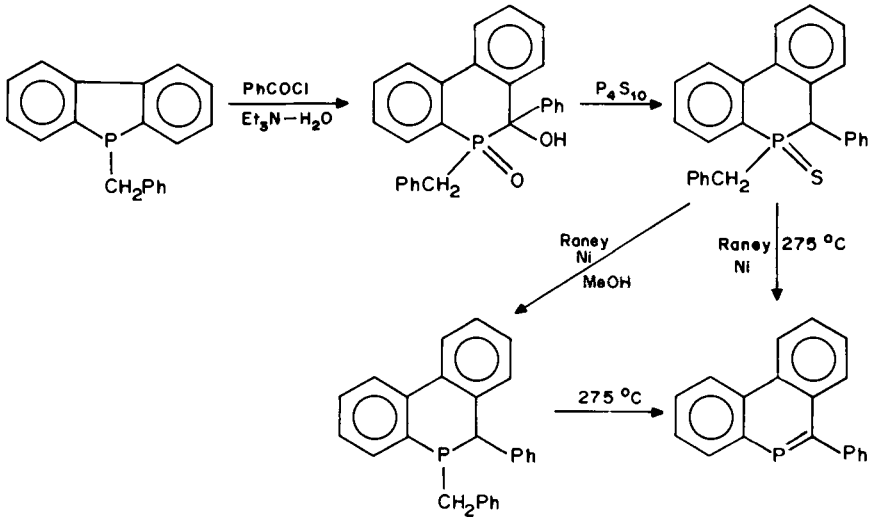
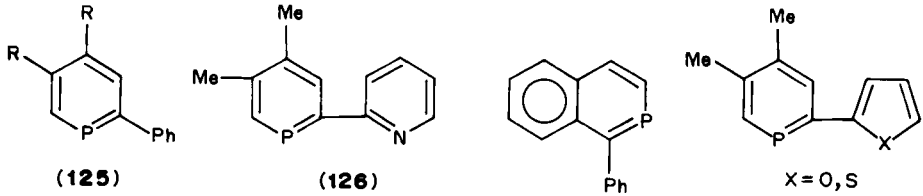


(165)

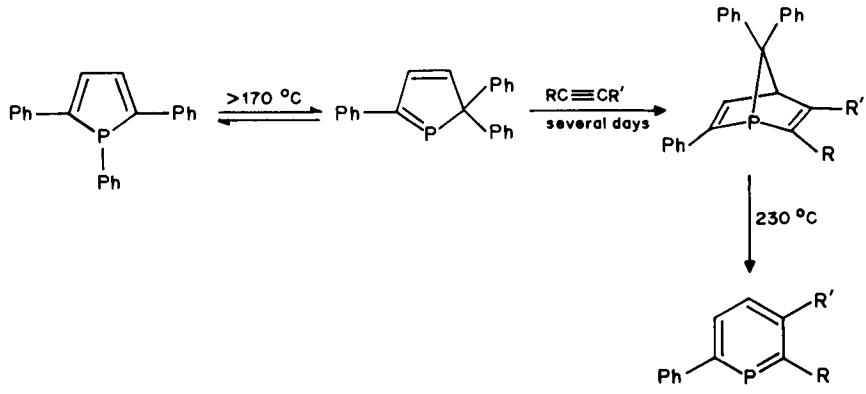
early example of this synthesis is shown in equation 165[305]. The last step of this synthesis is, therefore, another example of a thermal elimination reaction of a 1,2-dihydrophosphinine of the type already discussed.

The route is useful for the synthesis of a wide variety of λ^3-phosphinine derivatives including **125** (R = H)[215]. **125** (R = Me)[305], **126**[305], **127**[235] and **128**[215].



(125) **(126)** **(127)** **(128)**

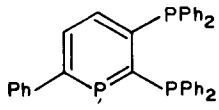
Another route to λ^3-phosphinines based on phosphole starting materials was also developed by Mathey's group. It is based on the observation (referred to in Section IV.B) that certain 1*H*-phospholes will, on heating, undergo [1,5] sigmatropic rearrangements to give 2*H*-phosphole derivatives (equation 109). Although most of these 2*H*-phospholes cannot be isolated, they can be trapped[229,306] in Diels–Alder-type reactions. Thermolysis



(166)

of the resulting adduct results in the formation[229,306] of a λ^3-phosphinine, usually in good yield. The process is outlined in equation[166].

In Mathey's studies, it was shown that in this reaction, considerable variation can be achieved for R and R' (R = R' = Ph, Et; R = Me, R' = Ph; R = H, R' = Ph) but that the bulkier substituent is always R'. Further, with very bulky substituents on the alkyne (as in, for example, $Me_3SiC{\equiv}CSiMe_3$), the cycloaddition will not normally occur. In an interesting extension of the reaction, **129** has been prepared[307] from 1,2,5-triphenylphosphole and bis(diphenylphosphino)acetylene. It should be noted in passing, that, in the ^{31}P NMR spectrum of **129**, the three-bond coupling between the two side-chain P atoms is 178 Hz. This extraordinarily high value has been attributed[307] to a 'through-space' coupling mechanism.



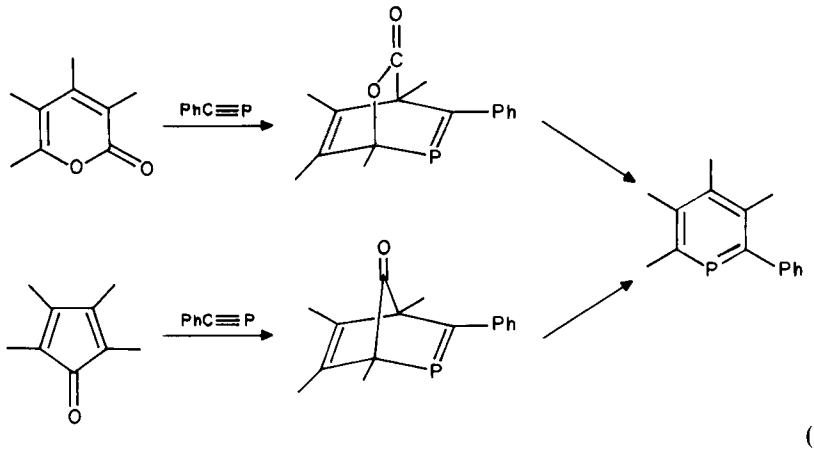
(129)

A third synthesis based on phosphole-type starting materials is more appropriately discussed together with related reactions as outlined below.

One further general route to λ^3-phosphinines, which is particularly useful in that it can sometimes be used to prepare functionally substituted systems, has been reported. In this type of synthesis, a phospha-alkene or phospha-alkyne undergoes a [4 + 2] cycloaddition with a suitable diene (cyclic or acyclic) and this is followed by one or more elimination reactions which may or may not be spontaneous. The first report came in 1982 by Märkl *et al.*[308], who showed that both α-pyrones and cyclopentadienones react with PhC≡P (derived thermolytically from $ClP{=}C(SiMe_3)Ph$) to give, ultimately, λ^3-phosphinines. The two reactions are summarized in equation 167; λ^3-phosphinines with a variety of alkyl or aryl substituents have been obtained by this procedure.

In a similar reaction, Rösch and Regitz[3] have shown that phosphole sulfides behave towards *t*-Bu C≡P in a similar manner to cyclopentadienones (equation 168).

Carrié and coworkers have carried out related cycloadditions using *P*-chlorophospha-alkenes and, by using a variety of modifications of the route and the conditions, achieved



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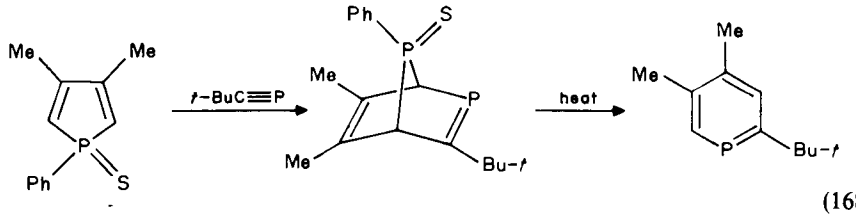

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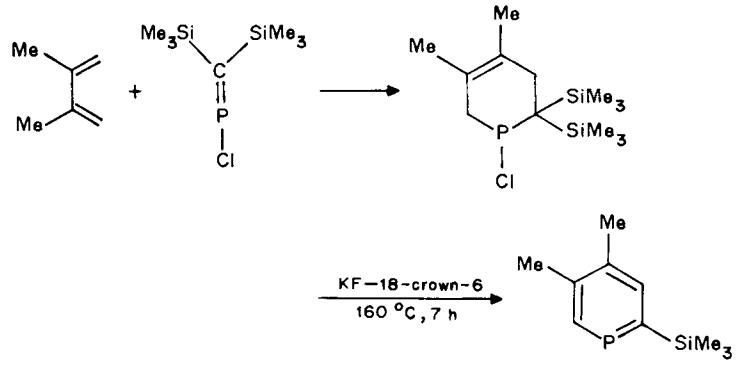
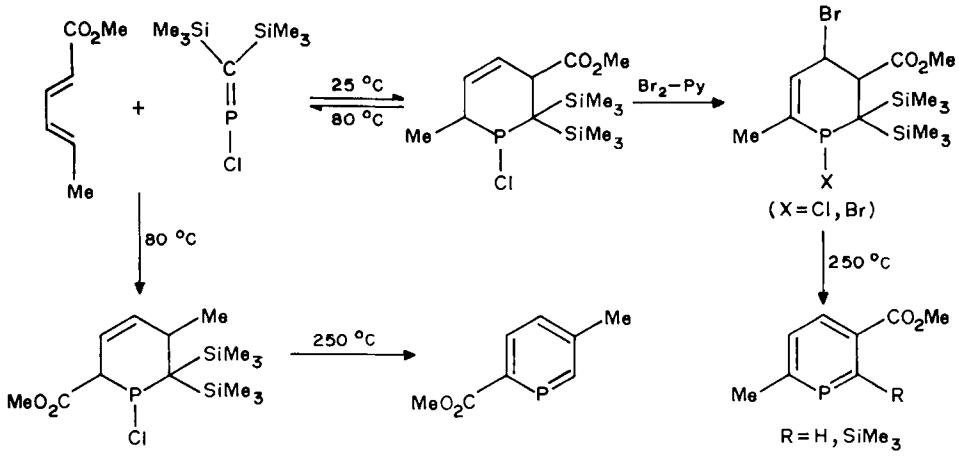


(169)

the synthesis of several functionally substituted λ^3-phosphinines. The first of these syntheses[128] is shown in equation[169]. However, although the yield was reasonable (30%), the product was not isolated and the conditions are such that the procedure has, at best, limited utility.

The synthesis was later modified[268,309] in several ways to yield a variety of functionally substituted λ^3-phosphinines (equations 170[309], 171[309] and 172[268,309]).

The acid and amide derivatives of **130** were also prepared[268] and a more detailed account of some of these syntheses has appeared recently[130].



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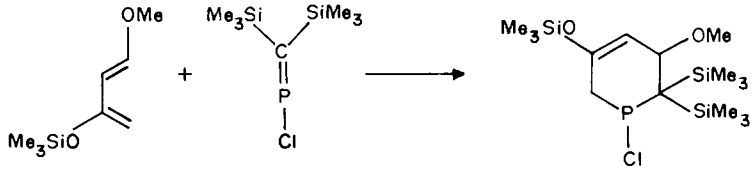

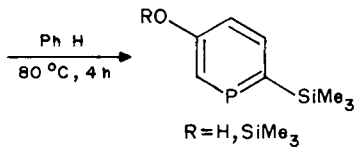

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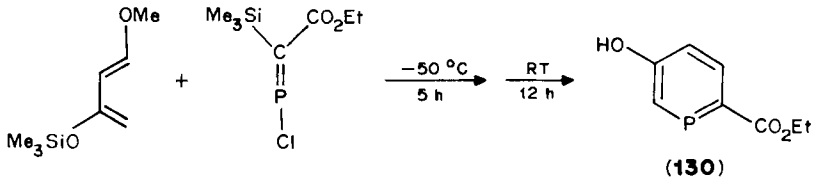


(130)

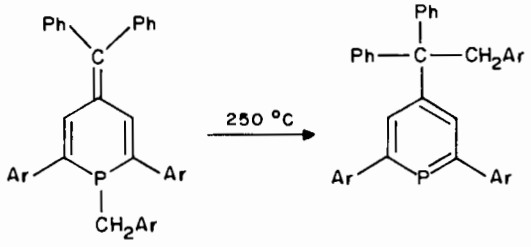
(172)

A few other, less general, syntheses of λ^3-phosphinines have been reported. These include the rearrangement shown in equation 173[293] and the 1,4-cycloaddition reaction of 2,4,6-triphenyl-3-aza-λ^3-phosphinine with dimethyl acetylenedicarboxylate (accompanied by the elimination of benzonitrile)[36], which was discussed in Section III.D.

The two remaining λ^3-phosphinine syntheses in the literature involve not so much the construction of the phosphinine ring but the conversion of one phosphinine into another. In the first of these[310], the 3-chloro-λ^3-phosphinines prepared by treatment of 5-oxo-1,2,5,6-tetrahydro-λ^3-phosphinines with PCl_5, as discussed earlier in this section, react

smoothly with lithiated secondary amines in addition–elimination reactions to give 3-dialkylamino-λ^3-phosphinines (equation 174).

The second of these λ^3-phosphinine interconversions is shown in equation 175[311]. More will be said later about the unusual phosphinine sulfide intermediate in this reaction.



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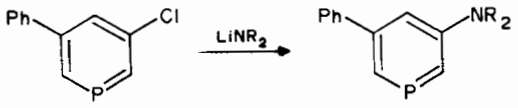

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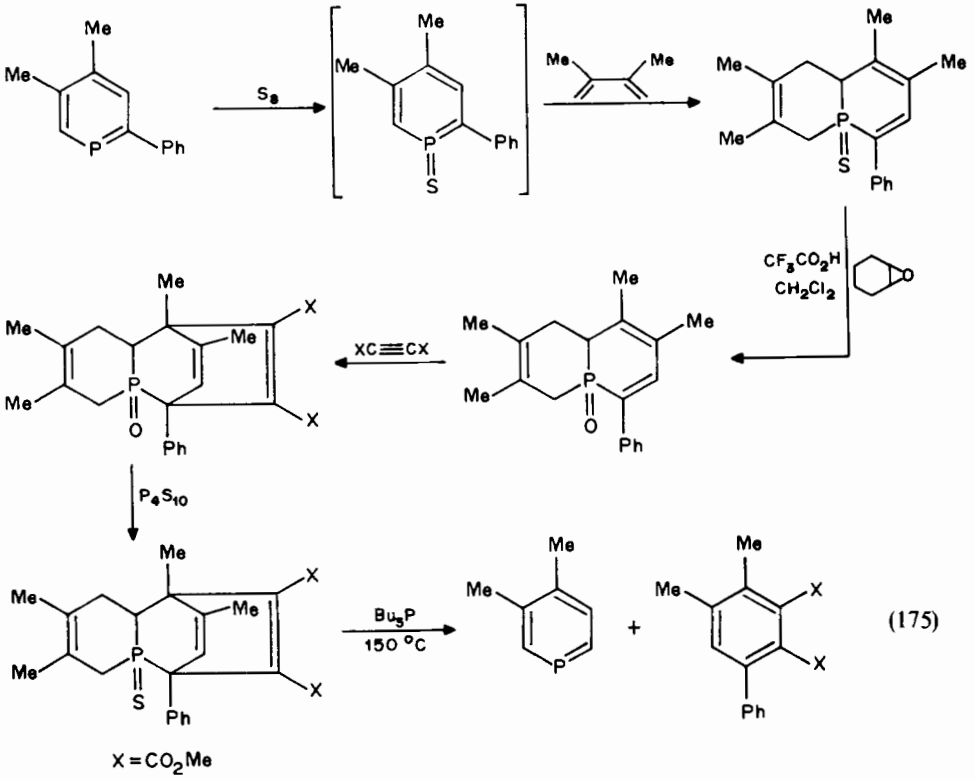
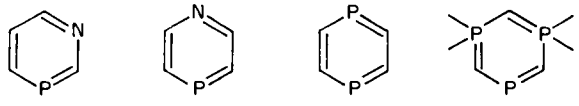


(175)

B. λ^3-Phosphinines Containing Additional Heteroatoms

Only four such systems are known: 3-aza-λ^3-phosphinines of type **131**, 4-aza-λ^3-phosphinines of type **132**, 1,4-λ^3,λ^3-diphosphinines of type **133** and $1\lambda^5$, $3\lambda^5$, $5\lambda^3$-triphosphinines of type **134**.



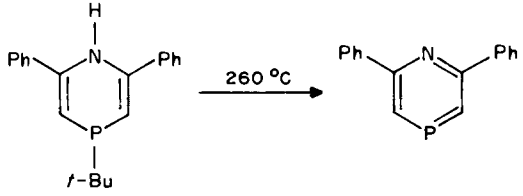
(131) **(132)** **(133)** **(134)**

The two azaphosphinine systems have been prepared by methods very similar to reaction sequences already described for the synthesis of simple λ^3-phosphinines and the approaches used are shown in equations 176[144] and 177[102].

The 1,4-diphosphinine system was synthesized from very heavily substituted bicyclic compounds either by thermolysis[312] (equation 178) or by treatment with 1,3-dipoles such as azides or diazo compounds (equation 179)[313].

The last of these systems (**134**) was prepared[314] by a novel ring expansion of a λ^5,λ^5-diphosphete as shown in equation 180.

(176)



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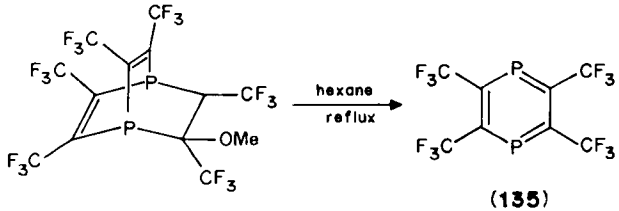
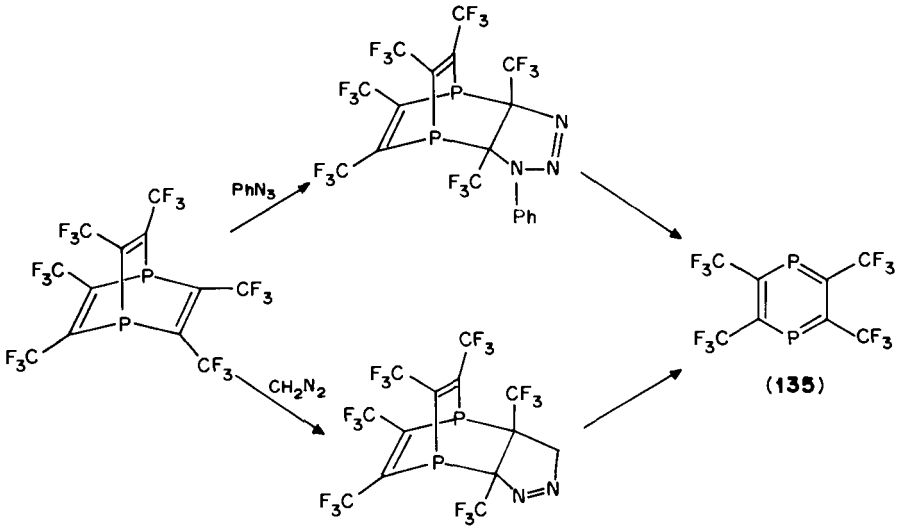


(135) (178)



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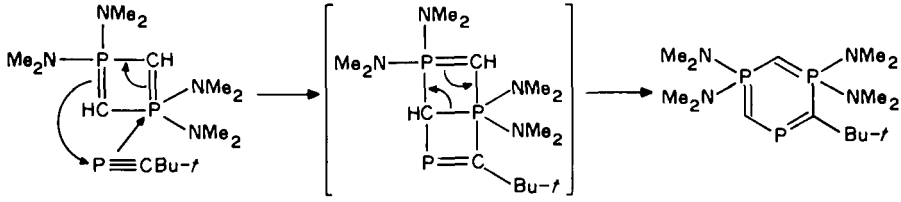


(180)

VI. SOME SPECIAL PROPERTIES OF FULLY UNSATURATED FIVE- AND SIX-MEMBERED λ^3 -PHOSPHORUS HETEROCYCLES

Since much of the reaction chemistry of 1*H*-phospholes and, to a lesser extent, of λ^3-phosphinines has been covered in some detail in earlier sections in a variety of contexts and, in addition, other properties of these systems have been reviewed extensively elsewhere, this section is intended to give only a brief overview of some of the more noteworthy properties of these heterocycles.

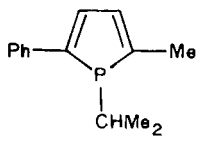
A. Electronic Structure

The apparent similarity of 1*H*-phospholes to the heterocyclopentadienes furan, pyrrole and thiophene on the one hand and of λ^3-phosphinines to benzene and pyridine on the other is obvious. What is not immediately clear, however, is how closely the electronic structures of the phosphorus heterocycles parallel those of their non-phosphorus counterparts, and much attention has been given to this interesting problem.

1. 1H-Phospholes

It has long been known that furan, pyrrole and thiophene are planar, 6π-electron Hückel aromatic systems having significant delocalization energies. At first sight, phosphole has the potential also to be such a system and, over a period of about 15 years, many studies (NMR, X-ray crystallographic, reactivity of the phosphorus non-bonding electron pair, theoretical) have been published regarding this problem. The matter has been thoroughly reviewed elsewhere[189-191] and the present position is that simple phospholes are pyramidal species (at room temperature) with only a small interaction of the phosphorus non-bonding orbital with the π system. The more significant observations and deductions are briefly summarized in the following discussion.

a. NMR studies. ^{31}P, ^{13}C and ^{1}H chemical shift data have been recorded for a variety of phospholes[189-191], but little can be deduced from them regarding the degree of electron delocalization in the system. The one NMR study which throws some light on this problem was carried out by Egan *et al*[217]. In this study, the pyramidal inversion barrier of the phosphorus atom in the dissymmetric phosphole derivative **136** was measured using the ^{1}H NMR coalescence technique. A value of about 67 kj mol^{-1} was obtained, which is considerably below that expected for a normal tertiary phosphorus atom constrained by a five-membered ring (ca 150 kj mol^{-1}). The implication is that there is some interaction between the phosphorus non-bonding pair orbital and the diene system but that the degree of delocalization in the planar inversion transition state is insufficient to change the phosphorus hybridization from sp^3 to sp^2.



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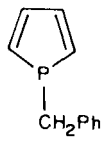

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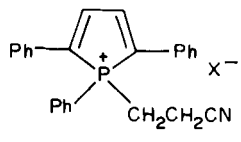

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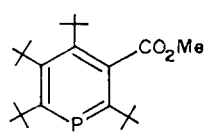


(139)

b. X-ray crystallographic studies. There have been four such investigations[228,315-317], but three of these were on heavily substituted phospholes and it is probable that only the study[315] on the very simply substituted phosphole **137** can make any contribution regarding the electronic structure of the phosphole ring. The most important feature of the molecular structure is that the ring P—C bonds are significantly shorter than one would expect from the sum of the single-bond covalent radii of the two atoms. Some small degree of delocalization may, therefore, be indicated and this is consistent with the low barrier to inversion at the phosphorus atom noted above.

c. Reactivity of the phosphorus non-bonding electron pair. Many reactions at the phosphorus atom of phospholes have been reported. These include oxidation, quaternization and metal complex formation (about which more will be said later). Oxidation and quaternization have been discussed at length elsewhere[189,190] and, in any case, these reactions offer little information regarding the electronic structure of phosholes. There are, however, two investigations which offer some information regarding the availability of the non-bonding pair for reaction. Thus, it has been found[200] that 1-methylphosphole has the unusually low pK_a value of 0.5 and phospholes are, therefore, much weaker bases than conventional tertiary phosphines. In addition, Farnham and Mislow[318] have established

that 1-(2-cyanoethyl)phospholium salts, such as **138**, undergo base-catalyzed retro-cyanoethylation reactions much more rapidly than do similar salts of other cyclic and acyclic phosphines, indicating again some degree of lone-pair delocalization. In passing, it should be noted in connection with the protonation studies referred to above that (a) phospholes, unlike the aromatic pyrroles, protonate[319,320] at the phosphorus atom and (b) it may be that the low basicity of phospholes arises, at least in part, from the possible degeneracy[321] of the n and highest π orbitals.

d. Theoretical studies. There have been at least nine theoretical treatments of the phosphole system. These too have been discussed thoroughly in earlier reviews[189,190] and only a summary is necessary here. Briefly, the results of these treatments have been largely mutually contradictory in that some have been interpreted as being consistent with a high degree of delocalization whereas others indicate a completely non-aromatic system. It is worth noting, however, that one of the most recent (1975) of these treatments[322], based on *ab initio* methods, indicates that the delocalization energy in phosphole is of the order of 54 kj mol^{-1}, which is consistent with the deductions from the NMR, X-ray and reactivity studies cited above. Computational techniques and theoretical treatments have improved enormously since 1975, however, and a more modern treatment may now be in order.

2. λ^3-Phosphinines

The situation is much clearer with λ^3-phosphinines than with 1*H*-phospholes. Again, the current position has been thoroughly reviewed[323] and only a brief digest will be given here. Essentially, all of the evidence is consistent with λ^3-phosphinines being 6π-electron Hückel-type aromatic systems in which the phosphorus atom enters into (3p–2p)π bonding. The ready availability of the unsubstituted system[285] has contributed greatly to the solution of the problem.

NMR data, although interesting and consistent with a significant degree of Hückel-type delocalization within the ring[323], offer no direct evidence for such an electronic structure. However, electron diffraction studies[324] show that the parent molecule is planar and symmetrical with P—C bond lengths of 1.73 Å, which is strongly supportive of the presence of a π electron system similar to that present in benzene and pyridine. Microwave data[325] give similar results.

X-ray measurements have been made on substituted λ^3-phosphinine derivatives such as 2,6-dimethyl-4-phenyl-λ^3-phosphinine[326]. As with the unsubstituted system, it was found that the phosphorus-containing ring is very close to planar, the ring is symmetrical and the P—C bonds are significantly shorter than the sum of the single-bond covalent radii. Recently, Maas *et al.*[326] examined the X-ray crystal structure of the very heavily substituted derivative **139**. This molecule is highly distorted with a twist-boat type of arrangement. The two P—C bonds are no longer equal, or nearly so, but are still short at 1.730 and 1.758 Å.

Another powerful tool for probing the electronic structure of molecules which are stable in the gas phase is ultraviolet photoelectron spectroscopy. Such measurements have been made for the parent λ^3-phosphinine[327] and also for certain substituted derivatives[328]. The results obtained for the unsubstituted system[327] are in excellent agreement with what would be expected for a molecule having a π electronic structure similar to that of benzene.

There have been several theoretical treatments of the λ^3-phosphinine system. Oehling and Schweig[329] used the CNDO/2 approach whereas others have used *ab initio*[330] and other[331] approaches. Although there are some differences in the deductions from the various approaches, they offer strong support for a Hückel-type 6π-electron structure.

As noted earlier, phospholes have an anomalously low basicity which is, perhaps, associated with some delocalization in the system. λ^3-Phosphinines, however, do not

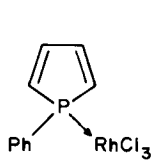
require the non-bonding pair for an aromatic structure and one would therefore expect that λ^3-phosphinines would have, like pyridine, appreciable basic character. This is not the case. Thus, λ^3-phosphinine (and its simple derivatives) will not form phosphininium salts, nor will it alkylate at the phosphorus atom[323]. This point has received considerable attention[143,323,329b,332]. Several explanations have been advanced, including an orbital sequence[329b] which places the non-bonding orbital below the highest π orbital in energy, leading to a pK_a value of -10 for the phosphininium ion. An alternative explanation[323] is that the ring system is unable to change its geometry in the required manner on protonation or alkylation. Evidence, based on a correlation between core ionization energies and proton affinities, has recently been presented[333] to support the latter view. In this connection, it should be mentioned that the proton affinity of λ^3-phosphinine has recently been measured[334] by the ion cyclotron resonance technique and it has been shown that protonation occurs at the phosphorus atom.

B. Metal Complex Formation

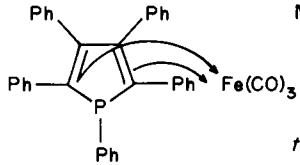
Both 1*H*-phospholes and λ^3-phosphinines form metal complexes and a wide variety of such complexes are now known. The topic has been reviewed extensively for both heterocycles[226,278,335] and only a brief outline of the main types of complex formed by each heterocycle will be presented here.

1. 1H-Phosphole complexes

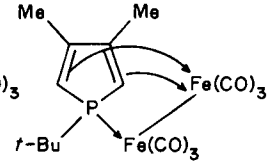
In the following discussion, the material presented will not be individually referenced as all relevant references can be found in the most recent review[226]. Briefly, 1*H*-phospholes can form three types of complex, viz. complexes in which the phosphole acts as a two-electron donor (σ complexes), as a four-electron donor (π complexes) and as a six-electron donor (σ,π complexes). Examples of these structural types are **140**, **141** and **142**.



(140)



(141)



(142)

By far the most common type of complex formed by phospholes is the two-electron donor σ complex. Such complexes have been prepared using a variety of phospholes, for chromium(0), molybdenum(0), tungsten(0), manganese(0), rhenium(III), iron(II), iron(0), ruthenium(III), ruthenium(II), cobalt(II), rhodium(III), rhodium(II), rhodium(I), iridium(III), iridium(I), nickel(II), nickel(0), palladium(II), platinum(II), copper(I) and mercury(II). In many instances, two or even three phosphole ligands may be attached to the metal center. Generally, then, phospholes interact well with soft acceptors.

Four-electron donor complexes, such as **141**, appear to be very rare, presumably because the phosphorus non-bonding pair in phospholes is too good a donor unless the substitution pattern renders the ligand particularly bulky.

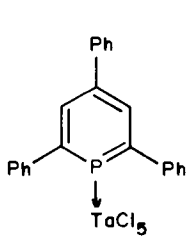
Similarly, relatively few complexes in which the phosphole ring acts as a six-electron donor are known and, in all instances, they involve metal(0) carbonyls (iron, manganese).

Clearly, the coordination chemistry of phospholes is a fertile area for further research and many of the complexes now known have obvious potential as catalytic systems.

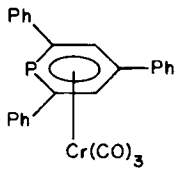
2. λ^3-*Phosphinine complexes*

Fewer metal complexes are known for λ^3-phosphinines than for 1*H*-phospholes. Even so, four basic structural types of complex are known[278] and examples are **143**, **144**, **145**, and **146**.

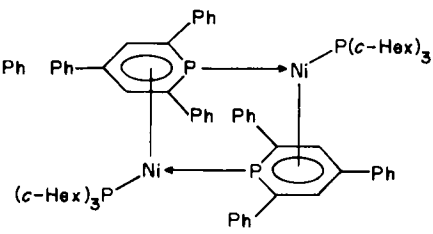
Complexes of type **143** may be formed with metal (0) or with metals in higher oxidation states. The remaining complexes are almost always with metal (0).



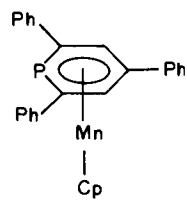
(143)



(144)



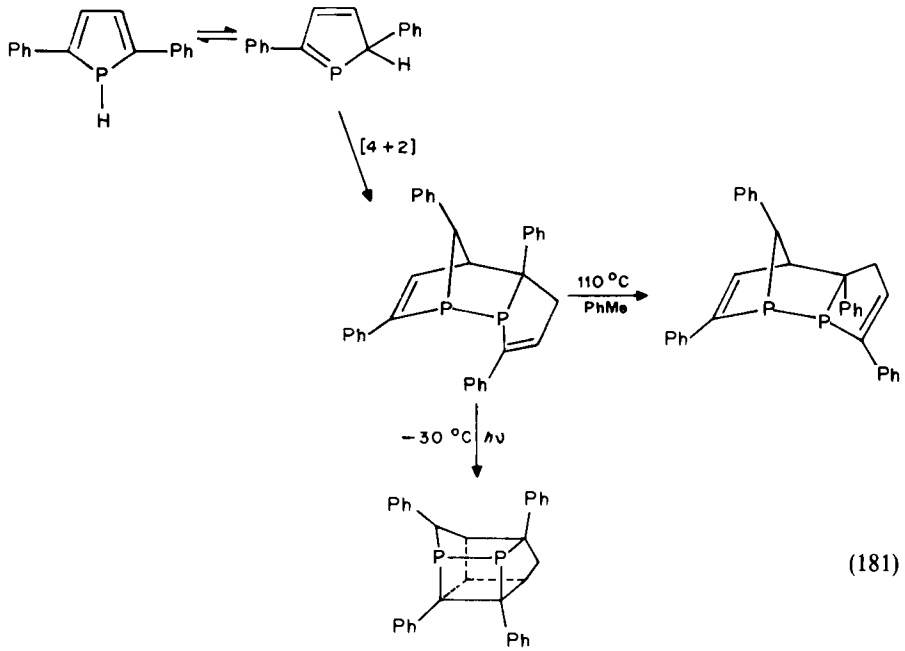
(145)



(146)

C. Reactions of Special Interest

In previous sections, most of the important reactions of 1*H*-phospholes have been covered directly or indirectly and some reactions of λ^3-phosphinines have also received attention. There are, however, a few particularly interesting reactions of both systems (more for λ^3-phosphinines) which should be mentioned.



(181)

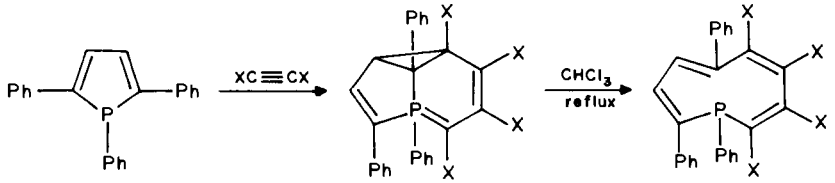
1. 1H-Phosphole reactions

Two reactions will be treated here. First, as mentioned in Section IV.B, 1*H*-phospholes bearing a hydrogen on the phosphorus atom rearrange below room temperature to the corresponding 2*H*-phosphole via a [1,5] sigmatropic rearrangement. Generally, these react further to give the 1,1′-biphospholyls already discussed (see, for example, equation 94). However, when there is suitable substitution on the ring, a Diels–Alder type of dimerization can occur to give an *endo* dimer containing a P—P bond. This, on heating, can rearrange to give the thermodynamically more stable *exo* dimer (equation 181)[185]. The *endo* dimer undergoes an intramolecular UV-induced [2 + 2] cycloaddition (equation 181).

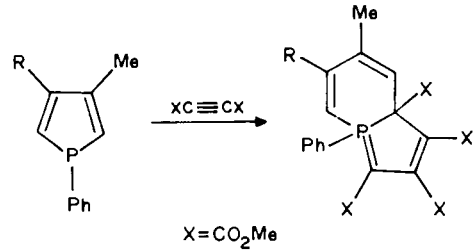
The second reaction of some interest is that of phospholes with dimethyl acetylenedicarboxylate to give, depending on the structure of the phosphole (or phosphindole), a variety of unusual phosphorus heterocycles. The conditions for and mechanisms of these reactions have been discussed extensively elsewhere[245] and it is necessary here only to illustrate some representative examples as shown in equations 182[336], 183[337] and 184[337].

2. λ^3-Phosphinine reactions

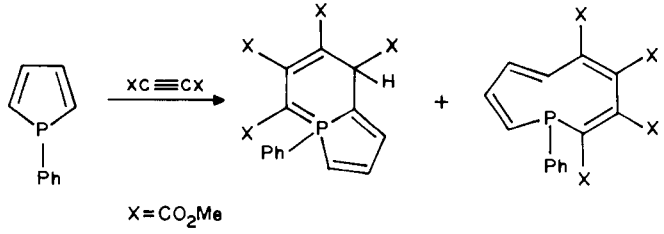
Several reactions require brief discussion here. As mentioned earlier, λ^3-phosphinines show little nucleophilic character towards alkylating agents and are not at all readily



(182)



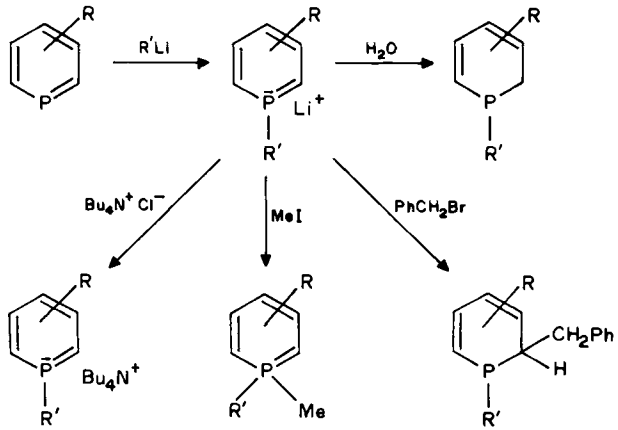
(183)



(184)

protonated. However, many reactions are known to take place at the phosphorus atom. Further, many of these reactions lead, ultimately, to the formation of λ^3-phosphinines and emphasis will be placed on such reactions.

One particularly interesting reaction is with organolithium compounds[292,332,338] (or with Grignard reagents[292,296]) in which the phosphorus atom acts as an electrophile. The process is illustrated in equation 185; the resulting anion can be trapped[339] as the tetrabutylammonium salt, hydrolyzed to give a 1,2-dihydro-λ^3-phosphinine, treated with alkyl halides via an S_N2 mechanism to give a λ^5-phosphinine or treated with alkyl halides via an S_N1 mechanism to give, again, a 1,2-dihydro-λ^3-phosphinine (equation 185).

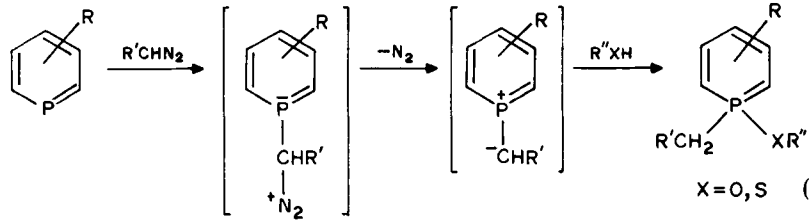


(185)

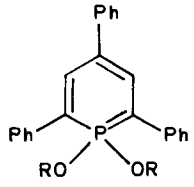
A similar reaction occurs with diazomethane[340]. However, the initially formed adduct readily loses nitrogen and the product of this reacts very rapidly with alcohols, thiols, phenols, etc., to give λ^5-phosphinine derivatives (equation 186)[340]. In aprotic solvents, the reaction proceeds in an entirely different manner to yield, finally[35], the 'chiropteradiene' discussed in Section III.D.

Radical additions to the phosphorus atom of λ^3-phosphinines also occur readily. These have been reviewed extensively elsewhere[276,278] and details will not be given here. However, by these various radical addition reactions, the structural types **147**, **148** and **149** have been prepared.

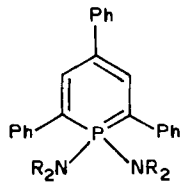
One last reaction of λ^3-phosphinines will be mentioned. As noted briefly in passing in Section V.A (equation 175), certain λ^3-phosphinines react[311] with sulfur in boiling xylene to give phosphinine 1-sulfides such as **150**. In the case already discussed (equation 175),



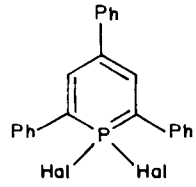
(186)



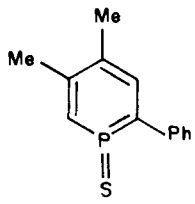
(147)



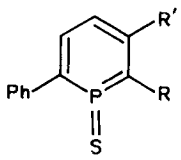
(148)



(149)

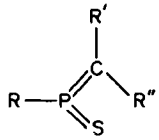


(150)



$R = P(S)Ph_2$, $R' = PPh_2$
or $R = PPh_2$, $R' = P(S)Ph_2$

(151)



(152)

150 is short-lived. It can apparently be characterized in solution (δ^{31}P 147) but it cannot be isolated. It has been trapped as shown in equation 175. However, very recently, the heavily substituted λ^3-phosphinine **129** has been shown[341] to react with sulfur at room temperature in benzene to give the phosphinine 1-sulfide **151**. Although this has not yet been isolated in pure form, it survives chromatography on silica gel and is stable in solution and the solid state for extended periods. These systems are of particular interest because they are heterocyclic relatives of the phospha-alkene sulfides, **152**, of which few examples are known. Low-coordination phosphorus compounds of this type are normally very highly reactive and short-lived. They are currently under intensive study and the chemistry of such systems has recently been reviewed[342].

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The Chemistry of Organophosphorus Compounds
FRANK R. HARTLEY

CHAPTER 11

Nucleophilic reactions of phosphines[a]

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[a]Dedicated to Dr William Gerrard OBE (1900–1990)

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I. INTRODUCTION

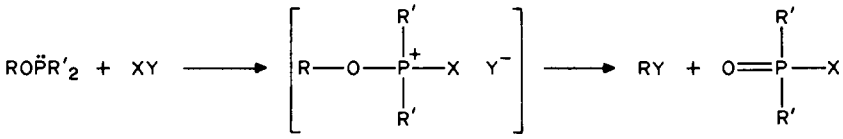
Phosphines are versatile nucleophiles. In addition to their reactions at saturated carbon and at sp^2 or sp hybridized carbon, they enter into nucleophilic reactions at many other centres, including attack at electronegative elements such as the halogens, nitrogen, oxygen and sulphur. The basis for their reactivity, which is higher than that of either the corresponding amines or arsines, has been discussed in detail[1]. Nucleophilic attack by a phosphine leads to an increase in coordination number to four and to the formation of a

$$R_3P: + R'X \longrightarrow R_3\overset{+}{P}R'\ X^-$$

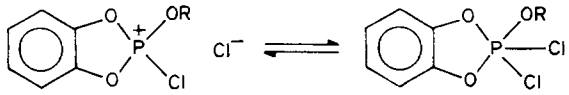
R = alkyl, aryl

SCHEME 1

phosphonium species. The latter may be a stable product (a phosphonium salt), e.g. in the reaction of a trialkyl- or triaryl-phosphine with an alkyl halide (Scheme 1)[2] or be merely a transitory intermediate en route to the formation of a tetracoordinate phosphorus(V) species if one of the ligands attached to phosphorus is an alkoxy group that can undergo facile alkyl—oxygen cleavage (Scheme 2)[3]. The latter reaction, known as the Michaelis–Arbuzov reaction, is important for the preparation of phosphonates, phosphinates and phosphine oxides[4]. Stable intermediates of the Michaelis–Arbuzov reaction have been isolated in cases in which the alkyl group is sterically hindered or is otherwise not easily susceptible to nucleophilic attack[5]. In certain examples, an equilibrium concentration of the corresponding phosphorane may also be formed (Scheme 3)[6].

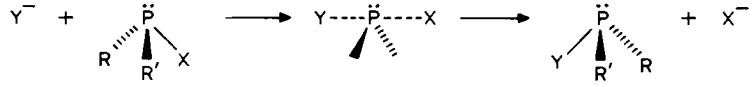


SCHEME 2



SCHEME 3

The higher polarizability of phosphorus compared with that of nitrogen and the availability of d orbitals leads to the possibility of nucleophilic attack by other reagents at phosphorus in cases where a suitable leaving group is present. Reactions of this type are exemplified by the displacement of halogen from halogenophosphines by alcohols, amines and organometallic reagents (e.g. Grignard reagents or organocadmium compounds)[7], the hydrolysis[8] or alcoholysis of esters or amides of phosphorus(III) acids[9] and displacements of aryl[10], benzyl[11,12], alkoxide or alkylthio groups[13] from trivalent phosphorus by organolithium compounds. Reactions of this type occur with total inversion of configuration at phosphorus, showing that pseudorotation in a hypervalent anion intermediate does not occur. A single-step $S_N(P)$ mechanism has been proposed (Scheme 4).



SCHEME 4

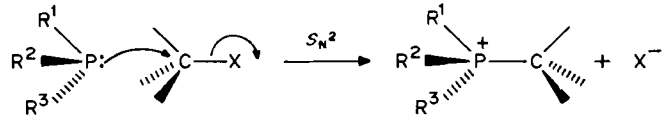
Biphilic reactions, in which both nucleophilic and electrophilic functions of phosphorus(III) are involved[14], are also well established in a number of processes, including the deoxygenation of dialkyl peroxides (see Section VIII.A.1) and cycloadditions to conjugated diene systems[14].

II. NUCLEOPHILIC SUBSTITUTION AT SATURATED CARBON

A. Nucleophilicity, Steric Factors and Solvent Effects

Nucleophilic reactions of phosphines at sp^3 carbon have been studied in considerable detail. Apart from the reactions of certain tertiary halides, e.g. triphenylmethyl

chloride[15,16] (for which a carbonium ion intermediate is involved; see Section III.A), the reactions are essentially of the S_N2 type leading to inversion of configuration at carbon and retention of configuration at phosphorus[17] (Scheme 5).



SCHEME 5

The greater nucleophilicity of trivalent phosphorus compared with that of either nitrogen or arsenic was first shown in 1934 by Davies and Lewis[18], who determined second-order rate constants in acetone or alcoholic media for the reactions of a series of aryl diethyl derivatives, $ArXEt_2$ (X = N, P, As), with ethyl iodide. Reaction rates were increased by the presence of electron-releasing substituents in the aromatic ring and decreased by electron-withdrawing substituents. Subsequent calculation of the Hammett parameters showed the phosphines ($\rho = -1.01$) to be less sensitive to substituent effects than the amines ($\rho = -2.77$), indicating a greater degree of conjugation with the aromatic ring in the case of the nitrogen[1]. This factor, together with the steric constraints imposed by the smaller nitrogen atom, is thought to account for the lack of reactivity shown towards methyl iodide by triphenylamine, whereas triphenylphosphine reacts rapidly. In the aliphatic series, the steric effect presumably accounts for the lower reactivity of triethylamine compared with that of triethylphosphine. The factors which combine to determine the reactivity of nucleophiles are complex, however, and include ionization potentials, bond energies and energies of solvation[19].

Studies on the rates of quaternization of triphenylphosphine and of triphenylarsine with methyl iodide and with various 4-substituted benzyl halides in acetonitrile have shown much less bond-making to be involved in the transition state in the case of the phosphines[20]. Triphenylphosphine is about 100 times more reactive than the arsine at 25 °C, the rate difference being due mainly to differences in the enthalpies of activation. Hammett plots for the various benzyl halides suggest that triphenylphosphine is involved in a 'tighter' transition state than triphenylarsine, which resembles the alkylamines in preferring a looser transition state. Kinetic studies of the rates of reaction between alkyldiphenylphosphines or alkyldiphenylarsines and methyl iodide and correlations of the nucleophilicities with the Taft scheme, indicated the operation of both inductive and steric effects[21].

Competitive S_N2 and $E2$ reactions of triphenylphosphine with cyclohexyl tosylate confirm the good nucleophilic affinity of triphenylphosphine for carbon[22]. Substitution occurs almost exclusively in various solvents at 75 °C. The phosphine is regarded as a typical neutral weak base; it is a poor reagent for elimination compared with anionic weak bases that are also good nucleophiles.

Solvation effects have been studied in the reactions of tributylphosphine and triphenylphosphine with a range of alkyl halides in a variety of protic and aprotic solvents[23,24]. For reactions of triphenylphosphine with benzyl chloride, a major contributing factor to the degree of reactivity was shown to be the electrophilicity of the solvent (53%), whereas lower contributions arise from polarity (35%) and polarizability (12%)[25]. In dipolar aprotic solvents (acetonitrile, propylene carbonate, dimethylformamide and dimethylacetamide), the reaction of triphenylphosphine with methyl iodide was shown to be less sensitive to solvent variation than was the reactivity of a tertiary aliphatic amine[26]. Solvation changes around the incipient phosphonium ion were found to be greater than around the anionic moiety and it was seen that three phenyl groups were

insufficient to shield the central phosphorus from the effect of the surrounding solvent molecules.

Other factors which influence the nucleophilicity of phosphines include the inductive effects of groups attached to phosphorus, the possibility of orbital overlap from neighbouring atoms carrying lone pairs and the constraints that may be imposed by the presence of the phosphorus atom in a ring system.

B. Inductive Effects of Substituents

The inductive effects of substituents have been shown to be of primary importance in determining the rates of reaction of many alkyl- and/or aryl-substituted phosphines with alkyl halides[27], the general order of nucleophilicity following that of the basicities. This result contrasts with that for amines, in which steric factors may be dominant because of the smaller size of nitrogen. For a wide range of tertiary phosphines [Ph_3P, Ph_2PEt, $(p\text{-}MeOC_6H_4)_3P$, $PhPEt_2$, Et_3P, Pr_3P, Bu_3P, Am_3P and Cy_3P], the rates of reaction with ethyl iodide in acetone at 35 °C fit a linear plot:

$$\log 10^5 k = 1.939 - 0.767\,\sigma^*$$

where σ^* is the sum of the Taft substituent constants for the various groups attached to phosphorus.

The value of -0.767 for ρ^* indicates a moderate inductive effect by which electron-releasing groups increase the nucleophilicity of the phosphorus lone pair. Resonance or steric effects within this series are small or constant. Surprisingly, the presence of a methyl group increases the nucleophilicity substantially beyond that which would be predicted from the above correlation and the order $Me_2PEt > MePEt_2 > Me_3P > Et_3P$ has not yet been explained. Whereas hyperconjugation might be considered to be a possible cause of the enhanced effect of methyl, the position of Me_3P in this series is anomalous. The low reactivity of triisobutylphosphine can be attributed to steric factors, whereas that for tris(2-cyanoethyl)phosphine is probably due to the electronic effect of the cyano group.

More recent studies have shown the very low reactivity of tris(cyanomethyl)phosphine to be due to the polar (field or $-I$) effect of the cyano group which reduces electron density in the region of the phosphorus lone pair[28]. The reaction rate for Me_2PCH_2CN with benzyl bromide in acetonitrile at 35 °C is close to that for triphenylphosphine, but decreases rapidly in the order $Me_2PCH_2CN > MeP(CH_2CN)_2 > P(CH_2CN)_3$, the tris(cyanomethyl)phosphine being less reactive than the monocyanomethyl derivative by a factor of about 20000. The strongly deactivating effect of cyanomethyl is also apparent in the reactions of phosphines of the type Ph_2PCH_2X with ethyl iodide[29]. Nucleophilicity decreases in the order $X = CONMe_2 > Me \approx CONH_2 > CO_2H \approx CO_2Et > CN$, with rates for $X = CO_2H$ and CO_2Et being comparable to that for triphenylphosphine. Although the reactivity order is consistent with inductive effects, the correlation with Taft substituent constants is poor and the results can be equally well explained on the basis of the ionization potentials of the phosphorus lone pair; other factors may also be involved.

Primary and secondary phosphines are significantly less nucleophilic than tertiary phosphines. The general order of reactivity $R_3P > R_2PH > RPH_2 > PH_3$ can be inferred from various sources, although exact rate measurements (other than for tertiary phosphines) have been made in only a few cases, e.g. for the secondary phosphines R_2PH (R = *n*-Bu, octyl, *i*-Bu)[27]. In some cases, e.g. for diphenylphosphine, the system is complicated by further reaction with a second molecule of alkyl halide, following dissociation of the first-formed hydrohalide (Scheme 6). Similarly, primary phosphines may give either secondary or tertiary phosphines by stepwise reactions, depending on the extent to which dissociation of the intermediate hydrohalide occurs (Scheme 7)[30,31].

$$Ph_2PH + RX \longrightarrow Ph_2\overset{+}{P}RHX^-$$
$$Ph_2\overset{+}{P}RHX^- \rightleftharpoons Ph_2PR + HX$$
$$Ph_2PR + RX \longrightarrow Ph_2\overset{+}{P}R_2X^-$$

SCHEME 6

$$RPH_2 + R'X \longrightarrow [RR'PH_2]^+X^-$$
$$[RR'PH_2]^+X^- \rightleftharpoons RR'PH + HX$$
$$RR'PH + R'X \longrightarrow [RR'_2PH]^+X^-$$
$$[RR'_2PH]^+X^- \rightleftharpoons RR'_2P + HX$$
$$RR'_2P + R'X \longrightarrow [RR'_3P]^+X^-$$

SCHEME 7

$$MePH_2 + MeI \rightleftharpoons Me_2\overset{+}{P}H_2I^-$$
$$Me_2\overset{+}{P}H_2 + MeOH \rightleftharpoons Me_2PH + MeOH_2^+$$
$$MePH_2 + MeOH_2^+ \rightleftharpoons Me\overset{+}{P}H_3 + MeOH$$
$$MeOH_2^+ + I^- \rightleftharpoons H_2O + MeI$$
$$Me_2PH + MeI \rightleftharpoons Me_3\overset{+}{P}HI^-$$

SCHEME 8

Whereas the individual alkylation steps proceed faster as the degree of alkylation increases, the dissociation of the hydrohalide becomes more difficult as the basicity of the phosphine also increases. Simple dialkylphosphines are obtained by the action of moderate heat on monoalkylphosphines together with methyl or *n*-alkyl iodides without solvent. Trialkylphosphines are readily obtained if the reaction is carried out in the alcohol corresponding to the alkyl halide as the solvent[30]. Under controlled conditions, both dimethyl- and trimethyl-phosphine can be isolated by the reaction of methylphosphine with methyl iodide in methanol (Scheme 8)[31].

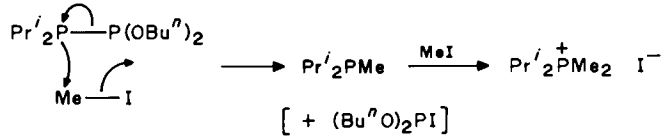
C. Effects of Lone Pairs on Neighbouring Atoms

The presence of lone pair electrons on atoms adjacent to phosphorus does not cause an increase in nucleophilicity comparable to the α-effect that is seen for oxygen nucleophiles. The dominant effect of alkoxy groups is in fact to decrease nucleophilicity by inductive electron withdrawal[32,33], so that reactivity with methyl iodide decreases in the order $Et_2POEt > EtP(OEt)_2 > (EtO)_3P$. Kinetic measurements have also demonstrated decreasing nucleophilic activity towards ethyl iodide as the number of alkoxy groups attached to phosphorus increases (Table 1)[33].

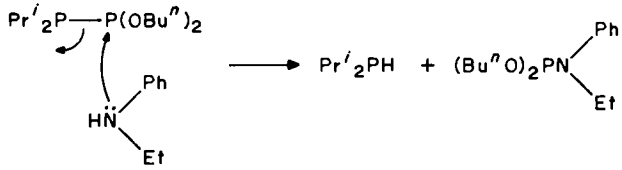
TABLE 1. Rates of reaction of phosphorus(III) derivatives with ethyl iodide (data from ref. 33)

	Ph_3P	Ph_2POEt	$PhP(OEt)_2$	$P(OEt)_3$
10^4k (60 °C)	5.18	2.39	1.79	0.20

Phenoxy groups reduce the reactivity still further[34]. Mesomeric interaction of the oxygen lone pairs with the d orbitals of phosphorus is therefore of less significance than inductive effects in determining the nucleophilic reactivity of phosphorus(III) compounds. A direct comparison of the reactivity of phosphorus atoms carrying alkyl and alkoxy groups can be seen in the reactions of certain diphosphines in which the phosphino phosphorus atom reacts preferentially with electrophiles, e.g. methyl iodide (Scheme 9), whereas the phosphorus atom to which alkoxy groups are attached reacts only with nucleophiles (Scheme 10)[35].



SCHEME 9



SCHEME 10

The effects of nitrogen ligands have been studied in the reactions of a number of tris(dialkylamino)phosphines with methyl iodide in acetonitrile (Scheme 11)[36]. Kinetic measurements at 25 °C showed these compounds to be amongst the most nucleophilic of phosphorus(III) compounds towards this alkyl halide. The least reactive (R_2N = morpholino) has a reactivity comparable to that of triphenylphosphine, whereas others in the series (R_2N = piperidino, Et_2N, Me_2N) are at least as reactive as tributylphosphine. Even so, π-electron transfer from nitrogen to phosphorus is not considered to be a major factor in the stabilization of the transition state for these compounds. Repulsive interaction between the nitrogen lone pairs and that of phosphorus may raise the energy of the latter, rendering it more basic (and more nucleophilic)[37]. The effect is relatively small, however, and the aminophosphines are not regarded as typical α-nucleophiles.

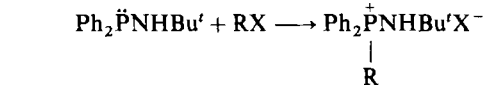
$$(R_2N)_3P: + MeI \longrightarrow (R_2N)_3\overset{+}{P}MeI^-$$

SCHEME 11

Although $d\pi$–$p\pi$ interaction between either oxygen or nitrogen that is directly attached to phosphorus appears to be of minor importance in determining the nucleophilic reactivity of phosphines, there is good evidence for such an interaction in the phosphonium salts that are produced. Oxygen—phosphorus and nitrogen—phosphorus bond lengths in the phosphonium salts are significantly shorter than the calculated single bond lengths and, in the case of the aminophosphonium salts, the nitrogen atom is sp^2 hybridized (planar)[38].

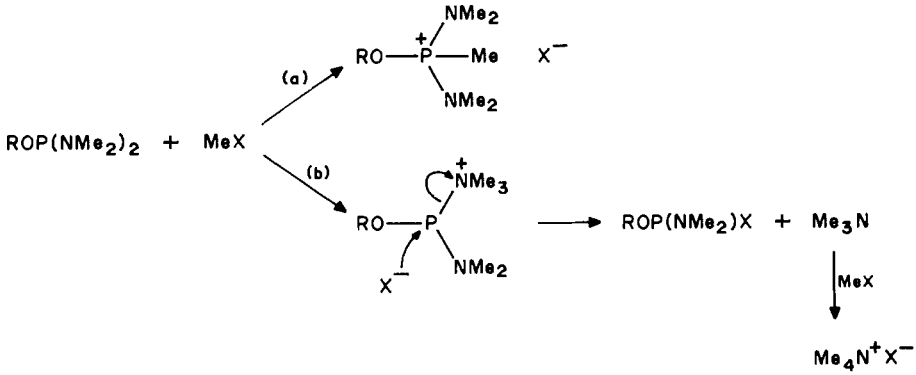
The evidence here, as in many other examples, points to a transition state for phosphonium ion formation that is reactant-like rather than product-like.

The greater nucleophilicity of phosphorus than of nitrogen towards saturated carbon is shown by preferential quaternization at phosphorus only in reactions of aminophosphines with benzylic chlorides (Scheme 12)[39], although a trend towards competitive quaternization at nitrogen has been reported in certain cases as the hardness of the halide reagent increases in the order I < Br < Cl (Scheme 13)[40]. Quaternization at both nitrogen and phosphorus may be possible if the nitrogen is not directly attached to phosphorus, depending on the groups attached to nitrogen (Scheme 14)[41].

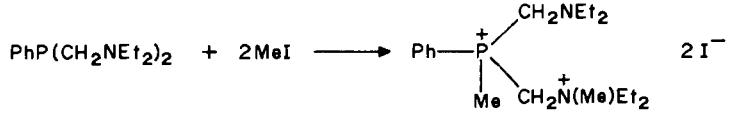


RX = benzyl chloride or other benzylic halide

SCHEME 12



SCHEME 13

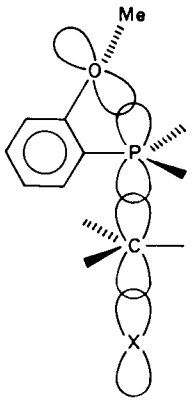


SCHEME 14

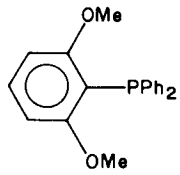
D. Through-space Orbital Overlap

A significant enhancement of nucleophilic reactivity in phosphines has been demonstrated in a number of cases in which *o*-anisyl (*o*-methoxyphenyl) groups are present[42–45]. Also, the rates of reaction with benzyl chloride and with butyl chloride differ by a factor of no more than 20, which is one of the lowest rate differences known for S_N2 reactions of these halides. The effect is attributed to a through-space interaction of the 2p electrons of the *o*-anisyl oxygen atom and the empty 3d (or hybrid) orbital of phosphorus in an early

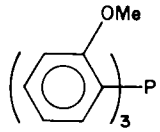
transition state (**1**). The effect is even more pronounced if two *o*-methoxy groups are present in the same ring. Thus, 2,6-di-*o*-methoxyphenyldiphenylphosphine (**2**) undergoes quaternization faster than tri-*o*-anisylphosphine (**3**) or di-*o*-anisylphenylphosphine (**4**), a result that has been discussed in terms of the effect of the 6-substituent on the C—P—C bond angle which is decreased in the transition state and allows more effective overlap of the p orbitals of the 2-methoxy group with phosphorus[45]. The importance of 2p–3d overlap in the activating effect of an *o*-methoxy group has been confirmed by studies on a series of 5-aryldibenzophospholes (**5**), for which it was found that maximum acceleration results when the 5-aryl group containing an *o*-methoxy substituent can be orthogonal to the dibenzophosphole ring (e.g. for V = Z = MeO; X = Y = H)[46].



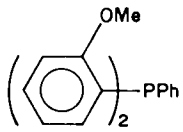
(1)



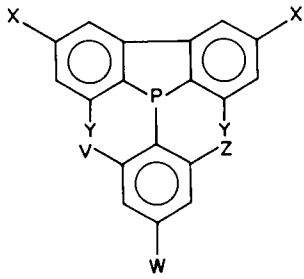
(2)



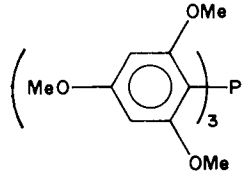
(3)



(4)



(5)

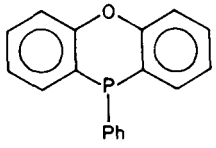


(6)

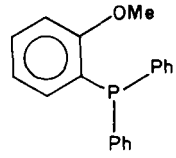
A further example of the effect of *o*-methoxy substituents is given by the unusually high reactivity of tris(2,4,6-trimethoxyphenyl)phosphine (**6**), which is one of the most nucleophilic (and most basic) phosphines known[47].

For *ortho* substituents other than methoxy, rate effects can generally be interpreted in terms of the geometry of transition states, the HSAB principle and ordinary substituent effects. *o*-Methylthio is thus much less able to promote reaction than is *o*-methoxy because sulphur is a softer nucleophile and is less able to donate electron density to the developing hard phosphonium centre. The methylthio group is also larger and may be less favourable sterically[44]. In the case of the dibenzophosphole (**7**), interaction of the 2p electrons of oxygen with the phosphorus 3d orbitals is inhibited by constraints of the ring system. A

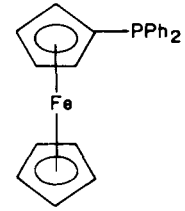
transannular P···O distance of 3.11 Å has been measured for the corresponding *p*-bromobenzyl bromide salt[48]. Quaternization of the phosphole (**7**) with phenacyl bromide is 20 times slower than that for *o*-methoxyphenyldiphenylphosphine (**8**) and is five times slower than for triphenylphosphine.



(**7**)

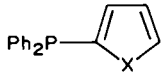


(**8**)



(**9**)

Evidence for an early transition state in quaternization is given by the absence of a significant rate increase for ferrocenyldiphenylphosphine (**9**) which should be capable of conjugative stabilization of the developing phosphonium ion[44]. Similarly, no significant involvement of the π-excessive heterocyclic ring was observed in reactions of phosphines having a heterocyclic substituent (**10**) with phenacyl bromide[49].



X=O,S,NH,NHMe

(**10**)

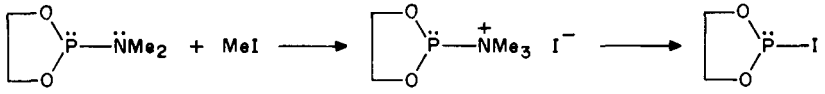
$Ph_2P(CH_2)_nOMe$ (**11**)

$Ph_2P(CH_2)_nNMe_2$ (**12**)

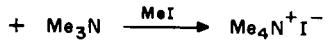
Some evidence for 2p–3d interactions involving either oxygen or nitrogen in open-chain systems has been found in the modest rate increases that are observed for reactions of ω-methoxyalkyldiphenylphosphines (**11**; $n = 1$–4)[45] and of ω-dimethylaminoalkyldiphenylphosphines (**12**; $n = 1$–4)[50] with benzyl chloride. The effect is, however, outweighed in the methoxy compound **11** ($n = 1$) by the large $-I$ effect of oxygen which renders the phosphine unreactive.

E. Effects of Ring Size

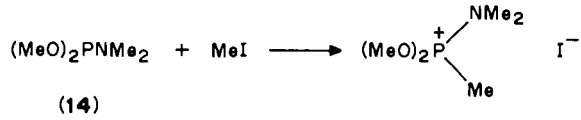
The nucleophilic reactivity of cyclic phosphorus(III) compounds may be modified by the effect of ring size[51,52]. Thus, the nucleophilic reactivity of the phosphorus atom in ethylene *N,N*-dimethylphosphoroamidite (**13**) towards methyl iodide is reduced to an extent that allows nucleophilic attack by the nitrogen atom to occur with consequent



(**13**)



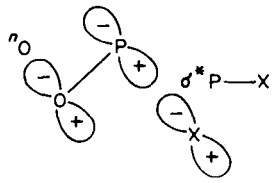
SCHEME 15



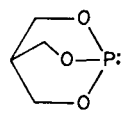
(14)

SCHEME 16

P—N cleavage (Scheme 15), whereas dimethyl *N,N*-dimethylphosphoramidite (**14**) reacts only at phosphorus to give the phosphonium salt (Scheme 16)[51]. The decreased nucleophilic reactivity of phosphorus(III) in five- and six-membered rings may be a consequence of a restriction in bond angle at phosphorus which, in an open-chain compound, may increase from ca 100 to ca 109° in the transition state leading to the phosphonium structure. Entropy factors were also considered to have a possible significance, associated with the restrictions imposed on the motions of the ring on passing from the relatively non-rigid tervalent compound to a less flexible four-coordinate species[52]. The low nucleophilicity of trivalent phosphorus in bicyclic phosphites[53] has been attributed to a stereoelectronic effect. *Ab initio* calculations show that an oxygen lone pair that is antiperiplanar to the phosphorus lone pair (**15**) would be expected to raise the energy by 13.8 kj mol^{-1} compared to a configuration, such as that of a bicyclic phosphite (**16**), in which the antiperiplanar arrangement is absent[54].



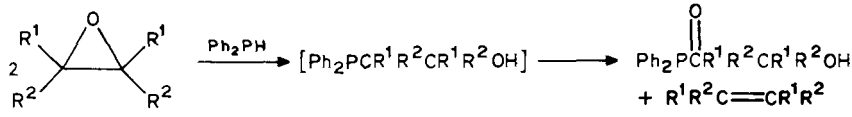
(15)



(16)

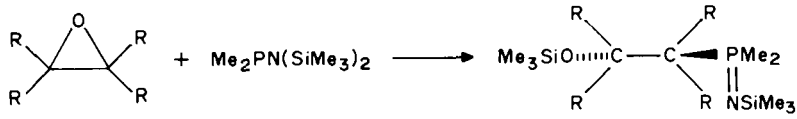
F. Miscellaneous Reactions at Saturated Carbon

Nucleophilic attack by phoshines or phosphide anions can result in the ring opening of epoxides. Secondary phosphines[55] and bis(trimethylsilyl)aminophosphines[56] give the corresponding addition products (Schemes 17 and 18) with diphenylphosphine, propylene



R^1=H, CN; R^2=H, Ph

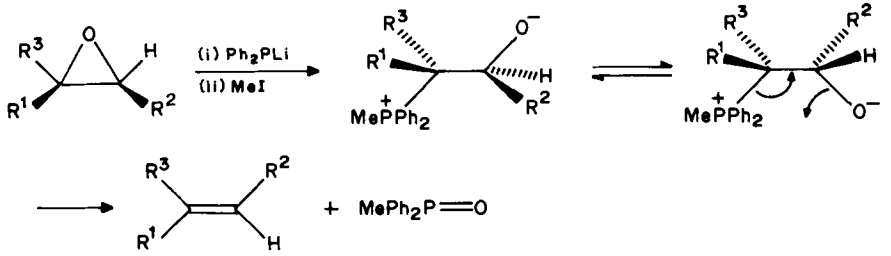
SCHEME 17



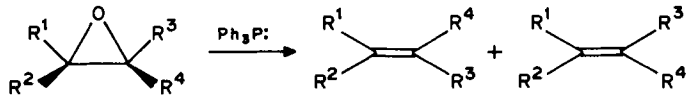
R=H, Me, Ph

SCHEME 18

oxide gives, surprisingly, the α-hydroxyphosphine oxide[55]. Ring opening by lithium diphenylphosphide followed by reaction with methyl iodide yields phosphonium betaines, which undergo elimination with the formation of alkenes having the opposite sterochemistry to that of the starting epoxides (Scheme 19)[57]. The reaction sequence is useful for bringing about inversion of alkene stereochemistry[58]. Triphenylphosphine similarly gives the corresponding elimination product[59], although the reaction is not stereospecific[60]. In addition to the main reaction pathway, leading to an alkene with inversion of configuration (Scheme 20), direct attack at oxygen is thought to account for the 20–30% of product that is formed with retention (see Section VIII.A). The highly nucleophilic tris(2,6-dimethoxyphenyl)phosphine has been used for ring opening of terminal epoxides, giving phosphonium species that were characterized as the perchlorate salts[61]. Trialkylphosphines have also been shown to bring about the ring opening of cyclic sulphonate esters to give the corresponding phosphoniosulphonate betaines (Scheme 21)[62].

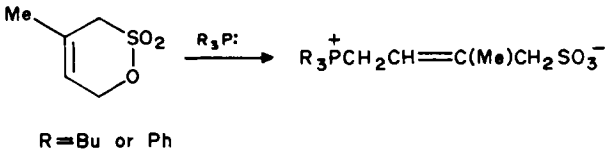


SCHEME 19



$R^1=R^3=Me$; $R^2=R^4=H$	81	:	19
$R^1=R^4=Me$; $R^2=R^3=H$	72	:	28

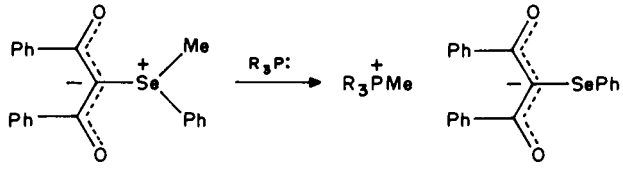
SCHEME 20



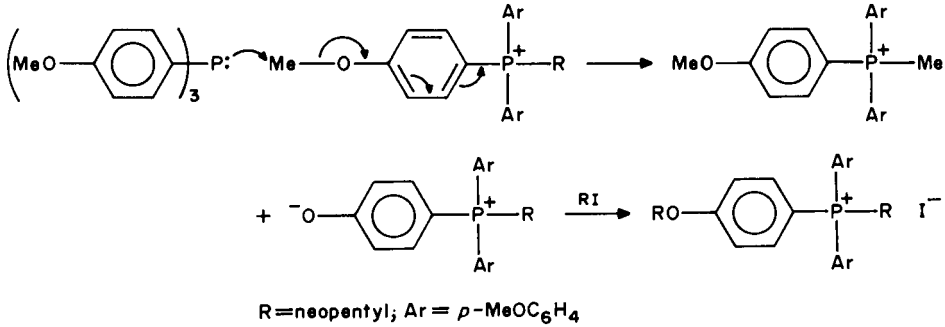
SCHEME 21

Tertiary phosphines are effective in the demethylation of a variety of methyl derivatives including quaternary salts of heterocyclic bases[63,64] and methylsulphonium or methylselenonium ylides (e.g. Scheme 22)[65–67]. The demethylation of quaternary ammonium iodides by triphenylphosphine is, however, thought to proceed by reaction of the phosphine with free methyl iodide, present in low concentration in solutions of the quaternary iodides, rather than by direct attack on the *N*-methyl compound[68]. Debenzylation of benzyloxypyridines has also been reported[69]. In the quaternization of

tris(*p*-methoxyphenyl)phosphine with neopentyl iodide, the *p*-methoxy groups become activated to nucleophilic attack by unreacted phosphine (Scheme 23), leading to the formation of eight phosphonium salts, having all possible combinations of methyl and neopentyl groups attached to phosphorus and/or oxygen[70]. Both tributylphosphine and triphenylphosphine demethylate dibromotrimethylantimony to form the corresponding methylphosphonium dibromodimethylantimonates[71]. ω-Chloroalkylphosphines undergo anchimerically assisted intramolecular cyclization (Scheme 24), the ease of ring formation decreasing in the order $5 > 6 > 3 > 4$[72].

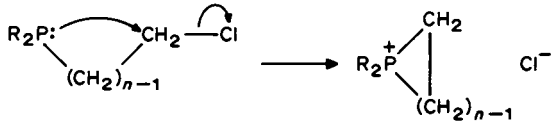


SCHEME 22



R=neopentyl; Ar = *p*-$MeOC_6H_4$

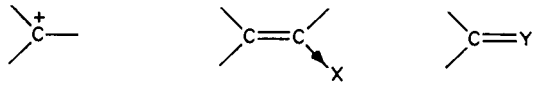
SCHEME 23



SCHEME 24

III. NUCLEOPHILIC ATTACK AT sp^2 HYBRIDIZED CARBON

Examples of nucleophilic reaction at sp^2 hybridized carbon are numerous and include reactions with carbonium ions (**17**), activated alkenes (**18**; X = electron-withdrawing group), and polarized groups such as carbonyl, thiocarbonyl, selenocarbonyl and imino (**19**; Y = O, S, Se, NR).



(17) (18) (19)

A. Carbonium Ions

Although phosphines do not attack simple alkenes under neutral conditions, reaction of the parent phosphine, PH_3, may occur at 30–60 °C under pressure, in the presence of an acid catalyst[73]. Primary phosphines and small amounts of secondary phosphines are obtained. Tertiary alkenes react most readily and it is thought that a carbonium ion mechanism is involved[74]. Because of the basicity of the primary phosphine, which is obtained as the phosphonium salt (Scheme 25), stoichiometric amounts of catalyst are required. Further reaction of the primary phosphine with alkene to give the dialkylphosphine, R_2PH, (Scheme 26) is slow as the equilibrium concentration of free primary phosphine that is present is small. Secondary and tertiary phosphines are too basic to react under these conditions. Tertiary phosphines will, however, react with carbonium ions under neutral conditions, e.g. the triphenylcarbonium ion (derived from triphenylmethyl chloride) adds directly to *tert*-phosphines (Et_3P, $PhPMe_2$ and Ph_3P)[15,16] to give the corresponding phosphonium salts (Scheme 27). Nucleophilic substitution into the benzene ring may also occur with triphenylphosphine and with sterically hindered phosphines [Ph_2PMe, Ph(*t*-Bu)PMe]) (see Section III.C)[15]. Dithiolium perchlorates (**20**) yield the corresponding phosphonium perchlorates by reaction with tributylphosphine in acetonitrile at 20 °C (Scheme 28)[75]. Triphenylphosphine adds directly to 2,6-diphenylpyrilium perchlorate (**21**) to give the corresponding pyranylphosphonium salt (Scheme 29)[76]. The

$$R_2C{=}CH_2 + H^+ \rightleftharpoons R_2\overset{+}{C}CH_3$$
$$R_2\overset{+}{C}CH_3 + PH_3 \rightleftharpoons CH_3CR_2\overset{+}{P}H_3$$

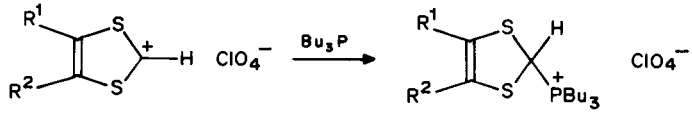
SCHEME 25

$$CH_3CR_2\overset{+}{P}H_3 \rightleftharpoons CH_3CR_2PH_2 + H^+$$
$$CH_3CR_2PH_2 + R_2\overset{+}{C}{-}CH_3 \rightleftharpoons (CH_3CR_2)_2\overset{+}{P}H_2$$

SCHEME 26

$$Ph_3C^+ + Ph_3P \longrightarrow Ph_3C\overset{+}{P}Ph_3$$

SCHEME 27

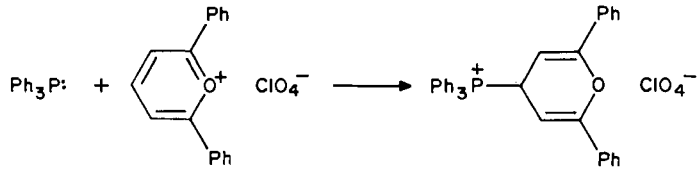


(20)

$R^1{=}R^2{=}Me$ or $R^1R^2{=}$ —CH=CHCH=CH—

SCHEME 28

nucleophilic reactions of triphenylphosphine and of trialkylphosphines with anodically generated cation radicals have also been shown to give the corresponding phosphonium salts[77].



SCHEME 29

B. Activated Alkenes

1. Additions of primary and secondary phosphines to activated alkenes

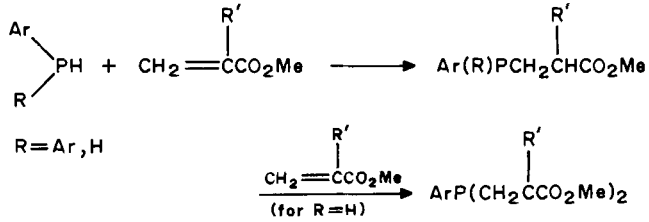
Phenylphosphine and diphenylphosphine react readily with acrylonitrile under the influence of heat and in the absence of a catalyst (Schemes 30 and 31)[78–80]. The process is a nucleophilic addition and appears to be intermediate in character between the acid-catalysed cyanoethylation of amines and the base-catalysed cyanoethylation of arsines[78]. Additions to acrylate and methacrylate esters (Scheme 32) and to a number of allylic derivatives also occur when the reactants are heated under neutral conditions[79–82]. Some examples of what appear to be uncatalysed additions to non-conjugated terminally unsaturated carboxylic esters have also been reported (Scheme 33)[83].

$$PhPH_2 + CH_2{=}CHCN \longrightarrow PhPHCH_2CH_2CN \xrightarrow{CH_2=CHCN} PhP(CH_2CH_2CN)_2$$

SCHEME 30

$$Ph_2PH + CH_2{=}CHCN \longrightarrow Ph_2PCH_2CH_2CN$$

SCHEME 31



SCHEME 32

$$PhPH_2 + CH_2{=}CH(CH_2)_{n-2}CO_2R \longrightarrow PhPH(CH_2)_nCO_2R$$

$$\xrightarrow{CH_2=CH(CH_2)_{m-2}CO_2R} PhP[(CH_2)_nCO_2R][(CH_2)_mCO_2R]$$

$m = 2\text{–}4$, $n = 2\text{–}4$, $R = C_4H_9$

SCHEME 33

The possible effect of acids as catalysts in these types of reaction is not clear. Although acetic acid was found to have no catalytic effect on the addition of diphenylphosphine to acrylonitrile[78], it was used in the analogous reaction of *m*-methoxyphenyl (phenyl)phosphine[82].

Base-catalysed additions of primary and secondary phosphines to activated alkenes are well known. Phosphine will react with a variety of α,β-unsaturated compounds (acrylonitrile, acrylamide, nitroethylene, mesityl oxide and acrylate esters) to give primary, secondary or tertiary phosphines according to the conditions[84,85]. Phenylphosphine behaves similarly[85]. These reactions are assumed to take place by Michael addition, involving the corresponding phosphide anions (Scheme 34). α,β-Unsaturated ketones undergo similar additions with primary phosphines in the presence of base[86,87], and with alkali metal dialkylphosphides[88] (Scheme 35). Low yields of addition products have also been obtained in the reactions of potassium diphenylphosphide with 1,1-diphenylethylene and with stilbene[89].

$$PH_3 + OH^- \rightleftharpoons PH_2^- + H_2O$$
$$PH_2^- + CH_2{=}CHCN \longrightarrow H_2PCH_2\bar{C}HCN$$
$$H_2PCH_2\bar{C}HCN + H_2O \longrightarrow H_2PCH_2CH_2CN + OH^-$$

SCHEME 34

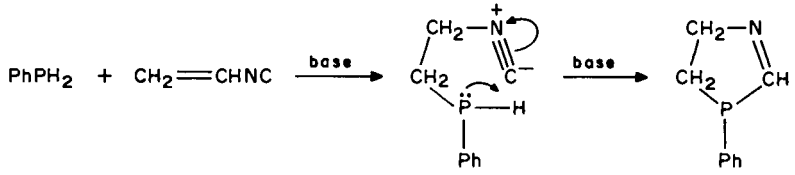
$$R_2C{=}CHCOR' \xrightarrow[\text{(ii) } H_2O]{\text{(i) } R''_2P^-M^+} R''_2PCR_2CH_2COR'$$

SCHEME 35

Base-catalysed addition of diphenylphosphine to vinyl isocyanide gives the expected product (Scheme 36), but phenylphosphine gives a phosphorus–nitrogen heterocycle resulting, presumably, from cyclization of the first-formed phosphine by intramolecular nucleophilic attack on the isocyanide group (Scheme 37)[90,91]. Group VIII metal chlorides, e.g. $NiCl_2$ or $PtCl_4$, have also been used under alkaline conditions to give high yields of tris(2-cyanoethyl)phosphine in the reaction of phosphine with acrylonitrile[92].

$$Ph_2PH + CH_2{=}CHNC \xrightarrow{\text{base}} Ph_2PCH_2CH_2NC$$

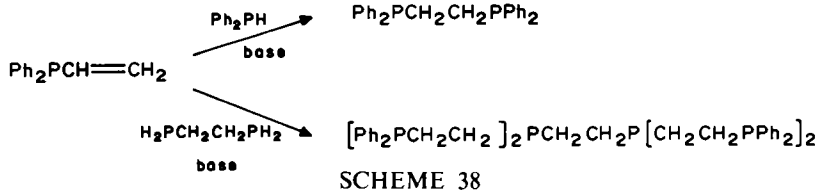
SCHEME 36



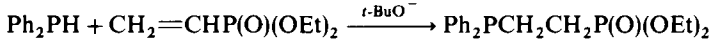
SCHEME 37

Phosphine, phenylphosphine and diphenylphosphine add readily to vinylphosphines in the presence of a base such as phenyllithium or potassium *tert*-butoxide[93]. The reactions are useful for the preparation of poly(tertiary phosphines) (Scheme 38). Base-catalysed

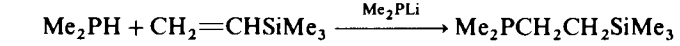
additions of diphenylphosphine to diethyl vinylphosphonate[94] and of dimethylphosphine to vinylsilanes[95] have also been reported (Schemes 39 and 40).



SCHEME 38

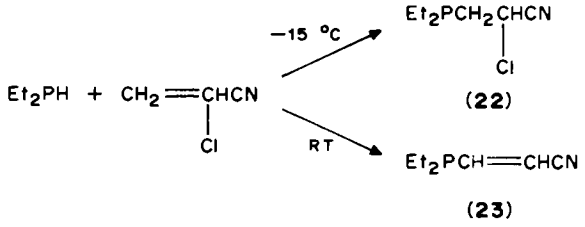


SCHEME 39

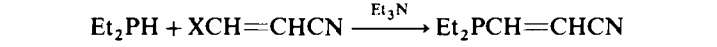


SCHEME 40

The reaction of diethylphosphine with α-chloroacrylonitrile occurs readily at −15 °C in the absence of added base to give a 1:1 adduct (**22**). At room temperature the elimination product (**23**) is formed (Scheme 41)[96]. β-Chloro- and β-benzylthio-acrylonitriles give analogous addition–elimination products by reaction with diethylphosphine in the presence of triethylamine (Scheme 42), but whether the base is essential to either the addition or the elimination stage is not clear.



SCHEME 41

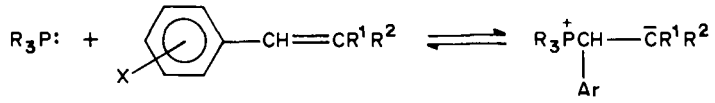


X = Cl or $PhCH_2S$

SCHEME 42

2. Reactions of tertiary phosphines with activated alkenes

Phosphonium betaines are formed by nucleophilic attack of trialkylphosphines on benzalmalonitriles or related derivatives (Scheme 43)[97,98]. The reaction is favoured and the product is stabilized by the presence of electron-attracting groups in the aromatic ring. K_e values ($R^1 = R^2 = CN$; R = Bu) vary from 1.74×10^4 for X = *p*-NO_2 to 190 for X = *p*-MeO[99]. The zwitterionic structure has been confirmed by high-resolution NMR spectroscopy[100]. In the reaction of triphenylphosphine with benzalmalonitrile, the equilibrium is so far to the left that no detectable phosphonium betaine is present; its formation, and

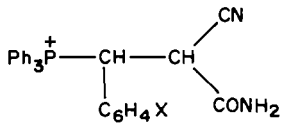


R = Me, Et, Bu; $R^1 = R^2 = CN$ or CO_2Et; $R^1 = CO_2Me$, $R^2 = CN$; $R^1 = NO_2$, $R^2 = CN$; $R^1 = NO_2$, $R^2 = Ph$

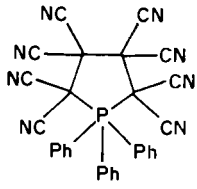
SCHEME 43

that of related triphenylphosphonium betaines, can, however, be inferred from the results of hydrolysis which gives the monoamide derivatives (**24**)[101].

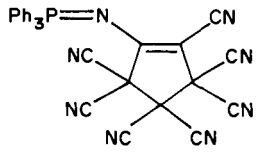
Tetracyanoethylene (tcne) is too reactive to form a 1:1 complex with simple triarylphosphines (Ar_3P; Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4), although spectroscopic evidence for a 1:1 charge-transfer complex has been obtained with the highly hindered trimesitylphosphine[102]. Triphenylphosphine reacts rapidly and exothermally with tcne in acetonitrile to give a 1:2 adduct, first formulated as octacyano-*P,P,P*-triphenylphosphacyclopentane (**25**)[103], but now known on the basis of X-ray diffraction and ^{13}C NMR studies to be the iminophosphorane (**26**)[104]. This reaction therefore involves nucleophilic attack of phosphorus at nitrogen (see Section VII.A), rather than attack at alkenic carbon.



(**24**)

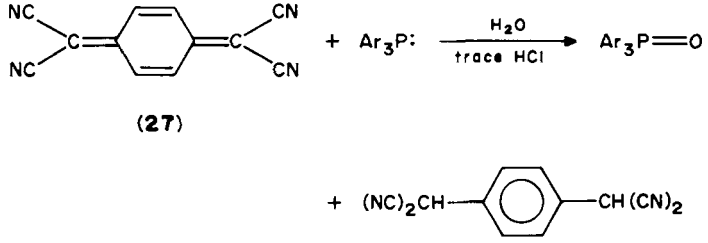


(**25**)



(**26**)

The reactions of 7,7,8,8-tetracyanoquinodimethane (**27**) with triarylphosphines proceed by a further different route. In the presence of water and a trace of hydrochloric acid, the reduced product is obtained in quantitative yield (Scheme 44)[105]. No betaine formation is involved and the reaction in this case is thought to proceed by way of a phosphinium radical cation intermediate.

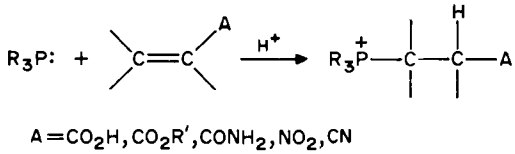


(**27**)

SCHEME 44

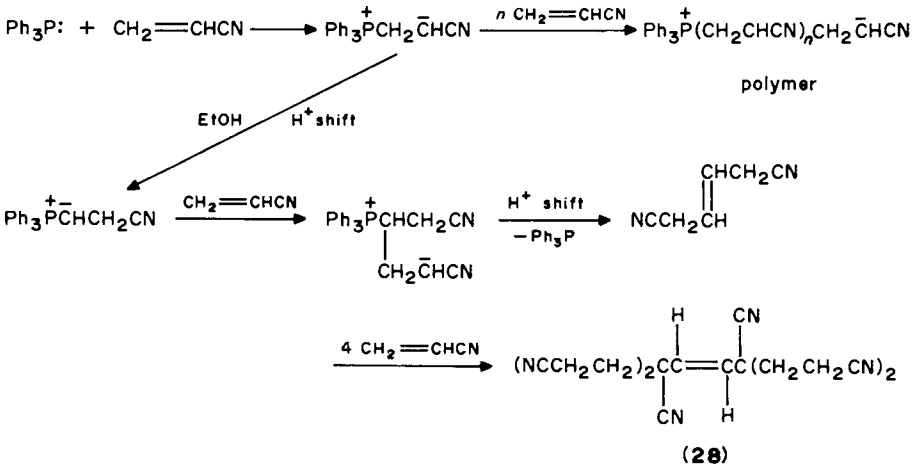
With simple vinyl derivatives (CH_2=CHX), tertiary phosphines form betaine intermediates that can react further in a number of ways. In the presence of acids, phosphonium salts are formed (Scheme 45)[106]. In the absence of other reagents, triphenylphosphine

initiates the polymerization of acrylonitrile to give an amorphous polymer of high molecular weight (Scheme 46)[107]. Hydroxylic solvents promote proton transfer processes which lead to ylid intermediates from which dimeric[108,109] and hexameric products[107] may be derived. The overall course of reaction is influenced by the nucleophilicity of the phosphine and by the proton acidity of the hydroxylic solvent[110]. With triphenylphosphine in ethanol, the crystalline hexamer (**28**) is obtainable[107], whereas *tert*-butanol favours the formation of the dimers, 2-methylglutaronitrile (**29**) and 1,4-dicyanobut-1-ene (**30**) (Scheme 47)[108,109]. Dimer is formed in particularly high yield (80% total) by the reaction of acrylonitrile with tri-*p*-tolylphosphine in triethylsilanol[110].

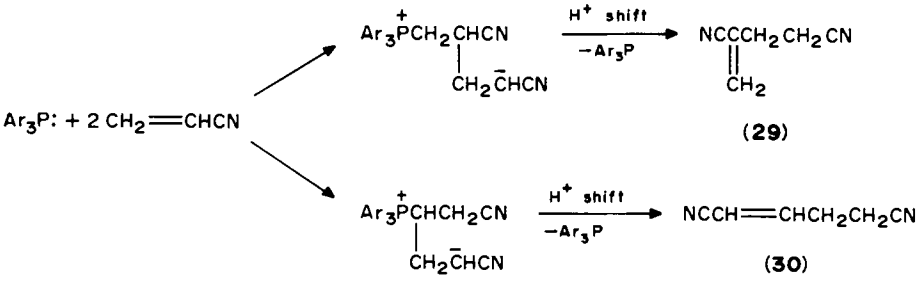


A = CO_2H, CO_2R', $CONH_2$, NO_2, CN

SCHEME 45

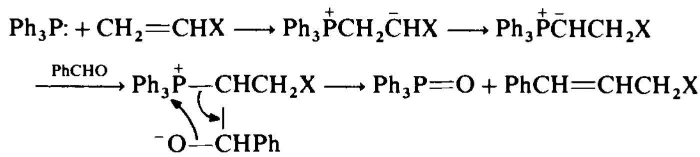


SCHEME 46



SCHEME 47

The formation of ylid intermediates in the reactions of triphenylphosphine with acrylonitrile and with related acrylic derivatives is also shown by their ability to enter into the conventional Wittig reaction with benzaldehyde (Scheme 48)[111].



SCHEME 48

Trialkylphosphines in anhydrous methanol may bring about the rapid and quantitative reduction of activated alkenes[112]. Ylid intermediates are thought to be involved (Scheme 49).

$$R_3P\colon + R'CH{=}CHR' \rightleftharpoons R_3\overset{+}{P}CHR'\overset{-}{C}HR' \rightleftharpoons R_3\overset{+}{P}\overset{-}{C}R'CH_2R' \xrightleftharpoons{MeOH}$$

$$R_3\overset{+}{P}CHR'CH_2R'\ OMe^- \rightleftharpoons R_3\underset{}{\overset{OMe}{\overset{|}{P}}}CHR'CH_2R' \xrightleftharpoons{MeOH} R'CH_2CH_2R' + R_3P{=}O + Me_2O$$

$$R = Et, Pr, Bu;\ R' = CO_2Me, COPh$$

SCHEME 49

With tricyclohexylphosphine, however, the initial betaine reacts directly with aldehydes[113] and with fumaric acid or fumaric esters[114] to give the corresponding addition products (Scheme 50). Betaines are also presumed to be involved as intermediates in the phosphine-catalysed dimerizations of alkyl vinyl ketones[110,115] and in the polymerization reactions of cyanoacrylates[116] and maleic anhydride[117].

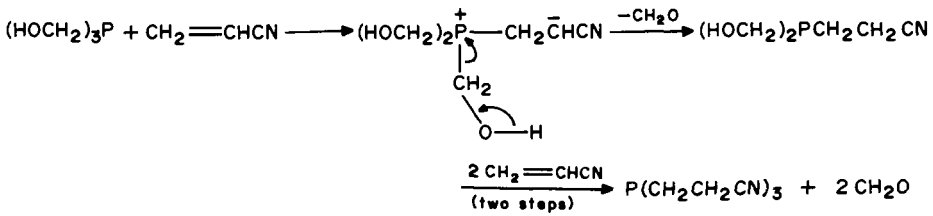
$$(C_6H_{11})_3P\colon + CH_2{=}CHX \rightleftharpoons (C_6H_{11})_3\overset{+}{P}CH_2\overset{-}{C}HX \xrightleftharpoons{RCHO} (C_6H_{11})_3\overset{+}{P}CH_2CHXCH\underset{\underset{R}{|}}{}O^-$$

$$\rightleftharpoons (C_6H_{11})_3\overset{+}{P}CH_2\overset{-}{C}XCHOHR \xrightarrow{-(C_6H_{11})_3P} CH_2{=}CXCH(OH)R$$

SCHEME 50

Tris(hydroxymethyl)phosphine reacts with acrylonitrile to give tris(2-cyanoethyl) phosphine[118]. The reaction appears to require the initial formation of a betaine by addition, followed by proton transfer and loss of formaldehyde (Scheme 51).

Tributylphosphine is an effective catalyst for Michael reactions, as exemplified by the addition of 2-nitropropane to acrylate esters and acrylonitrile derivatives[119]. Triphenylphosphine is suitable if used in the presence of an excess of the nitro compound. The proposed mechanism involves nucleophilic catalysis by attack of the phosphine on the activated alkene to give a betaine, which then acts as a base for generation of a carbanion



SCHEME 51

from the nitroalkane (Scheme 52). The phosphine is therefore playing a different role from that of a conventional base catalyst which attacks the nitroalkane directly.

$$R_3P: + CH_2{=}CHX \longrightarrow R_3\overset{+}{P}CH_2\bar{C}HX \xrightarrow{YH} R_3\overset{+}{P}CH_2CH_2X + Y^-$$

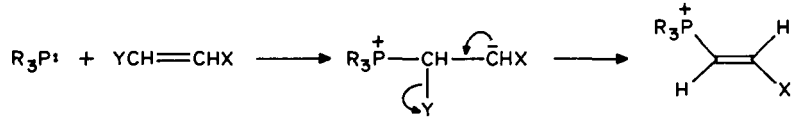
$$Y^- + CH_2{=}CHX \longrightarrow YCH_2\bar{C}HX$$

$$YCH_2\bar{C}HX + YH \longrightarrow YCH_2CH_2X + Y^-$$

$$X = CN,\ CO_2R;\ Y = Me_2CNO_2$$

SCHEME 52

β-Haloacrylic derivatives (*cis* or *trans*) undergo reaction with triphenylphosphine or tributylphosphine to give *trans*-vinylphosphonium salts, probably via elimination from the first-formed betaine[120]. *trans*-β-Bromovinyl phenyl sulphone behaves in an analogous fashion but with phenylsulphinate as the leaving group (Scheme 53)[121].

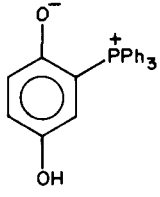


$Y = Cl, Br;\ X = CO_2H, CO_2Me, CN$

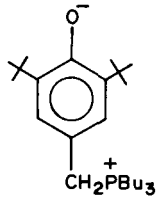
$Y = SO_2Ph;\ X = Br$

SCHEME 53

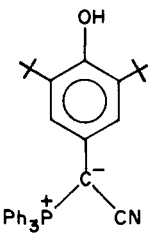
Stable betaines (**31** and **32**) are obtained by the conjugate addition of tertiary phosphines to *p*-benzoquinone[122] and to 4-methylene-2,6-di-*tert*-butylcyclohexa-2,5-dienone[123], respectively, with concomitant aromatization. With an electron-attracting cyano substituent in the 4-methylene position of the latter, a stabilized ylid (**33**) is



(**31**)

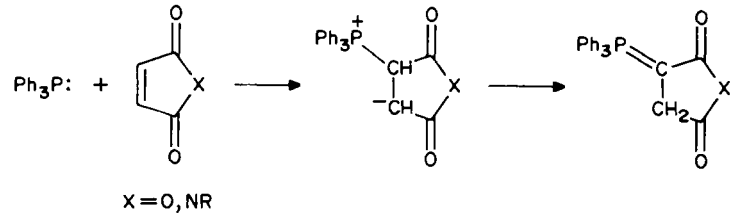


(**32**)



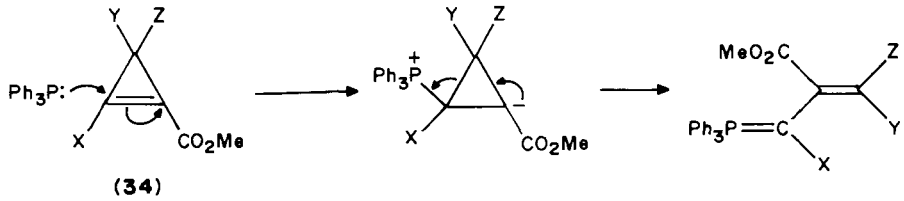
(**33**)

obtained[124]. Stabilized ylids are also formed in the reactions of triphenylphosphine with maleic anhydride[125] and with *N*-substituted maleimides[126] (Scheme 54). Isomaleimides give the same betaines as those obtained from the maleimides, although the stage at which rearrangement occurs is not known. In the reaction of triphenylphosphine with *p*-benzoquinone, ESR evidence has indicated that a radical intermediate may be involved[127].

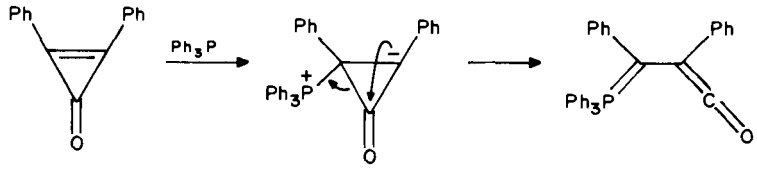


SCHEME 54

Activated cyclopropene derivatives and cyclopropenones readily undergo ring-opening reactions involving nucleophilic attack by a phosphine at an alkenic carbon atom. With triphenylphosphine the spiro[2.4]heptatrienes (**34**. XY = *o*,*o*'-biphenylene; X = H or CO_2Me)[128] and the tetramer of dimethyl acetylenedicarboxylate [**34**, Y = 1,2,3,6-tetrakis-(methyloxycarbonyl)-4-methoxy-7-oxanorborna-2, 5-dien-5-yl; X = Z = CO_2Me][129] undergo regiospecific addition involving cyclopropyl–allyl rearrangement (Scheme 55). Diphenylcyclopropenone gives α-triphenylphosphoranylidenebenzylphenylketene (Scheme 56)[130–132] and a similar ring opening occurs in the reactions of tertiary phosphines with diphenylthiiren-1,1-dioxide[133,134].

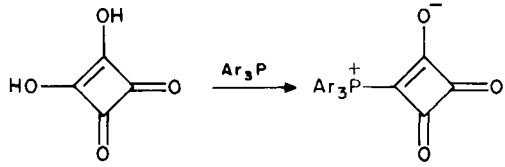


SCHEME 55



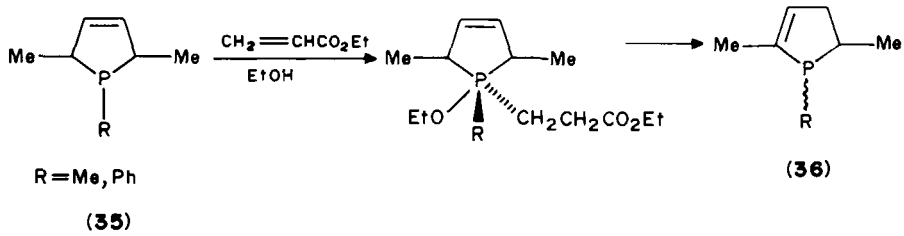
SCHEME 56

The cyclobutene derivative 'squaric acid' undergoes a displacement reaction with triarylphosphines to give betaine derivatives in which the cyclobutene ring is maintained (Scheme 57)[135,136].



SCHEME 57

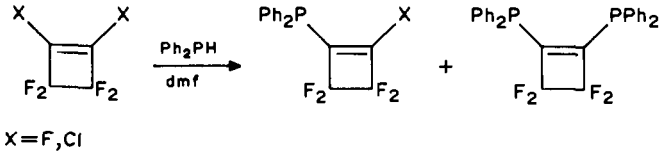
An interesting example of an acrylate-catalysed transformation of a phosphine derivative, is provided by the interaction of ethyl acrylate with a Δ^3-phospholene (**35**). Isomerization to the Δ^2-phospholene (**36**) is thought to occur via nucleophilic attack of phosphorus on the acrylate with the formation of a five-coordinate intermediate (Scheme 58)[137].



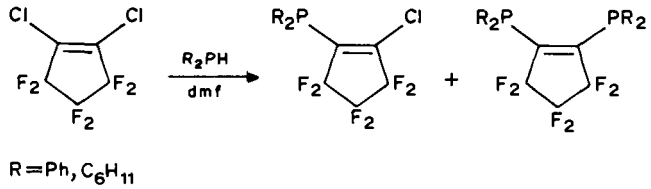
SCHEME 58

3. Reaction of phosphines with perhaloalkenes and perhalocycloalkenes

The nucleophilic attack of phosphines on perhaloalkenes and related compounds results in the displacement of halogen (fluorine or chlorine) from one or both of the alkenic carbon atoms. Diphenylphosphine yields either mono- or di-substitution products according to the conditions in its reactions with perhalocyclobutenes and perhalocyclopentenes (Schemes 59 and 60)[138–140]. In the reaction of dimethylphosphine with

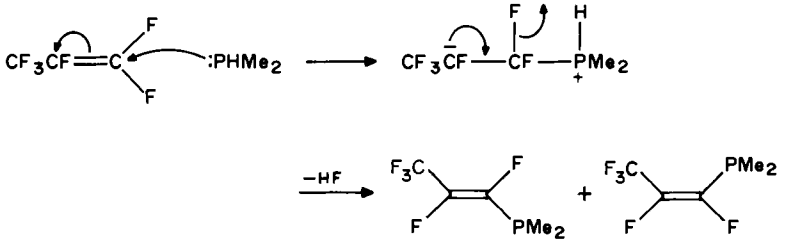


SCHEME 59



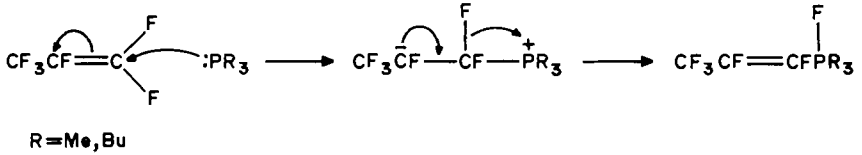
SCHEME 60

perfluoropropene, nucleophilic attack occurs at the terminal CF_2 group to give a mixture of the *cis* and *trans* isomers of perfluoropropenyldimethylphosphine (Scheme 61)[141,142]. The possibility that reaction occurs via the addition of PH to the olefinic double bond, followed by elimination, has been excluded[141]. Tetramethyldiphosphine reacts with perfluoropropene by a similar mechanism.

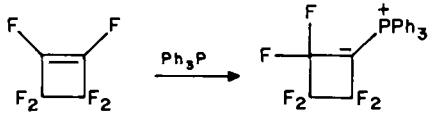


SCHEME 61

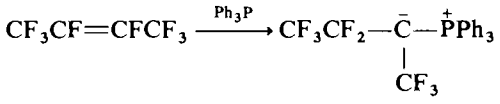
The attack of a trialkylphosphine on perfluoropropene proceeds initially by an analogous displacement, but is followed in this case (in which there is no proton to lose) by addition of the displaced fluoride ion to phosphorus giving a fluorophosphorane (Scheme 62)[142,143]. In reactions of triphenylphosphine with perfluorocyclobutene (Scheme 63) or perfluorobut-2-ene (Scheme 64), the final stage of the reaction is again different, the fluoride ion attaching to the β-carbon with the formation of a phosphonium ylid. This latter type of reaction appears to occur when there is no fluorine on the α-carbon (the potential anionic site). The structure of the product (**37**) derived from triphenylphosphine and perfluorocyclobutene has been confirmed by X-ray diffraction which revealed a typical ylid P—C bond length of 1.713 Å[144]. Compounds of this type readily undergo hydrolysis to give phosphonium betaines (Scheme 65)[145,146].



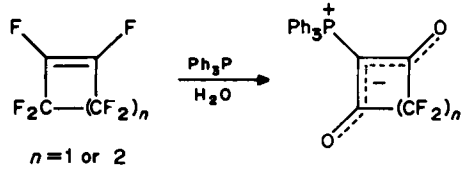
SCHEME 62



SCHEME 63

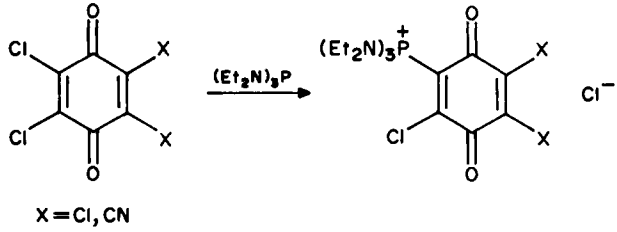


SCHEME 64



SCHEME 65

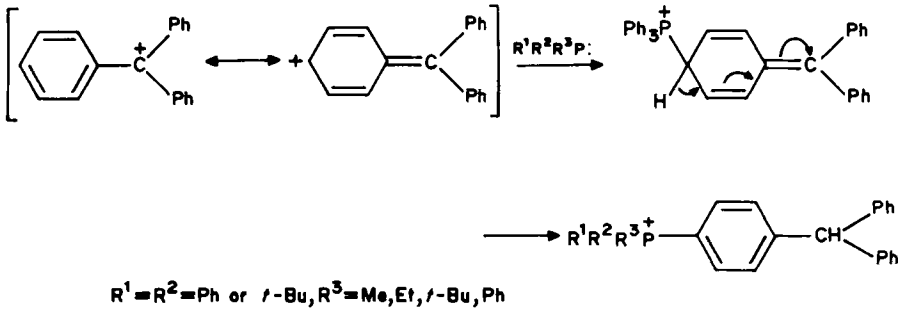
Nucleophilic displacement of chlorine from sp^2 carbon has also been observed in the reactions of trisdiethylaminophosphine with tetrachloro- and dichlorodicyano-*p*-benzoquinone (Scheme 66)[147].



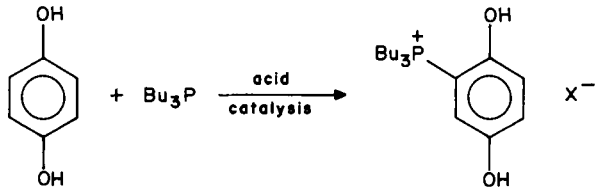
SCHEME 66

C. Nucleophilic Aromatic Substitution

The relatively stable triphenylmethyl carbonium ion, derived from triphenylmethyl chloride, is attacked by phosphines either at the carbonium centre (see Section III.A) or it may be subject to nucleophilic substitution in the benzene ring (Scheme 67)[15]. Substitution in the ring is more liable to occur in the case of more hindered phosphines [e.g. Ph_3P, Ph_2PMe or PhP(*t*-Bu)Me]. *p*-Quinol is reported to give the corresponding tri-*n*-butyl(2,5-dihydroxyphenyl)phosphonium salt by interaction with tri-*n*-butylphosphine in the presence of acid catalysts (Scheme 68)[148,149].



SCHEME 67

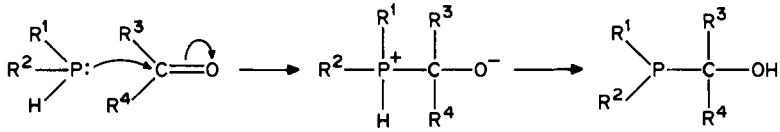


SCHEME 68

D. Additions of Primary and Secondary Phosphines to Carbonyl Compounds and Imino Compounds

1. Carbonyl compounds

Aldehydes and ketones undergo addition reactions with phosphine[150] and with primary or secondary phosphines[151–155] to give α-hydroxyphosphines as the initial products. The overall process may be considered to involve nucleophilic attack by phosphorus at the carbonyl carbon atom followed by proton transfer to oxygen (Scheme 69)[156]. The reaction may be acid catalysed[157–159], in which case protonation of oxygen is presumably the initial step. Several successive stages of reaction may occur if more than one P—H bond is present in the phosphine and the product may be obtained as a phosphonium salt or as the tertiary phosphine hydrochloride according to the conditions (Schemes 70 and 71)[159–161]. Aldehydes that are branched in the α-position react with phosphines in the presence of hydrochloric acid to give 1,3-dioxa-5-



SCHEME 69

$$4RCHO + PH_3 + HCl \xrightarrow{aq.} (RCHOH)_4P^+Cl^-$$

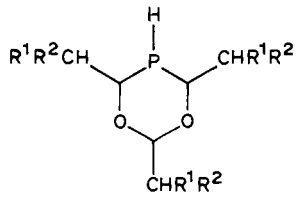
R = H, *n*-alkyl

SCHEME 70

$$2RCHO + R'PH_2 + HCl \xrightarrow{aq.} R'(RCHOH)_2\overset{+}{P}HCl^-$$

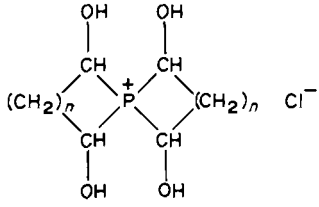
R = Ph, R′ = *i*-Bu; R = *i*-Pr, R′ = Ph

SCHEME 71



$R^1=R^2=Me;\ R^1=Et, R^2=Bu^n$

(38)



$n=2$ or 3

(39)

phosphacyclohexanes (**38**) whilst dialdehydes give spirophosphonium salts (**39**)[162]. Rearrangement of the α-hydroxyphosphonate to the isomeric phosphine oxide may also occur, particularly for products from aromatic aldehydes under strongly acidic conditions (Scheme 72)[163–168], whereas α-alkoxyphosphines are obtained if the reaction is carried out in the presence of an alcohol (Scheme 73)[164,165,167,169]. In the reaction of phenylph-

$$Ph_2PH + ArCHO \xrightarrow[\text{organic solvent}]{\text{dry HCl}} Ph_2P\overset{\overset{OH}{|}}{C}HAr \xrightarrow[\text{heat}]{\text{conc. HCl}} Ph_2PCH_2Ar\ (=O)$$

SCHEME 72

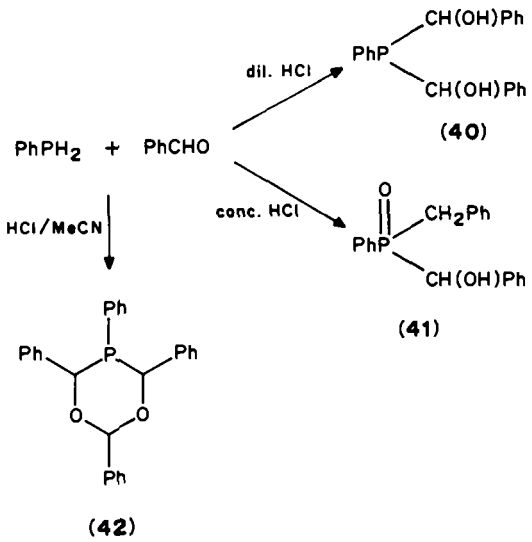
$$R_2PH + ArCHO \xrightarrow[HCl]{R'OH} R_2P\overset{\overset{OR'}{|}}{C}HAr$$

$R' = Me, Et, i\text{-}Pr, t\text{-}Bu$

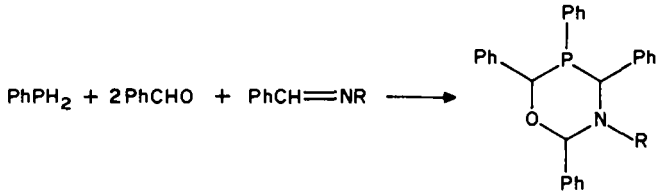
SCHEME 73

osphine with benzaldehyde a number of products are obtainable, viz. the bis(α-hydroxyphosphine) (**40**), the mixed α-hydroxyphosphine oxide (**41**) and the cyclic 1,3,5-dioxaphosphorinane (**42**), the formation of which involves condensation with three molecules of benzaldehyde (Scheme 74)[157,158]. A similar condensation of phenylphosphine with two molecular equivalents of benzaldehyde and one of a Schiff base leads to the formation of 1,3,5-azoxaphosphorinanes (Scheme 75)[170]. *o*-Aminobenzylphosphine cyclizes with carbonyl compounds to yield tetrahydro-1,3-benzazaphorines (Scheme 76)[171].

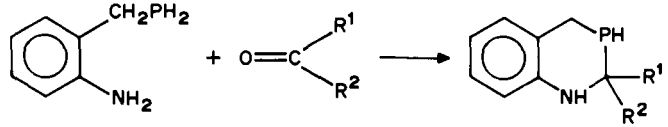
Intramolecular condensation involving the acid-catalysed reactions of ω-hydroxy-[172,173], ω-mercapto[174,175] or ω-amino-alkylphosphines[176,177] with aldehydes or ketones have been used in the synthesis respectively of 1,3-dioxa-, 1,3-dithia- and 1,3-diaza-phospholanes, phosphorinanes and phosphepans. The reactions are assumed to occur[168] by initial attack of phosphorus on the carbonyl carbon atom, followed by cyclization with elimination of water (Scheme 77, route a). Alternatively, an initial interaction between the ω-functional group and carbonyl could occur, followed by nucleophilic attack by phosphorus at a carbonium intermediate (Scheme 77, route b). Bicyclic phosphines are



SCHEME 74



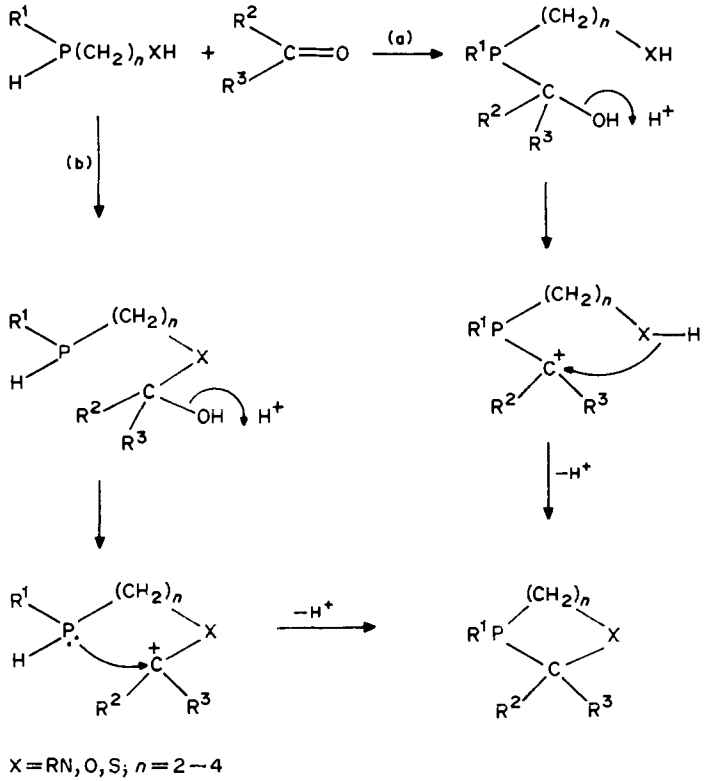
SCHEME 75



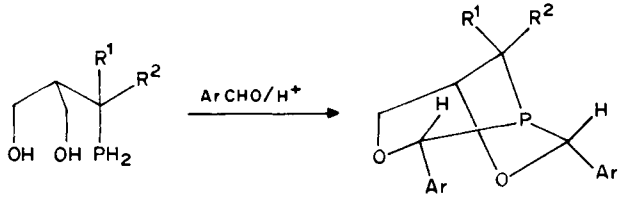
SCHEME 76

obtained by analogous interactions of 2-bis(hydroxymethyl)phosphines with benzaldehyde (Scheme 78)[178].

Methylphosphine, dimethylphosphine[179,180], dicyclohexylphosphine[181] and diphenylphosphine[156,181,182] undergo non-catalysed addition to carbonyl compounds that contain electron-withdrawing groups (e.g. CF_3COCF_3, CF_3COCH_3, hexafluorocyclobutanone, pyruvic acid, pentane-2,4-dione, CF_3COPh and C_6F_5CHO). Whereas an equilibrium mixture of reactants and products is obtained in the interactions of diphenylphosphine with either benzaldehyde or trifluoroacetophenone (Scheme 69,

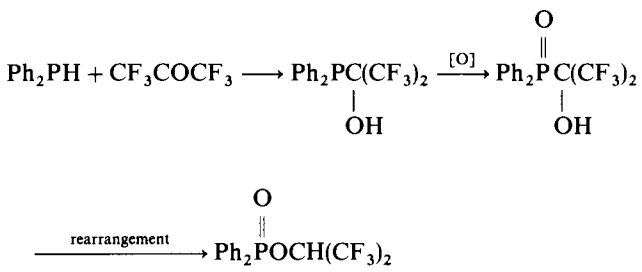


SCHEME 77



SCHEME 78

$R^1 = R^2 = Ph$, $R^3 = Ph$, $R^4 = H$ or CF_3), hexafluoroacetone ($R^3 = R^4 = CF_3$) and pentafluorobenzaldehyde ($R^3 = C_6F_5$, $R^4 = H$) undergo total conversion to products[156]. Ready oxidation to the α-hydroxyphosphine oxide may occur[182], especially in the case of those products derived from aldehydes[156], and further rearrangement may give the isomeric diphenylphosphinites (Scheme 79)[156,179–182]. The product derived from diphenylphosphine and methyl pyruvate was isolated only as the α-hydroxyphosphine oxide[183]. A number of additional products have been found to arise by further decomposition of the α-hydroxyphosphine derived from diphenylphosphine and hexafluoroacetone[156], involving, e.g., nucleophilic–electrophilic interaction of phosphorus(III) species.



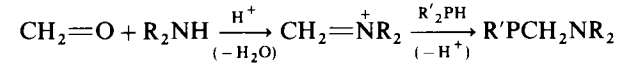
SCHEME 79

Different modes of rearrangement have been demonstrated for α-hydroxyphosphines having either one or two electron-attracting substituents on the α-carbon atom, tertiary phosphine oxides and phosphinite esters, respectively, being obtained[184]. These rearrangements occurred under the catalytic influence of tertiary phosphines whose effectiveness was found to be in the order of their nucleophilicities ($Me_3P > Me_2PPh > MePPh_2$); possible rearrangement mechanisms have been discussed[184].

The additions of dialkoxyphosphines to aldehydes give unstable α-hydroxyphosphines that cannot be isolated as such, although reaction with methyl iodide gives the expected Michaelis–Arbuzov products[185].

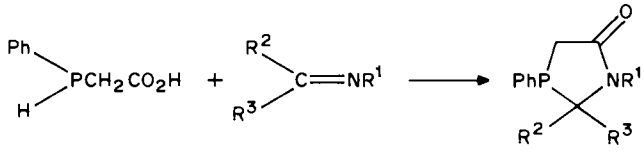
2. *Imino compounds*

Mannich-type reactions occur between phosphines and aldehydes (especially formaldehyde) in the presence of secondary amines and an acid catalyst[186–188]. It is likely that the phosphine enters into an addition reaction with a short-lived immonium intermediate (Scheme 80). Additions to more stable Schiff bases are exemplified by the reaction of diphenylphosphine with *N*-fluorosulphonyl imines (Scheme 81)[189], the cyclization of phenylphosphine with benzaldehyde and Schiff bases referred to above (Scheme 75)[170] and the formation of δ-lactams in the reactions of phenylphosphinylacetic acid with ketimines (Scheme 82)[190]. Alkali metal organophosphides also add readily to Schiff bases[191].



SCHEME 80

SCHEME 81

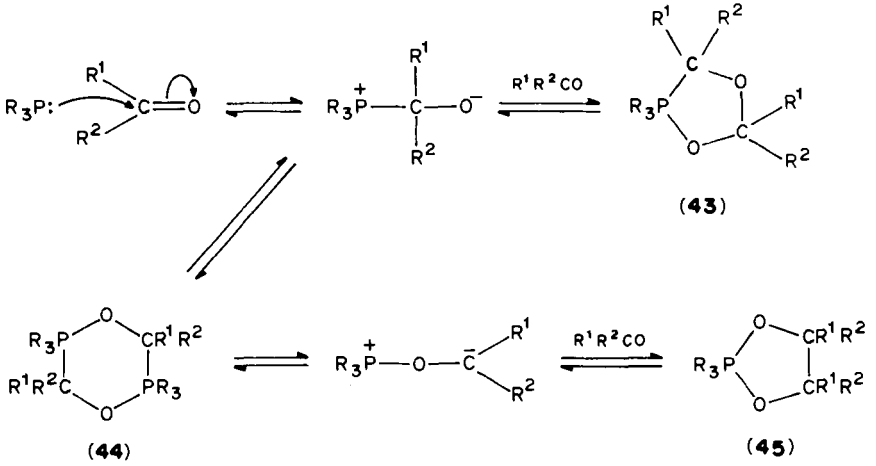


SCHEME 82

E. Reactions of Tertiary Phosphines with Carbonyl, Thiocarbonyl and Selenocarbonyl Compounds

1. Carbonyl compounds

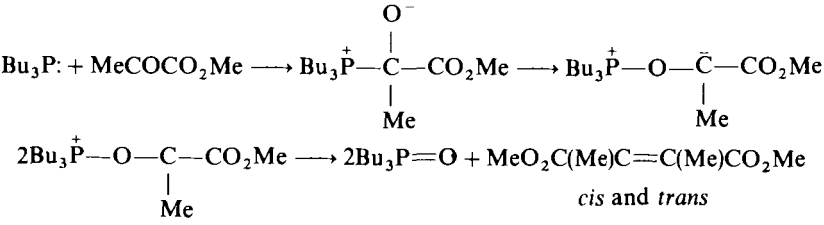
Although phosphorus(III) compounds generally do not form stable 1:1 adducts with aldehydes and ketones, further reaction of the first-formed betaine with a second molecule of the carbonyl compound may give either a 1,4,2-dioxaphospholane (**43**)[192,193] or a 1,3,2-dioxaphospholane (**45**) according to the substituent groups in the two reactants and the reaction conditions (Scheme 83)[156]. Formation of the 1,3,2-dioxaphospholane is thought



SCHEME 83

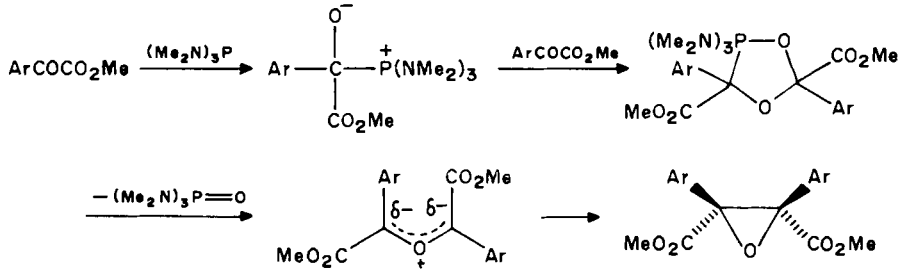
to occur via rearrangement of the first formed betaine to give the P—O—C structure before reaction with the second molecule of carbonyl compound (Scheme 83). Rearrangement of the betaine may possibly occur by a bimolecular process involving a six-membered oxyphosphorane intermediate (**44**)[156]. 1,4,2-Dioxaphospholanes may also be formed in a process involving the initial attack of phosphorus at the carbonyl oxygen atom in the reactions of certain quinones and 1,2-dicarbonyl compounds with phosphorus(III) reagents (see Section VIII.A.4)[194].

Tributylphosphine reacts with methyl pyruvate to give a mixture of *cis*- and *trans*-2,3-di(methoxycarbonyl)but-2-ene, thought to be formed from the betaine by rearrangement, followed by elimination of tributylphosphine oxide (Scheme 84)[195]. In contrast, methyl

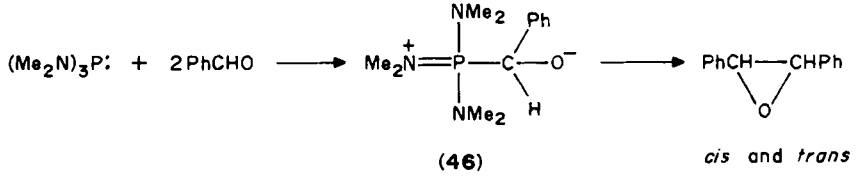


SCHEME 84

arylglyoxylates react with tris(dimethylamino)phosphine to give *cis*- and *trans*-stilbene oxides (Scheme 85), the highest yields being obtained when the aromatic rings contain electron-withdrawing groups[196]. Diastereomeric stilbene oxides are also obtained in the reaction of tris(dimethylamino)phosphine with two molecular equivalents of benzaldehyde (Scheme 86)[197] and in this case the initial betaine (**46**) can be isolated as a stable crystalline solid (characterized by X-ray diffraction). Similar mixtures of *cis*- and *trans*-epoxides are obtained from a number of aliphatic and heterocyclic aldehydes[197] and from pentafluorobenzaldehyde[198].



SCHEME 85



SCHEME 86

2. *Thiocarbonyl and selenocarbonyl compounds*

Nucleophilic attack by trimethylphosphine at the thiocarbonyl carbon atom occurs in the reactions of certain coordinated complexes with dialkyldithiocarbamates (Scheme 87)[199] and xanthates (Scheme 88)[200]. The reactions appear to involve the initial loss of trimethylphosphine which then attacks the coordinated thiocarbonyl ligand. Attack of phosphorus(III) on the thiocarbonyl group of a coordinated thioformate has also been reported[201].

The initial attack of triethylphosphine on selenoesters is thought to give unstable betaines (Scheme 89)[202]. In the absence of other reagents, deselenation gives rise to the

$$MOCl_2(PMe_3)_3 + 2NaS_2CNR_2 \longrightarrow MO(S_2CNR_2)_2(PMe_3) + 2PMe_3 + 2NaCl$$

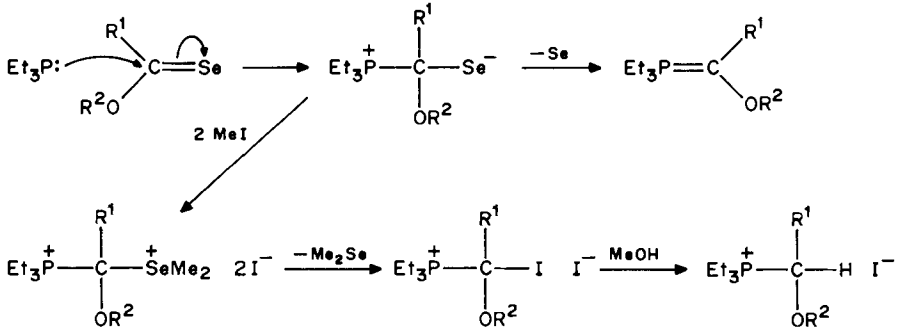
M = Mo, W; R = Me, Et

SCHEME 87

$$MOCl_2(PMe_3)_3 + 2KS_2COR \longrightarrow MO(S_2COR)_2(PMe_3) + 2PMe_3 + 2KCl$$

M = Mo, W; R = Me, Et, *i*-Pr

SCHEME 88



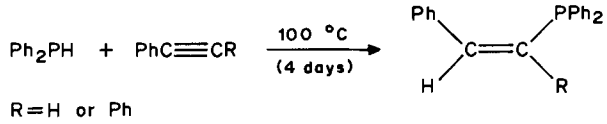
SCHEME 89

corresponding phosphorus ylides. The betaine can, however, be trapped by methyl iodide which initiates a sequence of reactions leading to unstable (iodoalkyl)phosphonium salts. The latter are converted to more stable phosphonium species by reaction with methanol.

IV. NUCLEOPHILIC ATTACK AT sp HYBRIDIZED CARBON

A. Addition of Primary and Secondary Phosphines to Alkynes

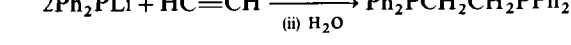
Non-activated alkynes are not susceptible to nucleophilic attack by primary or secondary phosphines. Diphenylphosphine adds slowly to phenylacetylene[203] and to diphenylacetylene[204] at 100 °C to give the products of *trans* addition (Scheme 90), but the



SCHEME 90

mechanism of addition has not been clearly established. The triple bond is apparently activated to some extent by conjugation with the phenyl substituents, since oct-1-yne is totally unreactive under similar conditions[203]. *Trans* addition is, however, consistent with a process of nucleophilic attack. In the presence of air, a change in mechanism is indicated by formation of the *cis*-addition product[203].

Lithium, or other alkali metal phosphides, add readily to acetylenic bonds. Whereas acetylene reacts with two molecular equivalents of lithium diphenylphosphide to give 1,2-bis(diphenylphosphinoethane) (Scheme 91)[203], the addition of alkali metal phosphides to phenylacetylene[203], diphenylacetylene[204,205] and oct-1-yne[203] gives the corresponding vinyl phosphines (Scheme 92). The stereochemistry of addition is influenced by the nature of the alkali metal and by the reaction conditions. It appears that *cis* addition is likely to occur with a more covalent reagent such as lithium diphenylphosphide, whereas *trans*



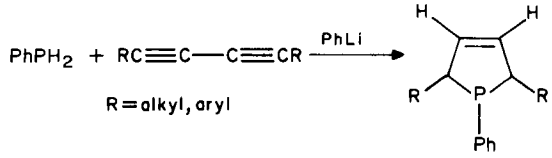
SCHEME 91

$$R^1C{\equiv}CR^2 \xrightarrow[(ii)\ H_2O]{(i)\ R_2P^-M^+} R_2P{-}\underset{\displaystyle R^1}{\underset{|}{C}}{=}CH{-}R^2$$

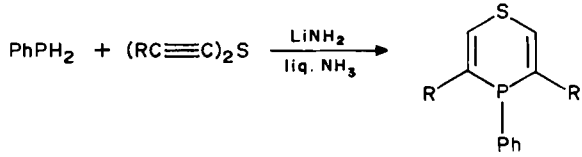
$R^1 = H$, Ph; $R^2 = Ph$
$R^1 = H$; $R^2 = n\text{-}C_6H_{13}$

SCHEME 92

addition is preferred with the more ionic sodium derivative[204]. The presence of a primary or secondary amine in the reaction mixture may change the mode of addition of the lithium reagent, possibly by complexing with the lithium to make the reagent more ionic in character[204]. The effect can be sensitive to the type of amine present, e.g. the reaction of lithium diphenylphosphide with diphenylacetylene in thf gives the *cis* product if diethylamine is present, but the *trans* product is formed in the presence of *n*-butylamine. Both products are obtained with a high degree of stereochemical purity. Phenylacetylene undergoes *trans* addition in the presence of either amine but *cis* addition in their absence[203]. Substituted buta-1,3-diynes add phenylphosphine in the presence of phenyllithium to give phospholes (Scheme 93)[206], whereas 1,4-thiaphosphorins are obtained by the reaction of phenylphosphine with di-1-alkynylsulphides under the influence of lithium amide in liquid ammonia (Scheme 94)[207].



SCHEME 93



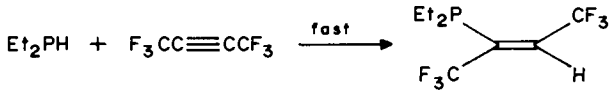
SCHEME 94

The presence of electron-attracting substituents in the alkyne causes activation to nucleophilic addition by phosphines. Diphenylphosphine thus adds readily to ethyl phenylpropiolate or to di(phenylethynyl)ketone to yield vinyl phosphines. The products are readily oxidized but may be converted to the corresponding vinylphosphonium salts by reaction with methyl iodide (Scheme 95)[208]. Diethylphosphine reacts vigorously at low

$$Ph_2PH + PhC{\equiv}CCOR \xrightarrow{HOAc} Ph_2PCPh{=}CHCOR \xrightarrow{MeI} [Ph_2\overset{+}{M}ePCPh{=}CHCOR]I^-$$

R = OEt or —C≡CPh

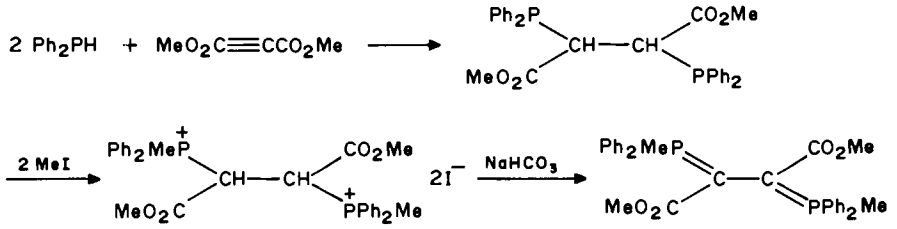
SCHEME 95



SCHEME 96

temperatures with hexafluorobut-2-yne to give the *trans*-addition product (Scheme 96)[209]. On the other hand, bis(trifluoromethyl)phosphine reacts only slightly at 105 °C because the nucleophilicity of the phosphine is reduced by the presence of the electron-attracting substituents (addition in this case occurs by radical attack under the influence of UV radiation). Nucleophilic addition of di-*n*-butylphosphine to di-*n*-butylethynylphosphine oxide, in which activation is caused by the phosphoryl substituent, gives the expected 1:1 adduct, although in only moderate yield[210].

Two molecular equivalents of diphenylphosphine add to dimethyl acetylenedicarboxylate to give a biphosphine, which by quaternization with methyl iodide followed by elimination gives a 1,2-alkylidenebisphosphorane (Scheme 97)[211]. In the case of diacylacetylenes, however, addition occurs preferentially at the carbonyl groups.

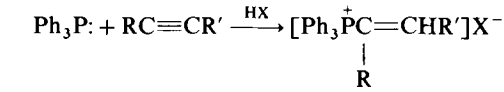


SCHEME 97

It is interesting that the reactions of primary phosphines with α-chloroalkynes[212] or of secondary phosphide anions with propargyl bromides[213] occur either by nucleophilic substitution of the halogen or by halogen abstraction, rather than by addition to the triple bond.

B. Reactions of Tertiary Phosphines with Activated Alkynes

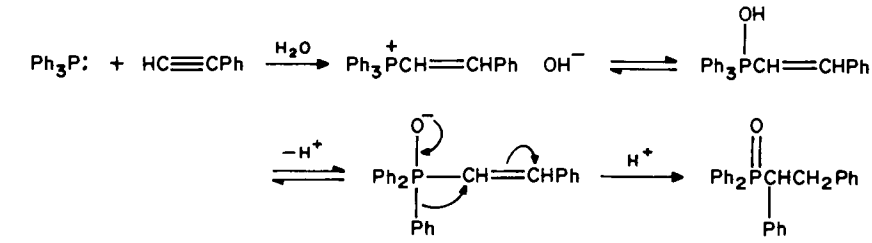
Tertiary phosphines do not enter into nucleophilic reactions with alkynes unless an activating group (e.g. CO, CN, or another electron-attracting group) is present. The initial stage of reaction is assumed to generate a 1:1 adduct, although this is generally unstable and may react further in a variety of ways. In the presence of mineral acid, vinylphosphonium salts are obtained (Scheme 98)[208,214].



R = Ph, R′ = CO_2H, CO_2Et, $CONH_2$, CHO, C≡CPh, COC≡CPh;
R = R′ = CO_2H; R = R′ = CO_2Me;
R = H, R′ = CO_2H; R = Ph, R′ = $P(Ph)_3Br$

SCHEME 98

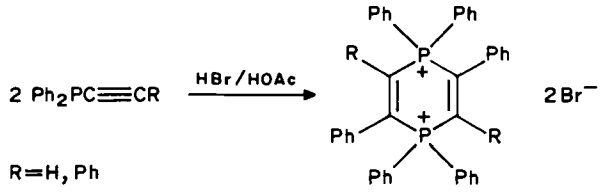
Phenyl or vinyl groups may provide sufficient activation by conjugation with the acetylenic bond. Thus triphenylphosphine reacts with phenylacetylene, in the presence of water, to give 1,2-diphenylethyldiphenylphosphine oxide[215] via a vinylphosphonium intermediate (Scheme 99)[216]. Dipolar intermediates have been reported in the reactions of



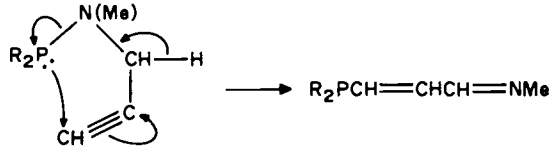
SCHEME 99

tributylphosphine with phenylacetylene[217], isopropenylacetylene[218] and vinylacetylene[219]. Activation by the ethoxy group is seen in the reactions of tributylphosphine with ethoxyacetylene. Both 1:1 and 1:2 adducts appear to be formed on the basis of the phosphonium salts that are obtained by trapping with acetyl bromide or ethyl bromide[220,221].

Self-condensation reactions of alkynylphosphines catalysed by hydrogen bromide in acetic acid yield substituted 1,4-diphosphoniacyclohexa-2,5-diene salts (Scheme 100)[222,223]. A number of mechanistic pathways are possible, including that of Michael addition[224]. Intramolecular nucleophilic attack of phosphorus(III) on an acetylenic carbon atom occurs also in the reactions of *o*-alkynylphenylphosphines in aqueous ethanol[225] and in the rearrangement of *N*-propargylaminophosphines (Scheme 101)[226].

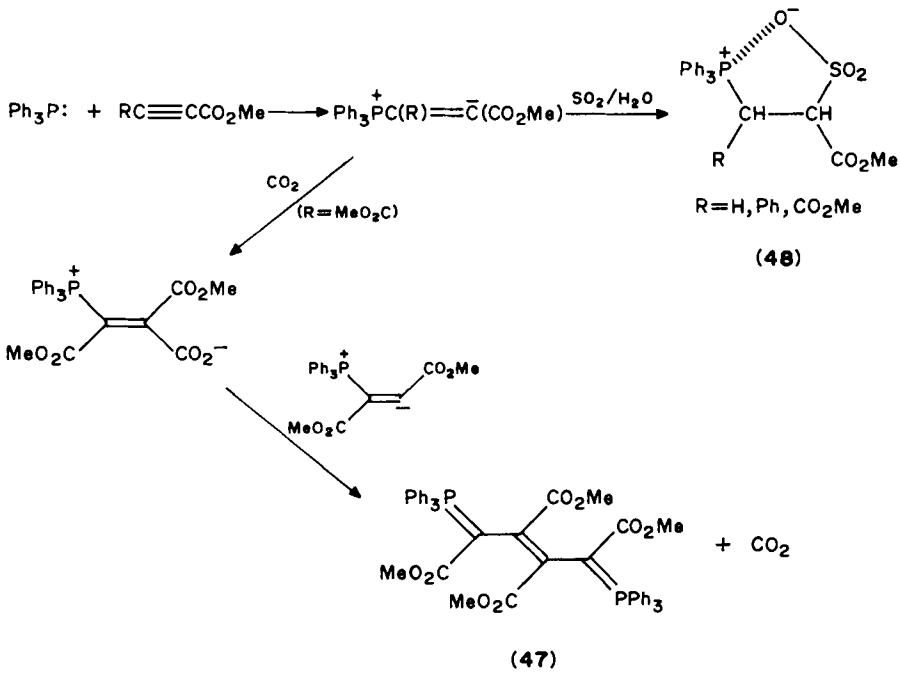


SCHEME 100



SCHEME 101

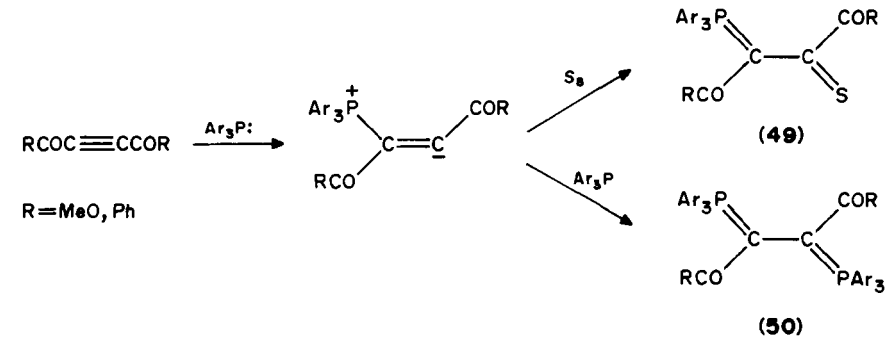
The addition reactions of acetylenes containing one or two carbomethoxy substituents have been studied in considerable detail and can gives rise to a remarkable range of products[227,228]. With triphenylphosphine, dimethyl acetylenedicarboxylate gives a 1:1



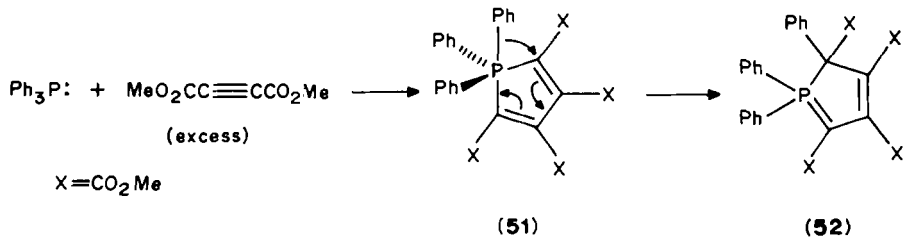
SCHEME 102

dipolar adduct which, although unstable and incapable of isolation as first reported[214], can be trapped by carbon dioxide[209] or by sulphur dioxide and water (Scheme 102) R = CO_2Me)[230]. Further reaction of the carbon dioxide adduct with a second molecule of the phosphine–acetylene adduct can then give a stable 2:2 adduct, which has been shown to be a 1,4-alkylidenebisphosphorane (**47**). The latter is also obtained by reaction of triphenylphosphine with the acetylene in polar solvents[229]. The sulphur dioxide–water adduct (**48**, R = CO_2Me) has been shown to crystallize in the *threo* configuration and to retain a cyclic conformation in solution. Similar phosphoniaethanesulphonates (**48**, R = H or Ph) are obtained from methyl propiolate and methyl phenylacetylenecarboxylate, respectively[230]. The 1:1 adduct of triphenylphosphine with dimethyl acetylenedicarboxylate, and that with dibenzoylacetylene, can also be trapped by reaction with sulphur, which gives stable ylides (**49**) (Scheme 103)[231]. 1,2-Alkylidenediphosphoranes (**50**) are obtained as 2:1 adducts in the reactions of an excess of triarylphosphine with dimethyl acetylenedicarboxylate[231,232], or diacylacetylenes[211,231].

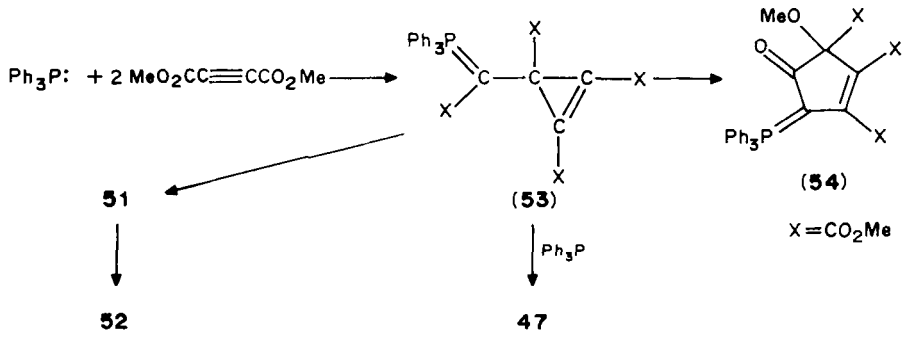
By heating triphenylphosphine with an excess of dimethyl acetylenedicarboxylate in diethyl ether, under reflux, a stable 1:2 adduct is obtained[233], shown to be a cyclic ylide (**52**) formed by 1,2-shift of phenyl in a cyclic phosphorane intermediate (**51**) (Scheme 104)[234]. A further, unstable 1:2 adduct (**53**) is formed initially at $-50\,^{\circ}C$[235]. Rearrangement may then give the phosphorane (**51**) and thence the ylide (**52**), which are otherwise obtained under reflux[234], or alternatively a cyclopentenylidenephosphorane (**54**) may be formed (Scheme 105)[235,236]. The structure of the latter type of product has been confirmed by X-ray diffraction in the case of the tri-*p*-tolylphosphine derivative[237]. Further confirmation of the proposed structure for the initial 1:2 adduct is given by its



SCHEME 103



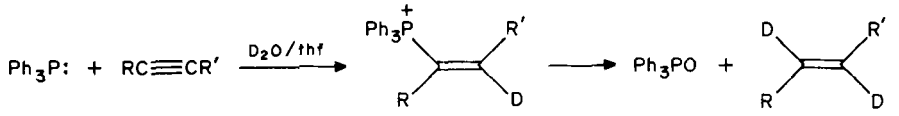
SCHEME 104



SCHEME 105

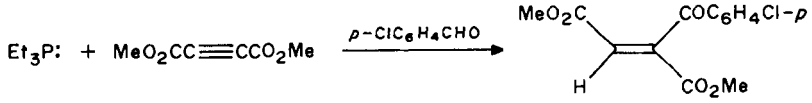
reaction with triphenylphosphine in methanol or chloroform to give the open-chain, 1,4-alkylidenebisphosphorane (47)[235].

Dimethyl or diethyl fumarate is obtained, together with the corresponding phosphine oxide, by the reaction of triphenyl- or triethyl-phosphine with dimethyl acetylenedicarboxylate in the presence of water[214,238,239]. It is assumed that the reaction proceeds via hydrolysis of the initially formed 1:1 complex. The use of deuterium oxide in this type of reaction provides a useful route for the preparation of dideuteriated alkenes (Scheme 106)[238]. In the presence of *p*-chlorobenzaldehyde, the 1:1 complex from



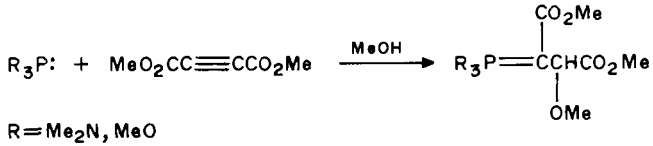
R=R′=CO_2Me; R=Ph, R′=CO_2Me, COPh

SCHEME 106



SCHEME 107

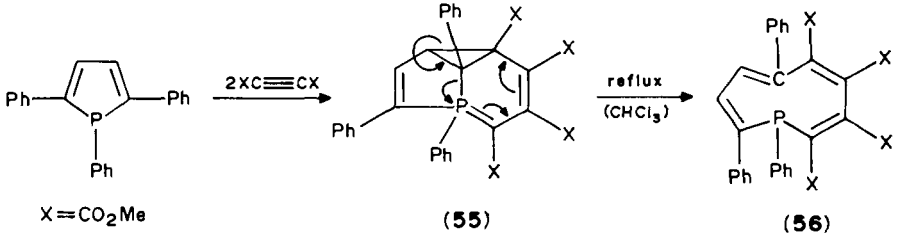
triethylphosphine gives the corresponding elimination product (Scheme 107)[239]. Evidence for the formation of a 1:1 adduct in the reaction of trimethyl phosphite and of trisdimethylaminophosphine with dimethyl acetylenedicarboxylate is provided by trapping with methanol to yield the corresponding ylide (Scheme 108)[240].



R=Me_2N, MeO

SCHEME 108

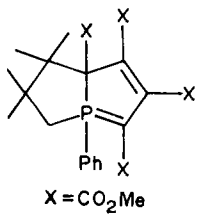
The interactions of cyclic phosphines and of bisphosphines with dimethyl acetylenedicarboxylate give rise to various heterocyclic products. 1,2,5-Triphenylphosphole yields a 1:2 adduct (**55**) that is stable at room temperature but undergoes isomerization to a second, more stable, 1:2 adduct (**56**) on heating in boiling chloroform (Scheme 109)[241].



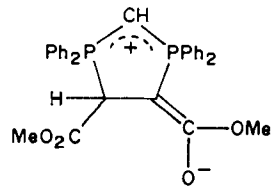
X=CO_2Me (**55**) (**56**)

SCHEME 109

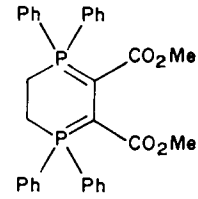
The structures of these two adducts have been established by NMR and IR spectroscopy[242]. Heterocyclic products (**57–62**) are also formed in the reactions of dimethyl acetylenedicarboxylate with 1-phenyl-2,2,3,3-tetramethylphosphetane[243], bis(diphenylphosphino)methane[244], 1,2-bis(diphenylphosphino)ethane[245], *cis*-1,2-bis(diphenyl-



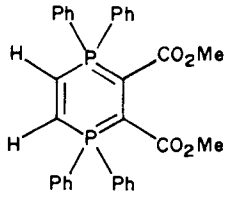
(57)



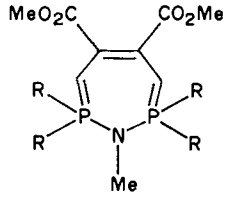
(58)



(59)

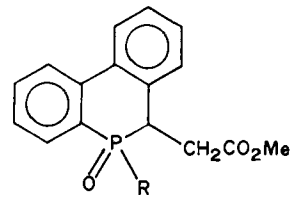


(60)



R=Me,Ph

(61)

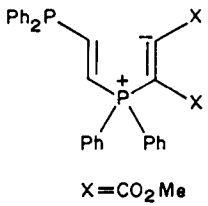


R=Me,Ph,PhCH2

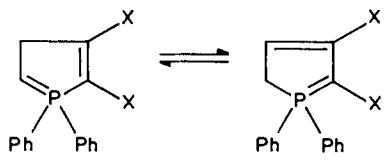
(62)

phosphino)ethene[244,246] and bis(dimethyl- or diphenyl-phosphino)methylamine[247], and in the reactions of dibenzophosph(III)oles with methyl propiolate in the presence of water[248], respectively. In each case the reaction is initiated by nucleophilic attack of phosphorus at the acetylenic carbon atom.

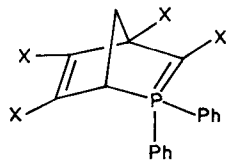
The *trans* isomer of 1,2-bis(diphenylphosphino)ethene gives an open-chain 1:1 adduct (**63**) on reaction with dimethyl acetylenedicarboxylate, whereas diphenylvinylphosphine gives 1:1 or 1:2 addition products (**64** and **65**)[246].



(63)



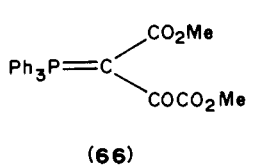
(64)



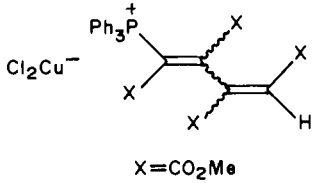
(65)

The tetrameric complex of triphenylphosphine and copper(I) chloride undergoes reaction with dimethyl acetylenedicarboxylate in benzene, under an atmosphere of nitrogen, to give approximately equal amounts of the 1,4-alkylidenebisphosphorane (**47**) and what appears to be an oxidized form of the 1:1 adduct (**66**)[249]. A small amount of a phosphonium chlorocuprate (**67**) is also obtained.

Triphenylphosphine reacts with dicyanoacetylene in acetonitrile to give a purple polymer, together with an orange crystalline adduct[103]. The latter has been shown by mass



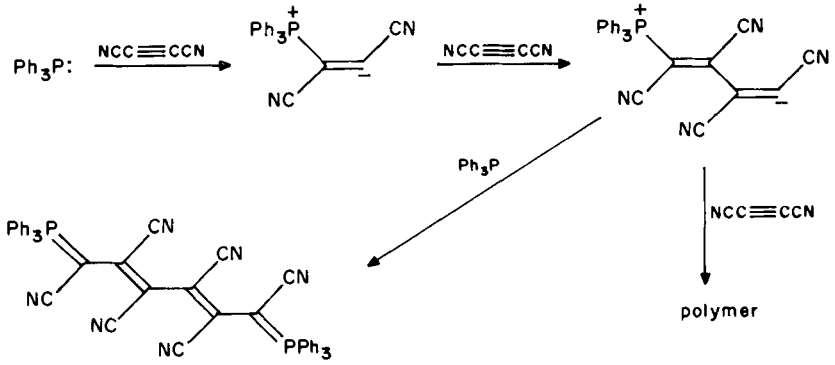
(66)



X=CO_2Me

(67)

spectrometry to be a 3:2 adduct, and has been assignd the structure of a 1,6-alkylidenebisphosphorane (**68**)[250]. The cyclic structure originally proposed is therefore incorrect. As in the related reactions of dimethyl acetylenedicarboxylate, the phosphine is thought to form an initial 1:1 adduct by nucleophilic addition. Further reaction may then lead to polymer formation or, alternatively, to the 3:2 adduct (Scheme 110). The preferred



(68)

SCHEME 110

formation of the latter (as opposed to the alternative 2:1 or 2:2 adducts that are obtained in other related systems) has been attributed to the highly electron-attracting character of the cyano group[250]. Bis(trifluoromethyl)acetylene, however, undergoes rapid polymerization at −78 °C on treatment with triphenylphosphine[209].

The reactions of halogenated alkynes with triphenylphosphine give ethynyl phosphonium salts through replacement of halogen by phosphorus (Scheme 111)[251]. The

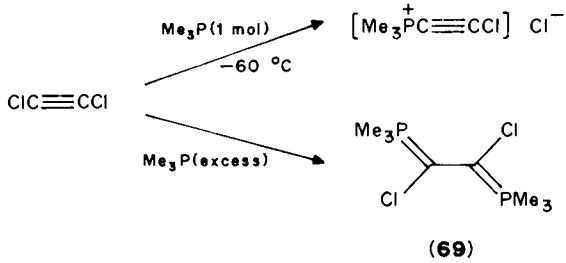
$$Ph_3P: + HalC{\equiv}CX \longrightarrow [Ph_3\overset{+}{P}C{\equiv}CX]Hal^-$$

X = H, Hal = F, Cl; X = Ph, COR, CH_2OH, CH_2O-pyranyl, Hal = Cl, Br; X = Hal = Cl

SCHEME 111

reactivity varies considerably with the substituents present and is especially high in the case of fluorine. A mechanistic study of the reaction between triphenylphosphine and phenylbromoacetylene[252] has shown that, in this case at least, the reaction probably proceeds via halogen abstraction to give a halogenophosphonium ion pair which collapses to give the phosphonium salt (see Section IX.B.5 for nucleophilic attack of phosphorus on

halogens). Trimethylphosphine gives an analogous phosphonium salt by reaction with dichloroacetylene at −60 °C, but with an excess of the phosphine addition occurs, giving a 1,2-bis-ylide (**69**) (Scheme 112)[253] analogous to the 1,2-bis-ylides obtained from disubstituted acetylenes containing other activating groups.

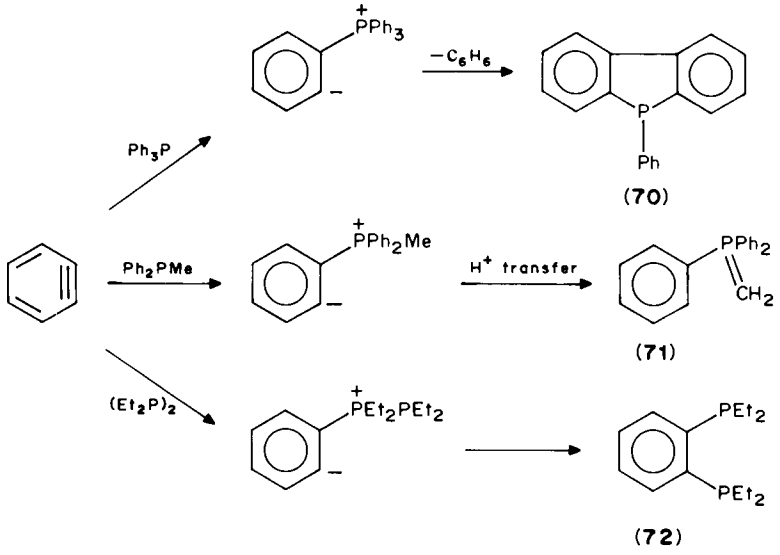


(**69**)

SCHEME 112

C. Reactions of Tertiary Phosphines with Benzynes

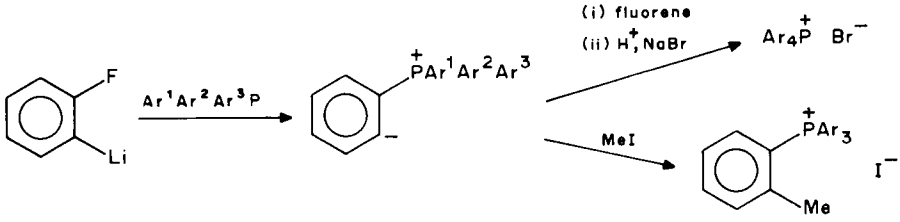
Benzyne, generated from *o*-bromofluorobenzene and magnesium, reacts with triphenylphosphine to give a low yield of phenylbiphenylenephosphine (**70**), presumably via addition followed by the elimination of benzene (Scheme 113)[254]. The betaine can



SCHEME 113

be trapped by reaction with triphenylboron. By a similar procedure, methyldiphenylphosphine yields a product which is assumed to be triphenylphosphinemethylene (**71**)[255], since further reaction with cyclohexanone yields the product of the Wittig reation, methylenecyclohexane. Tetraethyldiphosphine[256] gives an intermediate which becomes

stabilized through intramolecular rearrangement with the formation of *o*-phenylenebisdiethylphosphine (**72**). The reactions of triarylphosphines with a range of benzyne intermediates have been shown to give betaines that can be trapped by a proton donor such as fluorene, and thence converted to tetraarylphosphonium salts, e.g. acidification and the addition of sodium bromide yields tetraarylphosphonium bromides (Scheme 114)[257]. The initial betaine can also be trapped by reaction with methyl iodide.

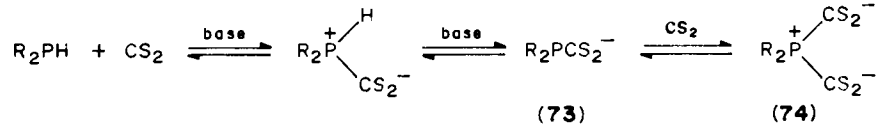


SCHEME 114

D. Reactions with Carbon Disulphide and Carbon Diselenide

Secondary phosphines react with ethanolic carbon disulphide in the presence of a base to give phosphinodithioformates (**73**) or phosphoniobisdithioformates (**74**) in two successive processes of nucleophilic attack by phosphorus (Scheme 115)[258,259]. The position of equilibrium is dependent on the inductive effects of the substituents. Whereas diphenylphosphine gives only the phosphinodithioformate, diethylphosphine gives the bisdithioformate. Tertiary phosphines give zwitterionic products (Scheme 116)[260,261]. In the reaction of a silylaminophosphine with carbon disulphide (Scheme 116, $R^1 = Me$, $R^2 = Me_3SiNR$), it was noted that an analogous betaine was formed without cleavage of, or insertion into, the P—N or Si—N bonds[262].

Carbon diselenide gives a stable cyclic ylide when allowed to react in excess with tributylphosphine (Scheme 117)[263].

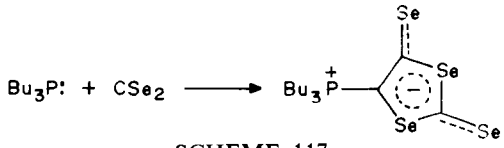


SCHEME 115

$$R^1{}_2R^2P: + CS_2 \rightleftharpoons R^1{}_2R^2\overset{+}{P}C\overset{S}{\underset{S^-}{<}}$$

$R^1 = Et$, Ph; $R^1 = Et$, $R^2 = Ph$;
$R^1 = Me$, $R^2 = Me_3SiN(R)$—

SCHEME 116



SCHEME 117

E. Reactions with Ketenes and Allenes

Primary and secondary phosphines add rapidly at low temperatures to the carbon—carbon double bond of ketenes to yield diacylphosphines (Scheme 118)[264] or monoacylphosphines (Scheme 119)[265–267], respectively.

With trialkylphosphines, allenecarboxylates give dipolar adducts in which the anionic charge is delocalized over the three-carbon allenic system (Scheme 120)[268].

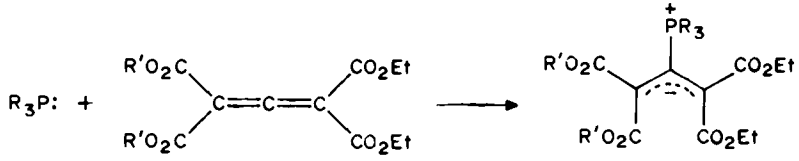
$$MePH_2 + 2CH_2{=}C{=}O \longrightarrow MeP(COMe)_2$$

SCHEME 118

$$R_2PH + R'_2C{=}C{=}O \longrightarrow R_2PCOR'_2$$

R = Me, Ph; R′ = H, CF_3

SCHEME 119

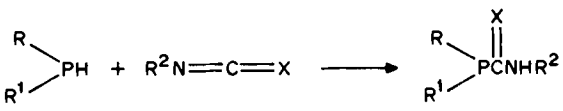


R=Ph, Me_2N; R′=Et, Me

SCHEME 120

F. Reactions with Isocyanates and Isothiocyanates

The reactions of primary or secondary phosphines with isocyanates and isothiocyanates have been widely used for the preparation of carbamoyl- and thiocarbamoyl-phosphines. Nucleophilic attack occurs at the carbonyl or thiocarbonyl carbon atom, with proton transfer to nitrogen (Scheme 121).



R=alkyl, aryl; R^1=alkyl, aryl, H; X=O, S

SCHEME 121

Cyanic acid (isocyanic acid) generated *in situ* from potassium cyanate reacts with primary or secondary phosphines, but not with phosphine, to give unsubstituted mono- and di-carbamoylphosphines (Scheme 122)[269–271]. The products are readily susceptible

$$R_xPH_{x-3} + (3-x)HOCN \longrightarrow R_xP(CONH_2)_{3-x}$$

R = alkyl, aryl; $x = 1$ or 2

SCHEME 122

to oxidation by atmospheric oxygen but may be recrystallized from degassed benzene under an atmosphere of nitrogen[271].

Aryl isocyanates react readily with phosphine in the presence of triethylamine to give tris(carbamoyl)phosphines (Scheme 123)[272]. The intermediate mono- and di-carbamoylphosphines cannot be isolated as the nucleophilic reactivity of phosphorus increases as hydrogen is progressively replaced by carbamoyl substituents. Similar

$$PH_3 + 3ArN{=}C{=}O \xrightarrow[2\text{-}4\ atm]{Et_3N} P(CONHAr)_3$$

SCHEME 123

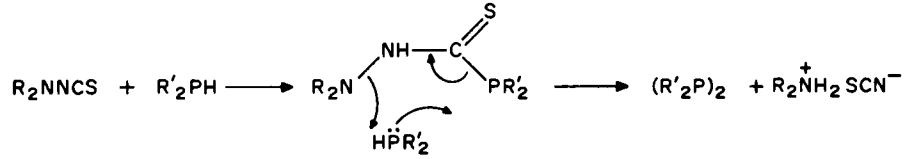
additions of primary or secondary phosphines to isocyanates give products in which all hydrogen atoms of the phosphine have been replaced[273-276]. Although phosphine itself does not react with phenyl isothiocyanate, primary and secondary phosphines react readily, in the absence of catalyst, to give thiocarbamoyl derivatives (Scheme 121; R = aryl, X = S)[277,278]. Secondary phosphines also react with isothiocyanic acid, generated *in situ*, to give the corresponding thiocarbamoylphosphines and, by oxidation or the addition of sulphur, the bisphosphinyl- or bisthiophosphinyl-iminomethyl sulphides (Scheme 124)[279].

$$Ph_2PH + HNCS \longrightarrow Ph_2PC(S)NH_2 + Ph_2P(X)\overset{NHNH}{\overset{\|\ \ \|}{C\ S\ C}}P(X)Ph_2$$

X = O, S

SCHEME 124

N-Isothiocyanatodiisopropylamine undergoes reaction with dimethyl- or diethyl-amine to give the corresponding tetraalkyldiphosphine and diisopropylammonium thiocyanate[280]. It is thought that the initial formation of a thiocarbamoylphosphine is followed in this case by further reaction with a second molecule of the phosphine, possibly as shown in Scheme 125.



R = *i*-Pr, R' = Me, Et

SCHEME 125

Zwitterionic products are generally obtained from the reactions of tertiary phosphines with isocyanates[281-284] and isothiocyanates[280,285,286]. The anionic charge is delocalized over the carbamoyl grouping and may be stabilized further by the presence of electron-attracting substituents on nitrogen (Scheme 126).

$$R_3P{:} + R'N{=}C{=}X \longrightarrow R_3\overset{+}{P}{-}\overset{X}{\overset{|}{C}}{=}N{-}R'$$

X = O, R' = SO_2F, CO_2H, CO_2Et, $CONH_2$, R = alkyl, aryl, Me_2N
X = S, R' = alkyl, aryl, COMe, COPh, R = alkyl or Me_2N

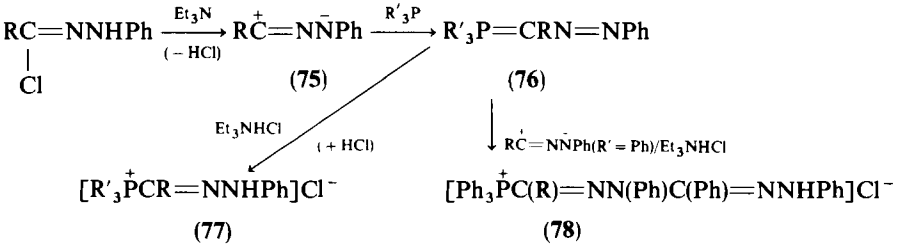
SCHEME 126

G. Reactions with Nitriles and Nitrilimines

There are no reports of reaction between the nitrile group and neutral phosphines. Alkali metal organophosphides will, however, attack nitriles containing no α-hydrogen to give products of addition to the carbon—nitrogen triple bond (Scheme 127)[191]. Only proton abstraction occurs if α-hydrogen atoms are present. Nitrilimines (**75**) react with aliphatic and mixed aliphatic–aromatic tertiary phosphines[287] and with phosphorus(III) amides[288] to give azomethylene adducts (**76**) (R = *p*-$O_2NC_6H_4$, CH_3CO or EtO_2C) or phosphonium salts (**77**) (R = Ph), according to the electronic effect of the substituent group R (Scheme 128). With triphenylphosphine, both 1:1 adducts (**76**)[289] and 1:2 adducts (**78**)[290] are obtainable.

$$R_2PLi + PhC{\equiv}N \longrightarrow R_2PC(Ph){=}NLi \xrightarrow{PhC{\equiv}N} R_2PC(Ph){=}NC(Ph){=}NLi$$

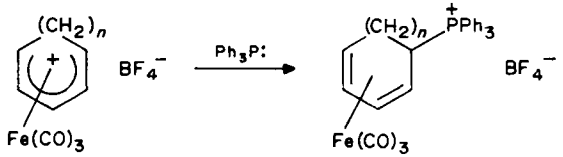
SCHEME 127



SCHEME 128

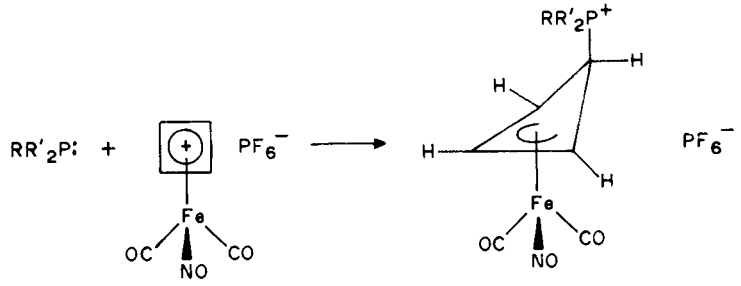
V. NUCLEOPHILIC ATTACK AT π-HYDROCARBON LIGANDS

The formation of a phosphonium ion by nucleophilic addition of a tertiary phosphine to the dienyl fragment of a π-hydrocarbon complex was first shown to occur in the reactions of triphenylphosphine with the cyclohexadienyl- or cyclopentadienyl-iron tricarbonyls (Scheme 129)[291]. The products were isolated by the addition of diethyl ether after reaction in methylene chloride at room temperature. Similar additions occur in the reactions of trialkyl- or triaryl-phosphines with many other π-hydrocarbon ligands, e.g. cyclobutadiene, benzocyclobutadiene, tropylium and homotropylium[292–295], and with coordinated arenes[296–299]. X-ray structure determination in a number of cases has shown

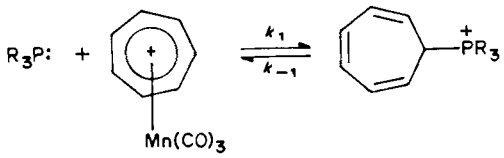


n = 1 or 2

SCHEME 129



SCHEME 130



SCHEME 131

the phosphine substituent to occupy the *exo* position (e.g. **79**, Scheme 130). Numerous reactions of this type, involving a wide range of π-hydrocarbon ligands (C_3H_5, C_4C_4, C_6H_6, C_6H_7, C_7H_7, C_7H_8, C_7H_9 and C_8H_{11}) have been studied kinetically and this general area of chemistry has been reviewed[300]. For reactions of this type (e.g. Scheme 131), the following general rate law has been found to apply:

$$\text{Rate} = k_1[\text{complex}][\text{Nu}] + k_{-1}[\text{complex}]$$

where Nu is the nucleophilic phosphine.

The forward reaction is fast, with $\Delta H^{\ddagger}$ values typically in the region of 14–50 kj mol^{-1}. Large negative entropies of activation ($\Delta S^{\ddagger} = -30$ to -130 J K^{-1} mol^{-1}) are consistent with a bimolecular reaction. The slower reaction of arene complexes compared with that of the analogous cycloheptatriene derivatives[301] may be attributed to the loss of resonance energy that occurs on formation of a phosphonium adduct from the former. The high reactivity of tri-*o*-anisylphosphine towards the coordinated 1-5-η^5-cyclohexadienyl system[302,303] parallels that shown by *o*-anisyl phosphines in their reactions with alkyl halides and is attributed to the anchimeric effect of the *o*-methoxy group (see Section II.D).

VI. NUCLEOPHILIC ATTACK AT BORON, SILICON, GERMANIUM AND TIN

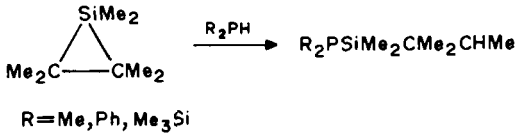
Tertiary phosphines readily donate their electron pair to boron in reactions with boranes to give a range of phosphine–borane adducts[304]. In addition, nucleophilic displacement of halogen from boron by a second molecule of phosphine can give rise to the formation of bis(phosphino)boronium ions, e.g. **80** (Scheme 132). The net displacement of chlorine from boron also occurs in the reactions of trimethylphosphine with certain chloro-*closo*-carboranes, followed by treatment with boron trichloride[305].

Nucleophilic attack at silicon occurs in the ring opening of hexamethylsiliran by primary or secondary phosphines (Scheme 133)[306]. With triphenylphosphine, the analog-

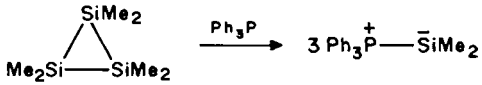
ous hexamethylsilacyclopropane undergoes fission of all Si—Si bonds to yield a phosphorus–silicon ylide (Scheme 134)[307].

$$Me_3P: + BH_3 \longrightarrow Me_3\overset{+}{P}—\overset{-}{B}H_3 \xrightarrow{HBr} Me_3\overset{+}{P}—\overset{-}{B}H_2Br \xrightarrow{Me_3P:} [Me_3P—BH_2—PMe_3]^+ Br^-$$

(80) SCHEME 132

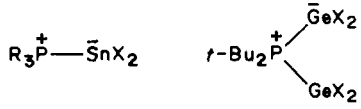


SCHEME 133

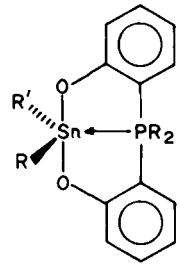


SCHEME 134

Phosphorus–tin ylides (**81**)[308] and phosphorus–germanium ylides (**82**)[309] are obtained in the reactions of tertiary phosphines with tin(II) or germanium(II) halides and a *trans*-annular phosphorus–tin bonds is formed in the products (**83**) of reaction between bis(hydroxyphenyl)phosphines and dimethoxystannanes[310].



(81) **(82)**



(83)

Nucleophilic displacement of halogen from trimethylsilyl chloride or trimethylgermyl chloride occurs in the reactions of these halides with allylphosphine in the presence of triethylamine (Scheme 135)[311].

$$CH_2{=}CHCH_2PH_2 \xrightarrow[Et_3N]{Me_3MCl} CH_2{=}CHCH_2P(H)MMe_3 \xrightarrow[Et_3N]{Me_3MCl} CH_2{=}CHCH_2P(MMe_3)_2$$

M = Si, Ge

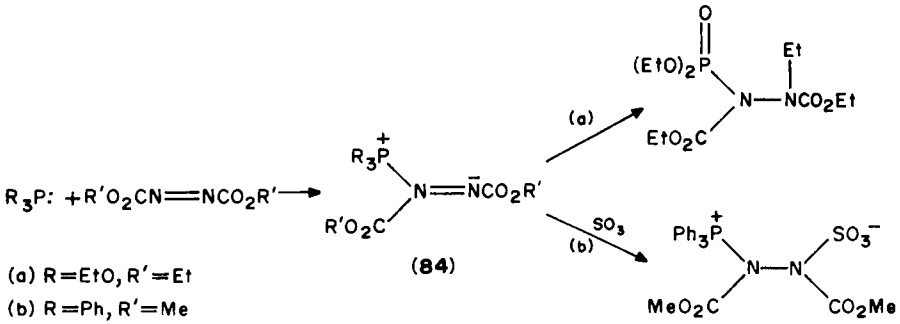
SCHEME 135

VII. NUCLEOPHILIC ATTACK AT GROUP V ELEMENTS

A. Nitrogen

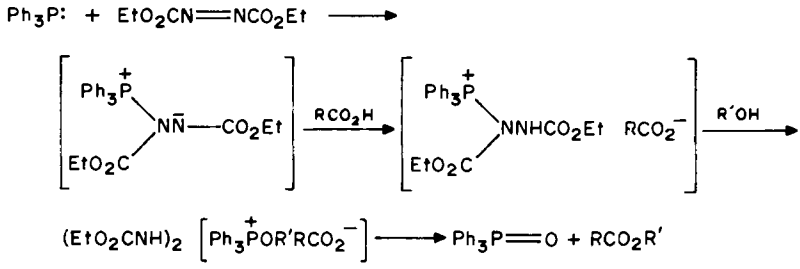
Nucleophilic attack at nitrogen occurs readily in compounds in which the nitrogen atom is multiply bonded and is adjacent to a conjugated system or electron-attracting moiety. Examples include the reactions of tertiary phosphines with dialkyl azodicarboxylates, organic azides, polyazines, azo compounds and diazonium salts.

Dialkyl azodicarboxylates give a reactive 1,3-dipolar intermediate (**84**)[312,313] whose structure has been confirmed *inter alia* by trapping with sulphur trioxide (Scheme 136)[313]. The triphenylphosphine adduct has found wide application as a reagent for intermolecular and intramolecular dehydrations and related reactions[314]. Examples include[314] the esterification of carboxylic acids and of phosphoric mono- and di-esters, the alkylation of phenols and heterocyclic compounds, the preparation of *N*-alkyl, *N*-alkoxy- and *N*-acyloxy-imides and of alkyl azides, the alkylation of active methylene compounds, numerous intramolecular dehydrations and dehydrosulphurizations, the alkylation of thioureas[315] and the preparation of alkyl halides[316], dialkyl carbonates[317], β-lactams[318] acid anhydrides[319], and a range of carbohydrate[320–326] and steroid[327] derivatives.



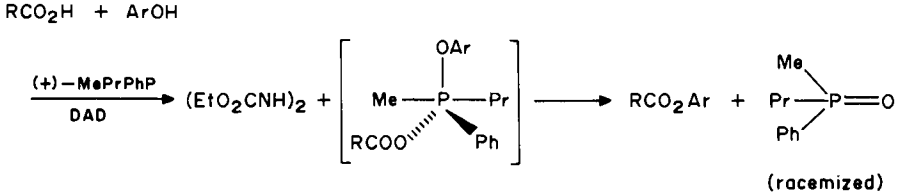
SCHEME 136

The overall process, in the case of esterification, for example, may involve protonation of the dipolar intermediate and the formation of an alkoxyphosphonium species which then eliminates phosphine oxide (Scheme 137)[314]. Such a mechanism is consistent with the inversion of configuration at carbon which accompanies *O*-alkyl fission in the final stage[328,329]. Alkoxyphosphonium salts have been isolated in the reactions of triphenylphosphine–diethyl azodicarboxylate (Ph_3P–DAD) with carbohydrates in the



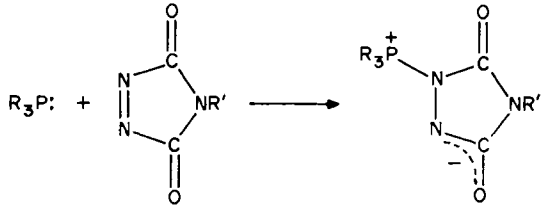
SCHEME 137

presence of alkylating or acylating agents[330]. Evidence has been discussed for the intermediacy of two phosphonium intermediates, one derived from the hydroxy group and one from the carboxy group, in the reactions of the reagent with β-hydroxy acids, which yield both lactones and alkenes[331]. Pentacoordinate (phosphorane) intermediates may also be involved, as shown by racemization at chiral phosphorus in the esterification of phenols and carboxylic acids by optically active methylphenylpropylphosphine–diethyl azodicarboxylate (Scheme 138)[332]. Racemization also occurs in the reaction of this same combination of reagents with tosylamide[333]. Phosphorane intermediates have been detected by ^{31}P NMR in the reactions of Ph_3P–DAD with alcohols[334] and stable phosphoranes have been prepared by the reactions of triphenylphosphine–diisopropyl azodicarboxylate with phenols[335] and with 1,3- or 1,4-diols[336].

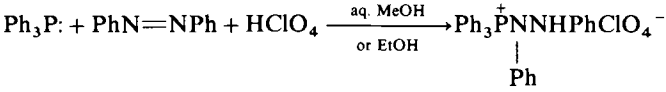


SCHEME 138

Reactive dipolar intermediates are also formed in the reactions of tris(dimethylamino)-phosphine with diethyl azodicarboxylate (Scheme 136; R = Me_2N, R′ = Et)[337], and of tertiary phosphines with 1,2,4-triazolidine-3,5-diones (Scheme 139)[338,339]. The interaction at room temperature of triphenylphosphine with equimolar amounts of azobenzene and perchloric acid in benzene gives a stable crystalline adduct, assumed to be formed by nucleophilic attack of phosphorus on nitrogen (Scheme 140)[340].



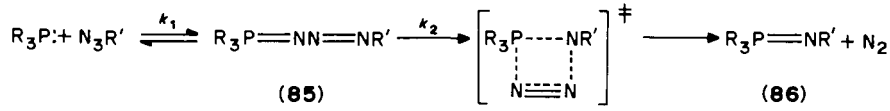
SCHEME 139



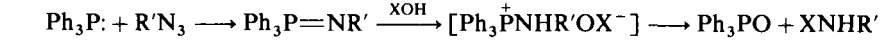
SCHEME 140

The formation of phosphinimines (λ^5-phosphazenes) (**86**) by the interaction of tertiary phosphines with organic azides (the Staudinger reaction)[341] has been studied extensively[342]. An intermediate phosphazide (**85**) is formed[343] and is thought to undergo decomposition via an intramolecular four-centre transition state (Scheme 141)[344,345]. Although many phosphazides decompose spontaneously with loss of nitrogen during the

course of reaction, stable types that can be isolated are also known. Some may be explosive[342]. The initial stage of reaction appears to occur by nucleophilic attack of phosphorus on the terminal nitrogen atom. The reaction is accelerated by the presence of electron-withdrawing groups in the azide[344,346,347] or electron-donating groups in the phosphine[344,348]. Neither radicals nor nitrenes are involved[342]. A detailed kinetic study of reactions of a wide range of phosphorus(III) compounds with phenylazide[349] has shown that the rate of attack is determined primarily by the inductive effects of the groups attached to phosphorus, the k_1 values being related linearly to the sums of the sigma parameters of the substituent groups. Decomposition of the intermediate phosphazide is, however, influenced by steric shielding of the phosphorus and by dative effects of substituents. Changes in solvent polarity have been shown to have little effect on the rate of reaction between triphenylphosphine and azidopyridine[350]. The reaction has been used widely in synthetic chemistry for the generation of λ^5-phosphazenes as reactive intermediates[342,351,352]. Examples include their use for the preparation of amines[353], amides[354] (Scheme 142) and various carbohydrate derivatives[355–357]. Heterocyclic

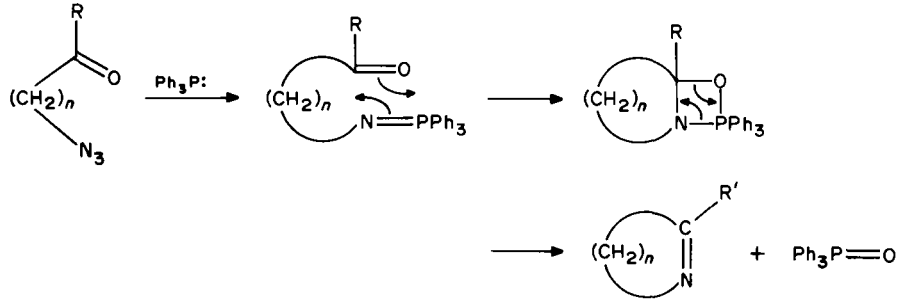


SCHEME 141

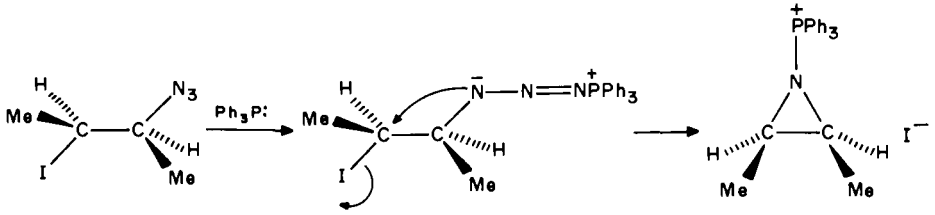


X = H or RCO

SCHEME 142

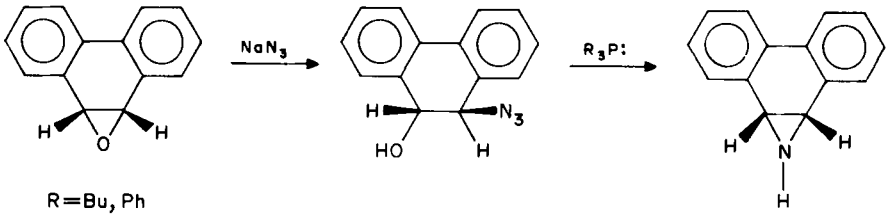


SCHEME 143

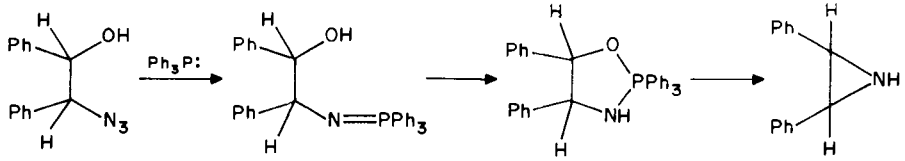


SCHEME 144

derivatives are obtained from azido ketones by means of the 'aza-Wittig reaction' (Scheme 143)[358–360]. Aziridines can be synthesised by the attack of tertiary phosphines on the azide group of 2-azidoalkyl iodides (Scheme 144) [361] or 2-azido alcohols[362,363], the latter reaction providing a useful step in the stereospecific conversion of oxiranes to the corresponding aziridines (Scheme 145). The reactions of 2-azido alcohols with triphenylphosphine have been shown to involve the formation of an intermediate oxazaphospholidine by cyclization of the corresponding phosphinimine (Scheme 146)[364], rather than by direct formation of the three-membered ring.

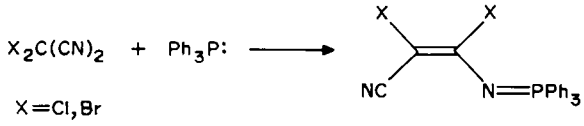


SCHEME 145



SCHEME 146

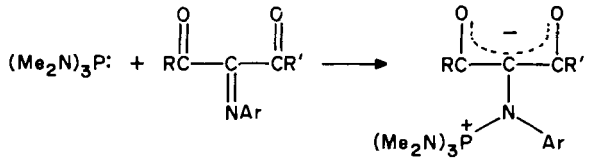
Nucleophilic attack of phosphorus at nitrogen also occurs in the reactions of tertiary phosphines with diazo compounds[365], diazonium salts[366], polyazines[367] and certain *gem*-dicyano compounds (Scheme 147)[368]. A similar attack on the nitrogen of the cyano group occurs in the reaction of triphenylphosphine with tetracyanoethylene(tcne), referred to in Section III.B.2.



SCHEME 147

Whereas Schiff bases are normally subject to nucleophilic attack at the imino carbon atom (see Section III.D.2), attack at nitrogen can occur if the polarization of the imino bond is reversed by the presence of electron-attracting groups (e.g. acyl or alkoxycarbonyl) on the carbon atom. Dipolar adducts are thus obtained (Scheme 148) in the reactions of tris(dimethylamino)phosphine with the anils of 1,2,3-triones[369,370] or of ethyl acetoacetate[371].

Phosphazenes are formed by attack at nitrogen, with ring opening and nitrogen—oxygen cleavage, in the reactions of triphenylphosphine with benzisoxazoles[372] and isoxazolones[373].



R=R'=Me,Ph; R=Me, R'=OEt

SCHEME 148

In the reactions of tertiary phosphines with nitronium hexafluorophosphate, the nitronium ion shows ambident reactivity towards phosphorus[374]. At low temperatures, an equilibrium between the nitrophosphonium and nitritophosphonium salts can be observed by ^{31}P NMR spectroscopy, with decomposition yielding the phosphine oxide as the temperature is raised (Scheme 149). Some evidence for ambident activity is also seen in the reactions of triphenylphosphine with thiocyanogen (Scheme 150), although the only product detectable by spectroscopy is the nitrogen-bonded isothiocyanatophosphonium thiocyanate **87**[375]. The formation of a small amount of the sulphur-bonded isomer (**89**), in equilibrium with the nitrogen-bonded species, is indicated however, by the reactions of the reagent with indoles and pyrroles to give cyano derivatives together with triphenylphosphine sulphide[376,377]. The triphenylphosphine–thiocyanogen combination and also the diisothiocyanatophosphoranes obtained from alkyl *o*-phenylene phosphites and thiocyanogen are useful reagents for the stereospecific conversion of alcohols to thiocyanates and isothiocyanates under mild conditions[375].

$$NO_2^+ PF_6^- \xrightarrow{R_3P} [R_3\overset{+}{P}NO_2\ PF_6^-] \rightleftharpoons R_3\overset{+}{P}ONO\ PF_6^-] \longrightarrow R_3P{=}O\ [+NO^+\ PF_6^-]$$

SCHEME 149

$$Ph_3P: + (SCN)_2 \longrightarrow Ph_3\overset{+}{P}NCS\,SCN^- \rightleftharpoons Ph_3\overset{+}{P}SCN\,SCN^-$$

(**87**) (**88**)

SCHEME 150

In the reactions of triphenylphosphine with certain bicyclic thiazolyl systems, attack appears to occur virtually exclusively at nitrogen[378].

B. Phosphorus and Arsenic

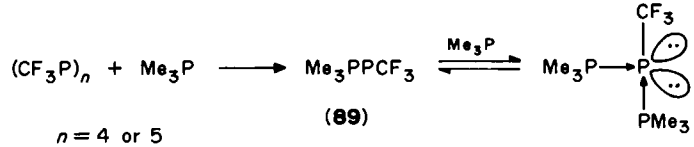
The ability of phosphorus to exhibit both nucleophilic and electrophilic activity (see Section I) gives rise to the possibility of phosphorus–phosphorus bond formation. Reactions which may involve nucleophilic displacement of halogen from one phosphorus(III) species by another have been reported in a number of cases[379–382]. Crystalline phosphonium salts result from the reactions of trimethylphosphine or dimethylphenylphosphine with dichlorophenylphosphine (Scheme 151)[383]. The products dissociate on heating under vacuum and are in equilibrium with the starting materials in solution.

$$Me_2PR + Ph_2PCl \rightleftharpoons [RMe_2PPPh_2]^+ Cl^-$$

R = Me, Ph

SCHEME 151

With an excess of trimethylphosphine, the homocyclic trifluoromethylpolyphosphines $(CF_3P)_n$ ($n = 4$ or 5) undergo ring opening to give a phosphine–phosphinidine complex (**89**), the latter undergoing further attack by the phosphine in a bimolecular exchange process thought to involve a transition state (**90**) as shown in Scheme 152[384].



SCHEME 152

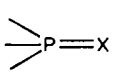
The interaction of tetramethyldiphosphine with tetramethyldiarsine at 25 °C in benzene involves a rapid exchange to give the tetramethylphosphinoarsine (Scheme 153)[385]. Nucleophilic attack of phosphorus at arsenic may be involved. Similar exchange reactions were not, however, observed between the diphosphine and the related distibine and dibismuthine derivatives.

$$Me_2PPMe_2 + Me_2AsAsMe_2 \rightleftharpoons 2\,Me_2PAsMe_2$$

SCHEME 153

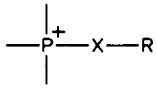
VIII. NUCLEOPHILIC ATTACK AT GROUP VI ELEMENTS

Tertiary phosphines are easily oxidized by elemental oxygen or elemental sulphur. In addition, they readily bring about the deoxygenation or desulphurization of a wide range of compounds that contain these elements[386] with the formation of the corresponding phosphine oxide or phosphine sulphide (**91**). Oxyphosphonium or thiophosphonium species (**92**) may also be formed, generally as reactive intermediates. Similar reactions occur with selenium or tellurium and their compounds, but have been studied to a lesser extent (see below).



X = O, S

(**91**)



X = O, S

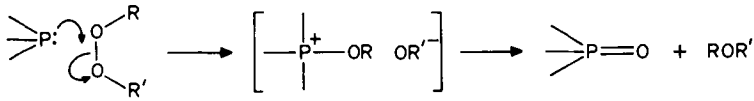
(**92**)

A. Oxygen

1. Reactions of phosphines with peroxo compounds

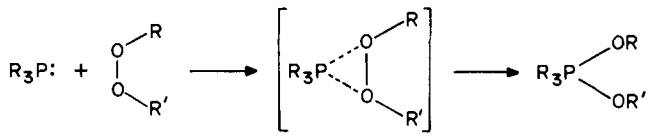
Whereas the oxidation of phosphines by elemental oxygen[387,388] or by di-*tert*-butyl peroxide at elevated temperatures[389] proceeds by a free-radical mechanism, the reactions

of peroxides under mild conditions, and in the absence of an initiator, involve nucleophilic or biphilic attack. Cleavage of the peroxo link by a phosphorus(III) reagent was first shown in the reaction of dibenzoyl peroxide with triphenylphosphine[390]. Horner and Jurgeleit[391] subsequently proposed a mechanism involving nucleophilic attack at oxygen for a wide range of organic peroxides. Although there are exceptions to this mechanism, there is good evidence based on ^{18}O-labelling and on stereochemical and kinetic studies for a process that involves nucleophilically induced cleavage in the reactions of phosphines with diacyl peroxides[392,393], alkyl hydroperoxides[394–397] and alkyl peresters[398,399] (Scheme 154). It is likely that the cleavage of dialkyl *tert*-butylperoxyphosphates[400] follows a similar pattern. The low dependence of reaction rates on solvent effects has, however, suggested the involvement of biphilic character in certain cases[398]. Considerable evidence has been presented in favour of a biphilic insertion mechanism for the reactions in aprotic media of phosphorus(III) reagents with dialkyl peroxides, in particular diethyl peroxide[401–406], 1,2-dioxetanes[407–409] and various bicyclic *endo*-peroxides[410], which yield pentacoordinate phosphoranes under relatively mild conditions (Scheme 155). Reactions of this type are generally not strongly influenced by solvent effects and the order of reactivity for a range of phosphorus nucleophiles is roughly the reverse of that for S_N2 displacements with alkyl iodides[401,402]. In alcoholic solution, diethyl peroxide reacts with tertiary phosphines to give products that are apparently derived from an alkoxyphosphonium intermediate (Scheme 156)[411]. The latter could be formed either by nucleophilic attack of phosphorus at oxygen or by dissociation of an initially formed phosphorane.



R=R′=acyl; R=H, R′=alkyl; R=acyl, R′=alkyl

SCHEME 154



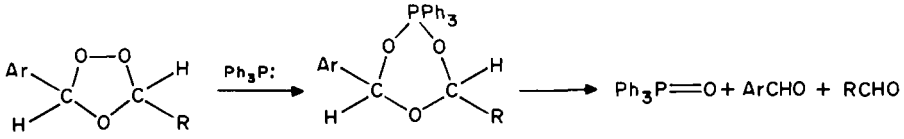
SCHEME 155

$$R_3P: + (EtO)_2 \xrightarrow{R'OH} R_3\overset{+}{P}\text{-}OEt + [OEt^-, OR'^-] \longrightarrow$$

$$R_3P{=}O + EtOH + R'_2O + R'OEt$$

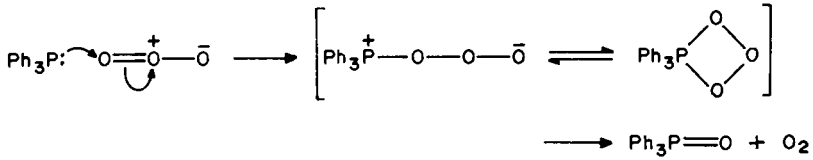
SCHEME 156

The cleavage of organic ozonides by phosphines may also involve biphilic character (Scheme 157). Attack occurs exclusively at peroxidic oxygen[412] and the rate of cleavage is not influenced to a significant extent by solvent effects[413].



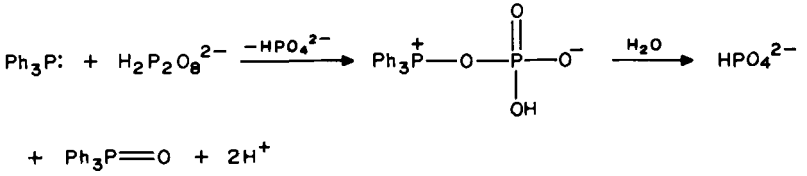
SCHEME 157

The oxidation of phosphines or phosphites by ozone[414,415] has been shown to be first order in each reactant at −90 °C, at which temperature triphenyl phosphite forms a stable ozonide[416]. No stable ozonide is obtained from triphenylphosphine, although the overall rate of oxidation is similar[416]. The mode of attack is not clear although the polar nature of the ozone molecule suggests that nucleophilic attack by phosphorus is likely (Scheme 158).



SCHEME 158

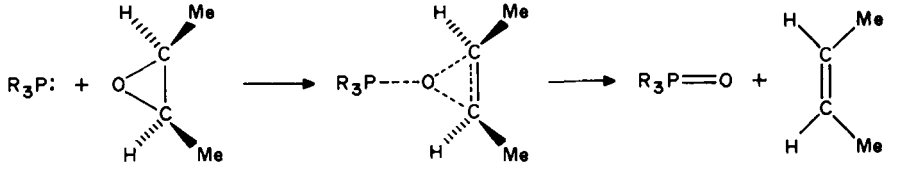
Clear kinetic evidence for rate-determining nucleophilic attack at oxygen has been obtained for the oxidation of triphenylphosphine by the peroxodiphosphate ion in various media[417,418]. The reaction involves the formation of a phosphonium intermediate which subsequently undergoes hydrolysis (Scheme 159). In the analogous peroxodisulphate oxidation, ^{18}O-labelling studies have shown that the oxygen in the phosphine oxide is derived from the peroxodisulphate[419].



SCHEME 159

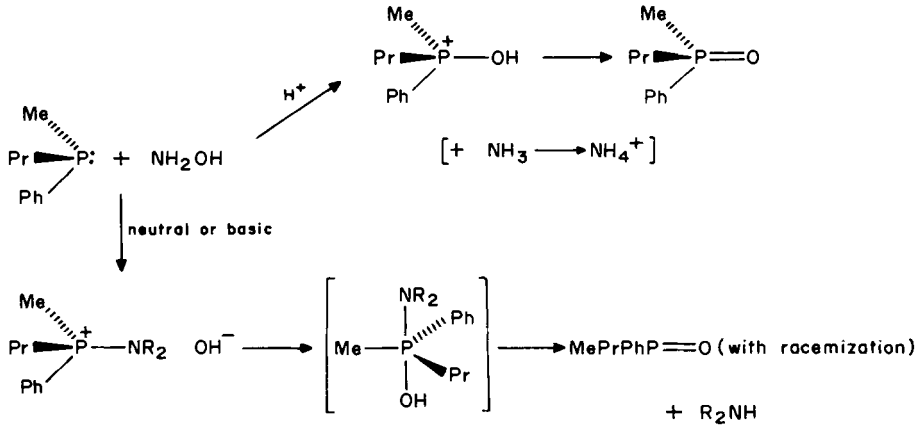
2. *Oxidation of phosphines by epoxides and by hydroxylamine*

Although the deoxygenation of epoxides by phosphines is thought to occur mainly via attack at carbon, followed by a Wittig-type elimination (see Section II.F), the lack of stereospecificity in this reaction has been attributed to concomitant attack at oxygen, leading to the formation of alkene (20–30%) with retained configuration (Scheme 160)[60].



SCHEME 160

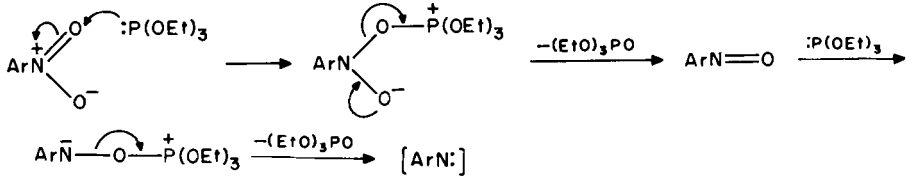
The oxidation of phosphines by hydroxylamine was discovered inadvertently in the course of the preparation of oximes from cyclic ketophosphines[420]. Studies with optically active methylpropylphenylphosphine have shown that under acidic conditions the reaction proceeds with complete retention of configuration at phosphorus, indicating direct nucleophilic attack at oxygen[421]. Under neutral or basic conditions, however, attack at nitrogen leads to an aminophosphonium intermediate and racemization via a hydroxyphosphorane (Scheme 161).



SCHEME 161

3. Deoxygenation of compounds containing doubly bonded oxygen

Oxygen abstraction from aromatic nitro and nitroso compounds[422] has been used extensively in the synthesis of heterocyclic compounds[423]. The reactions are best carried out by the use of a trialkyl phosphite and probably occur via the formation of nitrene intermediates (Scheme 162). Kinetic studies on the deoxygenation of nitroso compounds confirmed that a dipolar intermediate is formed initially by nucleophilic attack of phosphorus on oxygen[424,425], followed by the elimination of phosphine oxide. The initial formation of a radical ion pair by electron transfer has also been proposed on the basis of ESR studies of the reaction of triarylphosphines with nitroso compounds (Scheme 163)[426]. Whether this is an essential step on the main reaction pathway is not clear, however.

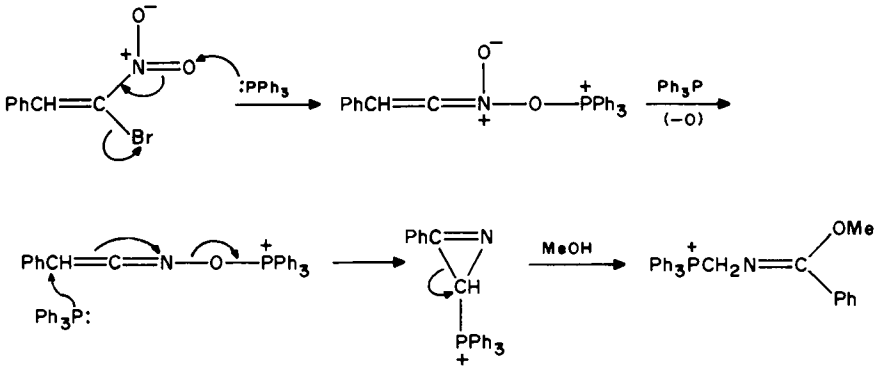


SCHEME 162

$$Ar_3P + O{=}NAr \longrightarrow [Ar_3\overset{+}{P}\cdot\ {}^{\cdot}O{-}\overset{-}{N}Ar] \longrightarrow Ar_3\overset{+}{P}{-}O{-}\overset{-}{N}Ar \longrightarrow Ar_3P{=}O + [{:}NAr]$$

SCHEME 163

Initial attack at oxygen is thought to occur in the reaction of triphenylphosphine with β-bromo-β-nitrostyrene in methanol (Scheme 164)[427].



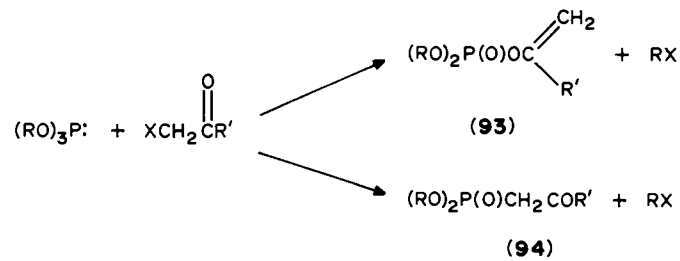
SCHEME 164

Tertiary phosphines are effective in the deoxygenation of sulphur dioxide[428,429], thionyl chloride[430,431], dimethyl sulphoxide[432], arylsulphonyl chlorides[433], selenoxides[434], *p*-chloroselenonic acid[435] and telluroxides[436]. Oxygen is also transferred from phosphine oxides[437] or arsenic oxides[438,439] to phosphines, but only at relatively high temperatures. The mechanisms of these deoxygenations are not always known with certainty but may involve nucleophilic attack at oxygen or, possibly, a biphilic interaction[432].

4. Additions to carbonyl compounds

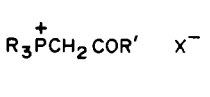
Products containing phosphorus—oxygen bonds are frequently obtained in the reactions of phosphorus(III) reagents with carbonyl compounds that have electron-withdrawing substituents in the α-position. Although such reactions can be formally represented as involving nucleophilic attack at the oxygen atom, the mechanism in many cases may involve initial attack at carbonyl carbon, followed by rearrangement. Other possibilities also exist that involve, e.g., initial attack at halogen in the case of certain α-halogenoketones (see below).

The formation of vinyl phosphates (**93**) in the reactions of phosphite esters with α-halogenoaldehydes[440–442] and α-halogenoketones[443,444] (the Perkow reaction) is well known and frequently occurs in parallel with the Arbuzov reaction, which gives ketophosphonates (**94**) by nucleophilic attack at the α-carbon atom (Scheme 165). The

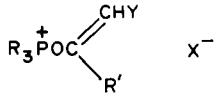


SCHEME 165

relative proportions of each product vary with the halogen present, the phosphorus reagent and the reaction conditions. With phosphines, α-halo ketones in general yield α-ketophosphonium salts (**95**), although enolphosphonium salts (**96**) are obtainable from α,α-dibromo- and α-halobenzyl ketones[446]. Phosphite esters, on the other hand, yield only vinyl phosphates (**93**) from α-chloroketones, but give mixed products with increasing proportions of the ketophosphonates (**94**) from α-bromo- and α-iodo-ketones.

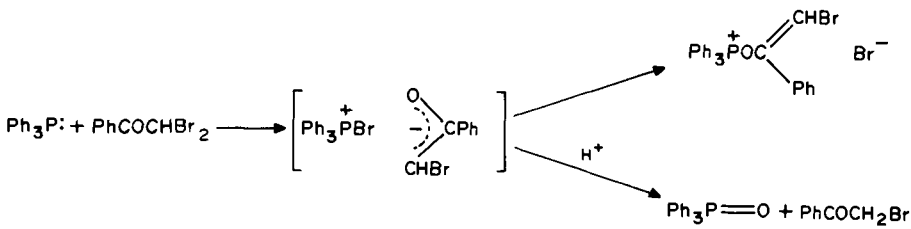


(**95**)

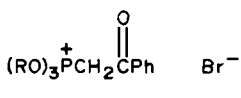


(**96**) Y=hal, aryl

The mechanism by which the P—O compounds are formed has been discussed in detail[445] but is not yet fully understood. It is probable that different reaction pathways may apply under different circumstances. Nucleophilic attack at halogen appears to occur in certain cases, since the halogenophosphonium enolate intermediate can be diverted in the presence of protic reagents to give the dehalogenated ketone and phosphine oxide (Scheme 166)[446,447]. This mechanism does not necessarily apply, however, in the formation of vinyl phosphates by the interactions of trialkyl phosphites with simple monohalogenated ketones. There is no evidence to support the suggestion[448] that the Perkow and Arbuzov products may both be formed from the same ketophosphonium intermediate. The isolation of ketophosphonium (**97**) and vinyloxyphosphonium (**98**) intermediates in these reactions and a study of their reactivities have shown that they are not interconvertible and that they lie on separate reaction pathways[38,449,450]. Nucleophilic attack at carbonyl carbon followed by rearrangement (Scheme 167) is generally considered to be the most likely route to Perkow products, although direct nucleophilic attack at oxygen has not been totally excluded[445]. In view of the biphilic character of phosphorus(III) reagents, a transition state that involves interaction at both carbon and oxygen is a possibility that should also be considered.

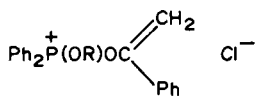


SCHEME 166

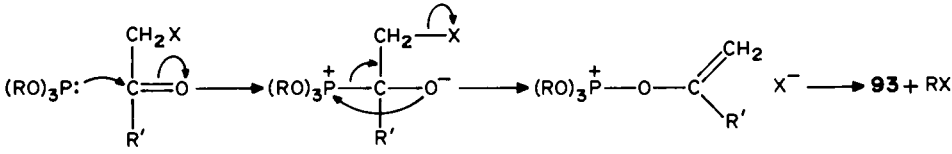


(**97**)

R=neopentyl

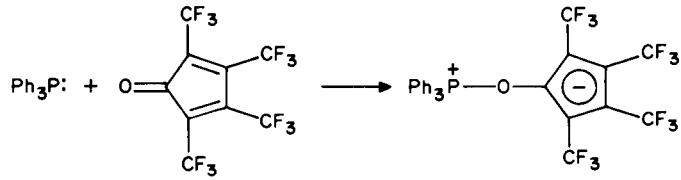


(**98**)

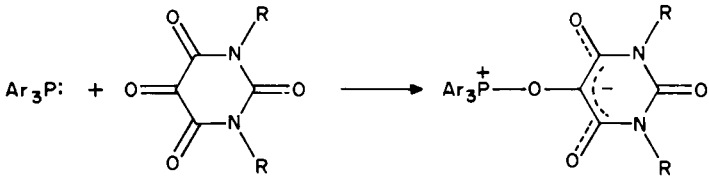


SCHEME 167

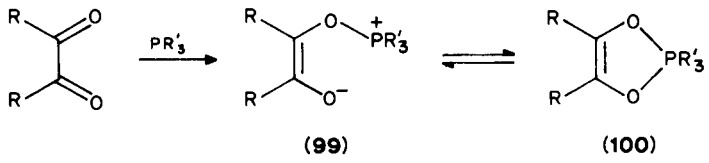
Further examples of carbonyl compounds which interact with phosphines to give oxyphosphonium species include cyclopentadienones that contain strongly electron-attracting substituents (Scheme 168)[451], alloxan derivatives (Scheme 169)[452], 1,2-diketones[194] and 1,2-quinones (Scheme 170)[194,453]. The zwitterionic products (**99**) obtained from 1,2-dicarbonyl compounds and tertiary phosphines may exist in equilibrium with the corresponding oxyphosphoranes (**100**)[194]; from phosphite esters the pentacoordinate structure is preferred because of the stabilizing effect of electronegative oxygen in an apical position.



SCHEME 168



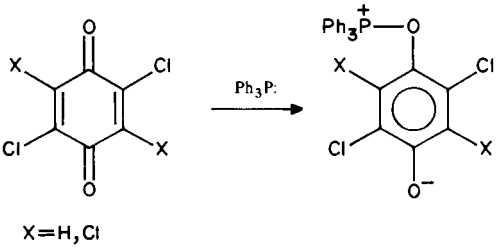
SCHEME 169



R=alkyl, aryl; R—R = —CH=CHCH=CH—

SCHEME 170

Whereas *p*-benzoquinone undergoes conjugate addition to the quinone ring in its reaction with triphenylphosphine (see Section III.B.2), attack at oxygen occurs in the case of the 2,5-dichloro and 2,3,5,6-tetrachloro (chloranil) derivatives (Scheme 171)[122].

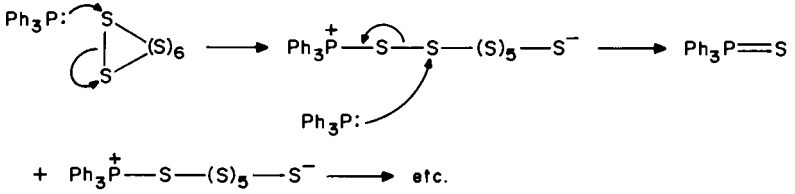


SCHEME 171

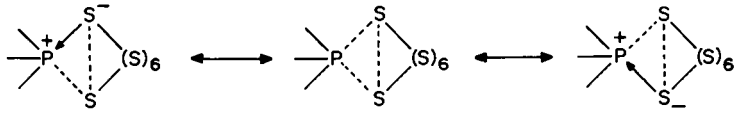
B. Sulphur

1. Elemental sulphur

Sulphur adds readily to tertiary phosphines to give the corresponding phosphine sulphides[454], and in the case of trialkyl or mixed alkyl aryl phosphines the reaction is extremely rapid[455]. Nucleophilic attack by phosphorus has been demonstrated for the reaction between triphenylphosphine and elemental sulphur (S_8), under nitrogen in benzene, and is considered to give rise to the formation of a zwitterionic intermediate (Scheme 172)[456]. A series of rapid bimolecular displacements along the sulphur chain then follow, with the elimination of triphenylphosphine sulphide. The reaction rate is increased strongly in ionizing solvents and by the presence of electron-releasing groups in the aromatic ring ($\rho = -2.5$). More recent studies with a range of phosphorus nucleophiles have suggested also that the reaction may have biphilic character, with relative rates in the order of those observed for reaction with dialkyl peroxides [$Ph_2POR > PhP(OR)_2 > P(OR)_3 > Ph_3P$][457]. A transition state with a high degree of polar character (**101**) was proposed.



SCHEME 172



(101)

2. Organic disulphides

In the absence of radical initiators[389,394], dialkyl and diaryl disulphides undergo nucleophilic cleavage on heating with phosphorus(III) reagents with the formation of phosphonium intermediates[458]. This process leads directly to the corresponding Arbuzov

product in reactions with phosphite esters (Scheme 173)[394,458]. The formation of a phosphonium species on heating triphenylphosphine with diphenyl disulphide in benzene, under reflux, is also indicated by the formation of triphenylphosphine oxide and benzenethiol on the addition of water (Scheme 174) (R = R′ = Ph)[459]. In protic media, the reactions of trialkyl- and triaryl-phosphines with dialkyl or diaryl disulphides occur readily at moderate temperatures to give high yields in each case of the corresponding phosphine oxide and thiol[460–462]. Kinetic studies in aqueous dioxane have confirmed the operation of a two-stage mechanism in the reactions of triphenylphosphine with dialkyl, diaryl and alkyl aryl disulphides[463–465].

$$(RO)_3P: + R'SSR' \longrightarrow (RO)_3\overset{+}{P}SR'\,SR'^{-} \longrightarrow (RO)_2P(O)SR' + R'SR$$

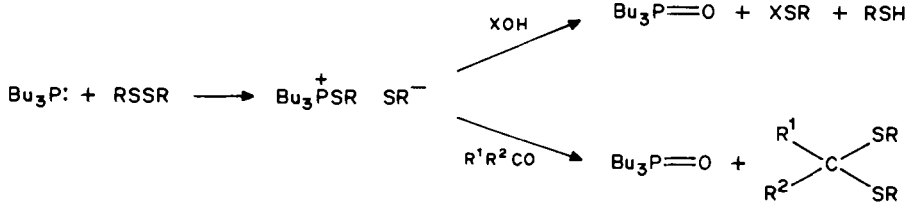
R = alkyl, R′ = alkyl, aryl

SCHEME 173

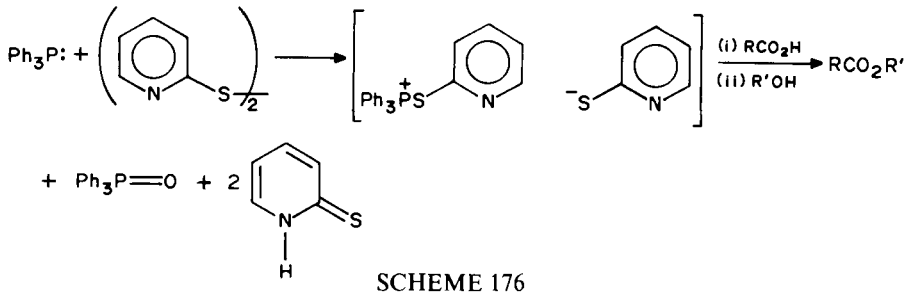
$$R_3P: + R'SSR' \longrightarrow R_3\overset{+}{P}SR'\,SR'^{-} \xrightarrow{H_2O} R_3P{=}O + 2R'SH$$

SCHEME 174

By related reaction sequences, various tertiary phosphine–disulphide combinations have been used for the introduction of alkylthio or arylthio groups into nucleoside derivatives[466,467] and the conversion of aldehydes and ketones to dithio-acetals and -ketals[468] (Scheme 175). Similar reagents bring about the reduction of arenesulphonic acids or alkanesulphonic acids to thiophenols and alkyl aryl thioethers, respectively, under relatively mild conditions[469]. The combination of triphenylphosphine and 2,2′-dipyridyl disulphide[470–472] has proved to be especially useful as a condensation reagent as possible interference by the thiol by-product is avoided and the need to incorporate a thiol scavenger is obviated (Scheme 176)[473]. The by-product from the disulphide in this case is



SCHEME 175



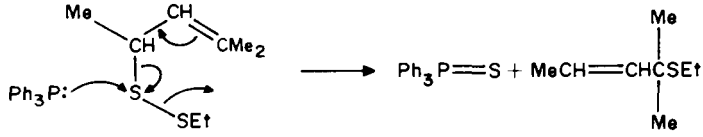
SCHEME 176

pyridine-2-thione. Applications have included the synthesis of esters, peptides[474,475], nucleotides, macrolides[473], lactones[476–478] and lactams[479,480]. Similar synthetic procedures have been based on triphenylphosphine in combination with bis(*O*-thiocarbonyl) disulphide[481] and 2,2′-dibenzothiazolyl disulphide[482]. Related reactions are involved in the reductive cleavage of S—S links in proteins by tributylphosphine[483,484] and in the preparation of thioesters from penicillin-related disulphides by reaction with triphenylphosphine in the presence of carboxylic acids[485].

In the absence of protic reactants, organic disulphides may undergo desulphurization via S—R cleavage (Scheme 177). The ease of reaction, however, is highly dependent on structure. Whereas acyl and thioacyl disulphides (R = PhCO, Me_2NCS, α-$C_{10}H_7S$) react readily with triphenylphosphine[459], alkyl and benzyl disulphides (R = Et, Pr^i, Bu^n, $PhCH_2$) are unreactive up to 140 °C[459,486]. The more ready desulphurization of allyl disulphides[486,487] is attributed to the possible formation of a cyclic S_Ni' transition state (e.g. Scheme 178). Desulphurization of diphenyl disulphide occurs only at high temperatures (250–300 °C)[488]. Although a two-stage ionic mechanism has been proposed for this reaction, the thermal instability of the disulphide at 300 °C suggests that decomposition to give sulphur could precede reaction with the phosphine[489].

$$Ph_3P: + RSSR \longrightarrow Ph_3\overset{+}{P}SR\,SR^- \longrightarrow Ph_3P{=}S + RSR$$

SCHEME 177

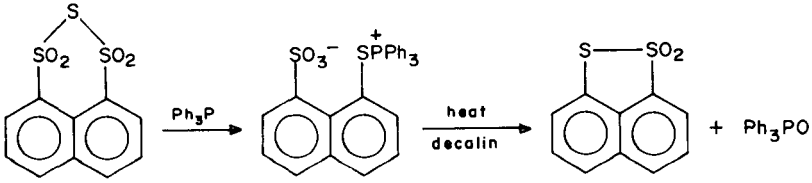


SCHEME 178

Trisdiethylaminophosphine brings about the smooth desulphurization of cyclic, benzyl, aralkyl and dialkyl (but not diaryl) disulphides 25–140 °C[490]. Although reaction is presumed to be initiated by nucleophilic attack at sulphur, the overall sequence is more complicated than suggested above (Scheme 177), as shown by the formation of all possible monosulphides in the desulphurization of mixed dibenzyl disulphides. The reagent has found use in the desulphurization of cystine derivatives[491], alicyclic thiosulphonates[492] and alkylphthalimido disulphides[493], and in the conversion of 1,2-dithiolan-3-ones to thiolactams[494].

3. Organic tri- and tetra-sulphides

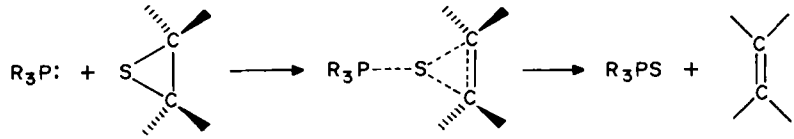
Trisulphides[495–497] and tetrasulphides[486] are readily reduced to the corresponding disulphides by triarylphosphines or trisdialkylaminophosphines under mild conditions. Sulphur is also removed in the conversion of a 1,2,3-trithiin-1,1,3,3-tetraoxide to the thiosulphonate (Scheme 179)[498].



SCHEME 179

4. *Miscellaneous reactions of sulphur compounds*

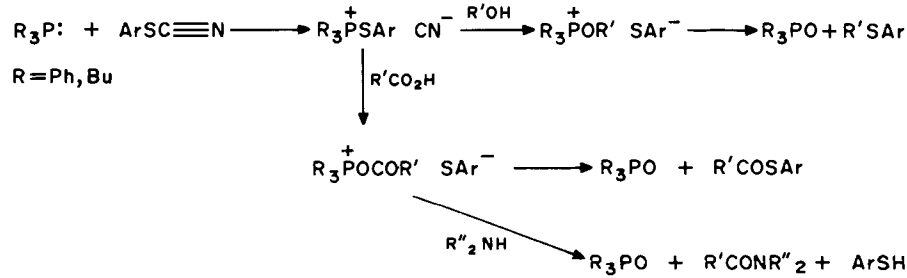
Nucleophilic attack at sulphur is presumed to occur in the reactions of tertiary phosphines with sulphenate esters (possibly a biphilic insertion reaction)[499,500], sulphenyl chlorides[473,501], sulphenamides[473], sulphimides[502–505], thietan-3-ones[506] and β-oxidosulphides[507] and in the desulphurization of thiirans (episulphides)[508–511], bridgehead sulphides[512], thioketones[513], sulphenyl thiocarbonates[514], 1,2,4-dithiazol-3-ones[515], epidithiodioxopiperazines[516], germadithiolanes[517], and many other compounds of sulphur[518]. Triphenylphosphine has also been shown to remove one sulphur atom from P_4S_9, to give the previously unknown P_4S_8[519] [desulphurization of P_4S_{10} by various phosphorus(III) reagents had previously been found to give P_4S_9 and P_4S_7 only]. The mechanism of desulphurization may involve nucleophilic attack at sulphur, but in most cases has not been investigated. The stereospecific formation of alkenes from episulphides and the small effect of solvents on rate have indicated, however, that direct attack at sulphur is involved in this reaction (Scheme 180)[509] without the formation of polar intermediates such as occur in the deoxygenation of epoxides.



SCHEME 180

5. *Thiocyanates*

Aryl thiocyanates undergo nucleophilic attack by tertiary phosphines with the displacement of cyanide to give quasiphosphonium intermediates of use for the replacement of hydroxyl by arylthio[520–522] and as condensing agents for the synthesis of amides from carboxylic acids and amines (Scheme 181)[523]. The reactions of alkyl or aryl



SCHEME 181

thiocyanates with tributylphosphine in the presence of aromatic aldehydes proceed through the initial formation of similar intermediates[524,525].

6. *Sulphur dioxide, thionyl chloride, sulphur trioxide and sulphuryl chloride*

The deoxygenation of sulphur dioxide (Scheme 182) and of thionyl chloride (Scheme 183) by tertiary phosphines has been formulated as proceeding via nucleophilic

$$R_3P: + SO_2 \longrightarrow R_3P{=}O + [SO] \longrightarrow \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

SCHEME 182

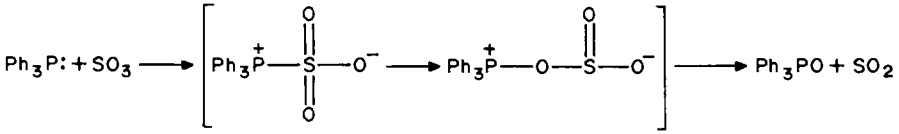
$$R_3P: + SOCl_2 \longrightarrow R_3P{=}O + SCl_2$$

$$Ar_3P + SCl_2 \longrightarrow Ar_3PCl_2 + S$$

$$Ar_3P + SCl_2 \longrightarrow Ar_3PCl_2 + Ar_3P{=}S$$

SCHEME 183

attack at sulphur followed by rearrangement[428,430,431], although biphilic attack involving oxygen in the initial step is a possibility. Sulphur trioxide and sulphuryl chloride both react with triphenylphosphine to give 1:1 adducts, that from sulphur trioxide[526,527] being shown by X-ray diffraction to have a P—S rather than a P—O bond[528]. Rearrangement in solution leads to the loss of sulphur dioxide and formation of the phosphine oxide (Scheme 184)[529]. Two adducts are obtained from sulphuryl chloride, one in which



SCHEME 184

phosphorus is bonded to sulphur and the other with phosphorus bonded to oxygen, on the basis of infrared evidence[530]. Preferential attack at oxygen is indicated by NMR spectroscopy in the case of sulphuryl chloride fluoride[529].

7. Selenium and tellurium

Tertiary phosphines react readily with elemental selenium and tellurium to give phosphine selenides and tellurides[454,531,532]. The transfer of selenium[533,534] and of tellurium[531,535] between phosphorus(III) species in solution is rapid on the NMR time scale (in contrast to the slower exchange rate for sulphur) and is a bimolecular process[534] for which a linear intermediate has been proposed (Scheme 185)[535]. Tertiary phosphines also deselenate organic isoselenocyanates[536] (whereas isothiocyanates undergo attack at carbon) and the selenocyanate ion[537–539] (Scheme 186).

$$R_3P{=}Y + PR_3 \rightleftharpoons [R_3P{-}Y{-}PR_3] \rightleftharpoons R_3P + Y{=}PR_3$$

Y = Se or Te

SCHEME 185

$$R_3P: + R'NCSe \text{ (or } SeCN^-) \longrightarrow R_3P{=}Se + R'NC \text{ (or } CN^-)$$

SCHEME 186

Aryl selenocyanates[540] and *N*-arylselenylphthalimides[541] behave in a similar manner to the aryl thiocyanates in forming quasiphosphonium intermediates that are useful (with some exceptions[542]) for the conversion of alcohols to arylselenides and of carboxylic acids

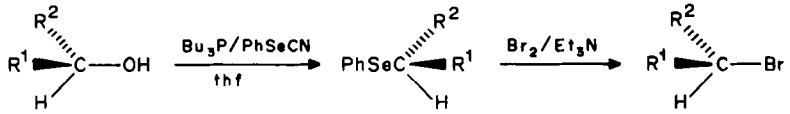
to selenoesters (Scheme 187). Optically active alcohols may thus be converted via the selenides to the corresponding bromides with retention of configuration (Scheme 188)[543].

The reaction of selenocyanogen with a tertiary phosphine is similar to that for thiocyanogen (see above). The reagent will thus convert alcohols to the alkyl selenocyanates although the latter are unstable (Scheme 189)[544]. A combination of triphenylphosphine with 2,2′-dipyridyl diselenide is an alternative to the corresponding disulphide reagent for condensation reactions[545].

$$Bu_3P: + ArSeX \longrightarrow Bu_3\overset{+}{P}SeAr\ X^- \xrightarrow{ROH} Bu_3\overset{+}{P}OR\ SeAr^- \longrightarrow Bu_3P{=}O + RSeAr$$

X = CN, *N*-phthalimido; R = alkyl, acyl

SCHEME 187



SCHEME 188

$$ROH \xrightarrow{Ph_3P/(SeCN)_2} RSeCN \longrightarrow R_2Se$$

SCHEME 189

IX. NUCLEOPHILIC ATTACK AT HALOGENS

A. Elemental Halogens and Interhalogen Compounds

Tertiary phosphines react rapidly with halogens[546–554] or with interhalogen compounds[553,554] to give halogenophosphonium halides and polyhalides (Scheme 190). The

$$R_3P: \overset{\curvearrowright}{X}\!\!-\!\!\overset{\curvearrowright}{Y} \longrightarrow R_3\overset{+}{P}X\,Y^- \xrightarrow{XY} R_3\overset{+}{P}X\ XY_2^-$$

R = alkyl, aryl, R_2N; XY = Cl_2, Br_2, I_2, ICl, IBr

SCHEME 190

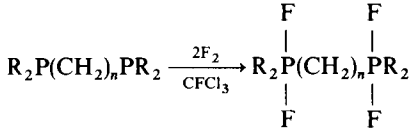
formation of bisphosphinoiodonium iodides has also been reported on the basis of conductometric measurements in the reactions of *tert*-alkylphosphines with iodine in acetonitrile (Scheme 191)[554]. The halogenophosphonium halides may exist in the

$$2R_3P + I_2 \xrightarrow{MeCN} (R_3P)_2I^+\,I^-$$

SCHEME 191

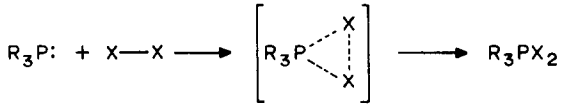
pentacoordinate form. Thus Ph_3PCl_2 has the phosphorane structure in benzene[555] and in nitrobenzene[548] but ionizes in acetonitrile[556,557] and is ionic in the solid state[558]. The corresponding bromide and iodide exist only in the ionic form[559], as do the trialkyl-[548,558]

and trisdialkylamino-phosphine adducts[551,552]. The pentacoordinate form appears to be favoured as the phosphorus ligands become more electron attracting, e.g. in Ph_2PCl_3 and $PhPCl_4$[558] and in the difluorophosphoranes, which can be obtained by direct fluorination under controlled conditions (e.g. Scheme 192)[560,561]. An insertion mechanism may possibly be involved, rather than nucleophilic attack, in the direct formation of pentacoordinate species (Scheme 193).



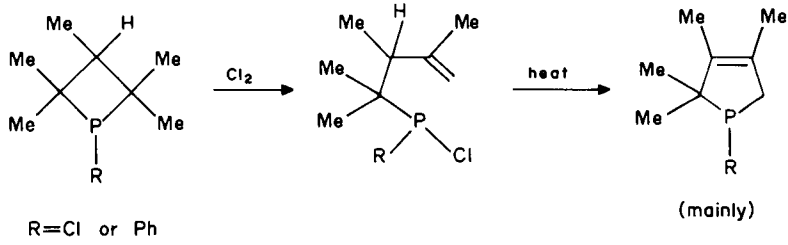
R = Me, Ph; $n = 1$–4

SCHEME 192



SCHEME 193

Halogenophosphonium halides are similarly formed in the additions of halogens to cyclic phosphines such as phosphetanes[562], phospholenes[563] and phosphorinanes[564]. The existence of a low equilibrium concentration of the corresponding dihalogenophosphoranes is indicated by rapid *cis-trans* isomerization of the products[562,563]. 2,2-Dimethylphosphetanes may also undergo ring opening with bromine or chlorine to give but-3-enylhalogenophosphines, which cyclize to phospholenes on heating (Scheme 194)[565].

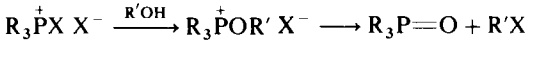


R=Cl or Ph

(mainly)

SCHEME 194

Phosphine–halogen reagents (e.g. Ph_3PX_2 or Bu_3PX_2) are useful for the replacement of hydroxyl by halogen (Scheme 195)[566,567] and, in combination with imidazole, in the halogenation of carbohydrates[568–570].



R = alkyl, aryl; X = Cl, Br, I

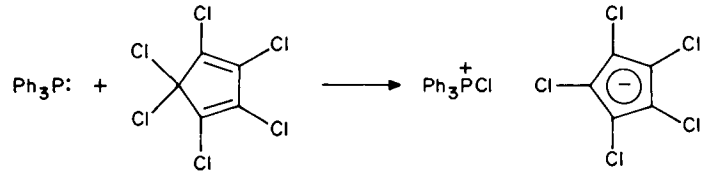
SCHEME 195

B. Other Positive Halogen Sources

Initial attack at halogen occurs in the reactions of phosphines with a wide variety of positive halogen sources[571]. Such compounds include those in which the halogen is attached to an electronegative element or group (O, N, CCl_3, etc.) or is α to an electron-withdrawing moiety such as carbonyl, sulphone, nitro or cyano.

1. *Chlorocyclopentadienes and trichloromethylcyclohexadienones*

In certain cases the halogenophosphonium ion is formed in association with a stable delocalized anion, as in the reactions of triphenylphosphine with halogenocyclopentadienes (Scheme 196)[572]. Under these circumstances no further reaction occurs, unless a



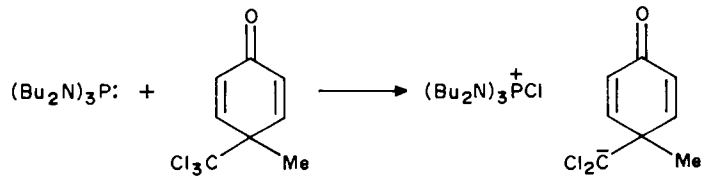
SCHEME 196

nucleophilic reagent such as an alcohol is present, in which case the latter is converted to alkyl chloride[572]. In reactions with trialkyl phosphites, the cyclopentadienide anion brings about dealkylation of the intermediate phosphonium ion to give the chlorophosphate (Arbuzov product) (Scheme 197)[573].

$$(RO)_3P: + C_5Cl_6(\text{or } C_5HCl_5) \longrightarrow [(RO)_3\overset{+}{P}ClC_5Cl_5^- \text{ (or } C_5HCl_4^-)]$$
$$\longrightarrow (RO)_2P(O)Cl + RC_5Cl_5 \text{ (or } RC_5HCl_4)$$

SCHEME 197

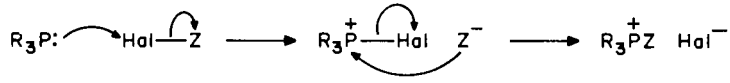
A stable chlorophosphonium species is also obtained in the reaction of tris(dibutylamino)phosphine with 6-methyl-6-trichloromethylcyclohexadienone (Scheme 198)[574].



SCHEME 198

2. *Halogen attached to oxygen or nitrogen*

In most reactions of tertiary phosphines with positive halogen sources, the halogenophosphonium ion is formed only as a transitory intermediate, undergoing rapid nucleophilic displacement of halide by the counter ion (Scheme 199). Further reaction may then ensue, depending on the nature of the group Z.



SCHEME 199

Hypochlorites thus give alkoxyphosphonium chlorides which decompose rapidly to the corresponding alkyl chloride and phosphine oxide (Scheme 200), unless sterically

$$R_3P: + R'OCl \longrightarrow R_3\overset{+}{P}ClOR'^{-} \longrightarrow R_3\overset{+}{P}OR'\,Cl^{-} \rightarrow R_3P{=}O + R'Cl$$

SCHEME 200

hindered[575–577]. The reactive intermediate may be diverted by the addition of a hydroxy compound. Thus, the combination of triphenylphosphine and *tert*-butyl hypochlorite, premixed at −78 °C, has been used for the conversion of 1,4-diols to tetrahydrofurans and 1,2-diols to chlorohydrins and epoxides (Scheme 201)[578].

N-Halogenoamines give stable aminophosphonium salts (Scheme 202)[579–581].

$$Ph_3P: + Bu^tOCl \longrightarrow Ph_3\overset{+}{P}ClBu^tO^{-} \rightleftharpoons Ph_3\overset{Cl}{\overset{|}{P}}OBu^t \rightleftharpoons Ph_3\overset{+}{P}OBu^t\,Cl^{-}$$

$$\xrightarrow{HOCHR(CH_2)_nOH} HOCHR(CH_2)_nCl + ClCHR(CH_2)_nCl + ClCHR(CH_2)_nCl + R\overline{CH(CH_2)_nO}$$

R = alkyl, Ph; n = 1–4

SCHEME 201

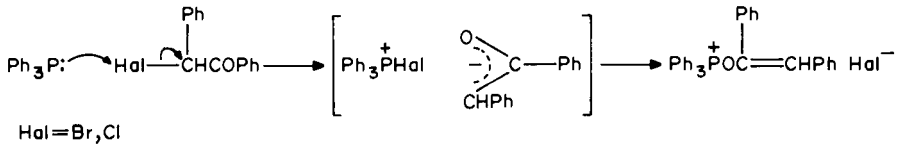
$$RR'_2P: + R''_2NCl \longrightarrow RR'_2\overset{+}{P}\overset{+}{P}ClNR''_2{}^{-} \longrightarrow RR'_2\overset{+}{P}NR''_2\,Cl^{-}$$

R = R′ = alkyl; R = alkyl, R′ = Me_2N

SCHEME 202

3. Halogen alpha to carbonyl, sulphone, nitro, cyano or other activating group

The reactions of phosphorus(III) reagents with α-halogenoketones are complicated by the possibility of attack at several alternative sites (see also Section VIII.A.4)[445]. The course of reaction varies according to the halogen, reagent type and reaction conditions. Nucleophilic attack at halogen has, however, been clearly established in the reactions of tertiary phosphines with α,α-dibromoketones[446] and may also occur with α-haloketones that have an aryl substituent in the α-position (Scheme 203)[582]. The

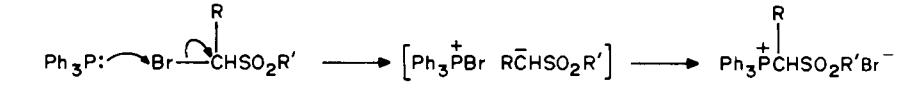


Hal = Br, Cl

SCHEME 203

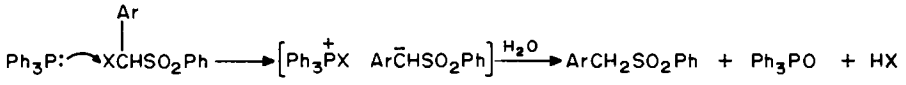
halogenophosphonium enolate that is formed collapses rapidly to give the enolphosphonium halide, but may be diverted by the presence of protic reagents to give the phosphine oxide and dehalogenated ketone (Scheme 166)[582,583]. In accord with this mechanism, the reaction of an optically active phosphine proceeds with inversion of configuration at phosphorus[446]. Nucleophilic attack at the α-carbon atom occurs with retention at phosphorus, as would also be expected for direct nucleophilic attack at oxygen.

Similar sequences occur in the reactions of tertiary phosphines with α-halogenobenzyl sulphones, except that the ion pair collapses with the formation of a C—P bond (Scheme 204)[584]. Reductive dehalogenation occurs in the presence of alcohols or water (Scheme 205)[584–587] and the phosphine oxide is formed (as with the α-halogenoketones



$R = p\text{-}O_2NC_6H_4$, $R' = p\text{-}CH_3C_6H_4$

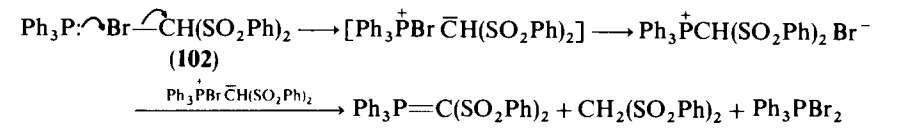
SCHEME 204



X = Cl, Br, I

SCHEME 205

above) with inversion of configuration at phosphorus[587,588]. α-Halogenopyridylmethyl sulphones react in a similar fashion[589]. The disulphone di(phenylsulphonyl)-bromomethane (**102**) reacts with triphenylphosphine to give the reduced product in aprotic media, the proton in this case being supplied by a second molecule of the bromophosphonium intermediate (Scheme 206)[584].



SCHEME 206

The reactions of tertiary phosphines with *N*-halogeno-amides and -imides[590–593], α-bromonitroalkanes[590,591,594], α-halogenonitriles[590,595], α-halogeno-α-nitrocarboxylates[596,597], α-halogeno-α-cyano- or α,α-dihalogeno-succinimide derivatives[598–601], β-bromovinyl ethers[602] and β-bromo-β-nitrostyrenes in which the aromatic group is electron attracting[603] are also thought to proceed via initial attack at halogen, although the mechanism of reaction has not been firmly established in all cases. Evidence for a radical intermediate has been obtained by trapping experiments in the reaction of triphenylphosphine with arylbromonitromethanes[604].

4. Perhalogenoalkanes and perhalogenoalkyl derivatives

The reactions of tertiary phosphines with tetrahalogenomethanes[605,606] have attracted considerable interest in view of the synthetic applications of these reagent combin-

$$R_3P: + CX_4 + R'OH \longrightarrow R'X + CHX_3 + R_3P{=}O$$

R = alkyl, aryl, R_2N; X = Cl, Br

SCHEME 207

ations[607,608]. In addition to their use for the replacement of alcoholic hydroxyl groups by halogen (Scheme 207)[609–613], these reagents have been shown to be effective for a wide range of halogenations, dehydrations and coupling reactions including peptide synthesis[608]. Hexachloroethane may also be employed[614].

In all cases, nucleophilic attack of phosphorus at positive halogen gives a reactive halogenophosphonium intermediate that interacts immediately with protic reagents, the anion being trapped to give the corresponding haloform (Scheme 208). The intermediate also reacts rapidly with carbonyl compounds (Scheme 209)[615–617]. In the absence

$$R_3P:\curvearrowright X\!-\!CX_3 \longrightarrow R_3\overset{+}{P}X\ CX_3^- \xrightarrow{YH} R_3\overset{+}{P}Y\ X^- + CHX_3$$

Y = R'O, R'S, R'CO_2, R'NH, R'$_2$N, etc.

SCHEME 208

$$(Me_2N)_3P \xrightarrow{CCl_4} (Me_2N)_3\overset{+}{P}Cl\ CCl_3^- \xrightarrow{RCOR'} (Me_2N)_3\overset{+}{P}Cl\ Cl^- + \begin{matrix} R & & Cl \\ & C & \\ R' & & Cl \end{matrix}$$

SCHEME 209

of other reactants, the halogenophosphonium ion is attacked rapidly by the counter ion to give the trihalogenomethylphosphonium halide as the first isolable intermediate (Scheme 210)[608,618,619]. Direct observation of the first intermediate (**103**) has been

$$R_3P: \xrightarrow{CX_4} R_3\overset{+}{P}X\ CX_3^- \longrightarrow R_3\overset{+}{P}CX_3\ X^-$$

(103)

SCHEME 210

reported only in the reaction of a sterically hindered phosphine, tri-*tert*-butylphosphine, with carbon tetrabromide at low temperatures[620], although analogous salts (**104, 105**) derived from the tin and germanium tetrahalides are stable at room temperature[621–623].

t-$Bu_3\overset{+}{P}X\ GeX_3^-$	t-$Bu_3\overset{+}{P}X\ SnX_3^-$
X = Cl, Br	X = Cl, Br
(104)	**(105)**

Kinetic evidence has suggested the possibility of a direct insertion mechanism (Scheme 211) in the interaction of triphenylphosphine with carbon tetrachloride, although

$$Ph_3P: + Cl{-}CCl_3 \longrightarrow \begin{matrix} & Cl & \\ Ph_3P & \vdots & \\ & CCl_3 & \end{matrix} \longrightarrow Ph_3\overset{+}{P}Cl\ CCl_3^- \text{ or } Ph_3\overset{+}{P}CCl_3\ Cl^-$$

SCHEME 211

reactions of more nucleophilic phosphines, e.g. trisdimethylaminophosphine, are thought to be more clearly ionic[608]. Ionic routes are also presumably more likely in reactions involving the more polarizable bromide and iodide.

A second molecule of tertiary phosphine will readily abstract positive halogen from the trihalogenomethyl phosphonium halide to give an ylide (**106**) (Scheme 212)[605,606,624-627],

$$Ph_3\overset{+}{P}CX_3\,X^- \xrightarrow{Ph_3P:} Ph_3P{=}CX_2 + Ph_3\overset{+}{P}X\,X^-$$

(**106**)

X = Cl, Br, I

$$Ph_3P{=}CX_2 \xrightarrow{Ph_3P:} [Ph_3P\cdots C(Cl)\cdots PPh_3]^+Cl^-$$

X = Cl (**107**)

SCHEME 212

and attack by a third molecule of phosphine has been shown in the Ph_3P–CCl_4 system to yield a stable methine-bridged phosphonium salt (**107**)[628,629].

Attack by phosphorus at halogen is also thought to occur in the initial stage of reaction between triphenylphosphine and benzotrichloride[630,631], trichloroacetamide[632], methyl trichloroacetate[633] and the trichloromethylpyrimidines[634].

5. *Halogenoalkenes and halogenoalkynes*

Reactions of phosphines with halogenoalkenes (including the perfluoroalkenes) generally involve nucleophilic substitution at carbon (see Sections III.B.2 and III.B.3). With perfluoroisobutene, however, triphenylphosphine removes fluorine with the formation of triphenylphosphine difluoride (Scheme 213)[635]. Nucleophilic attack at halogen is also

$$(CF_3)_2C{=}CF_2 \xrightarrow{Ph_3P:} (CF_3)_2C{=}C[CF{=}C(CF_3)_2]_2 + Ph_3PF_2$$

SCHEME 213

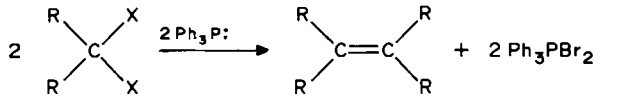
believed to occur in reactions of halogenoalkynes with phosphines (Section IV.B.; Schemes 111 and 112)[251-253] and is particularly rapid in the case of fluorine. The reaction of triphenylphosphine with phenylbromoacetylene has been shown to involve the initial formation of a bromophosphonium phenylacetylide ion pair which, in an inert solvent, collapses to yield the phosphonium salt. In the presence of water, however, hydrolysis of the intermediate gives phenylacetylene, triphenylphosphine oxide and hydrogen bromide (Scheme 214)[252].

$$PhC{\equiv}C{-}Br{\curvearrowleft}{:}PPh_3 \longrightarrow [PhC{\equiv}C^-\ Br\overset{+}{P}Ph_3] \begin{cases} \longrightarrow PhC{\equiv}C\overset{+}{P}Ph_3\ Br^- \\ \xrightarrow{H_2O} PhC{\equiv}CH + Ph_3PO + HBr \end{cases}$$

SCHEME 214

6. Elimination reactions

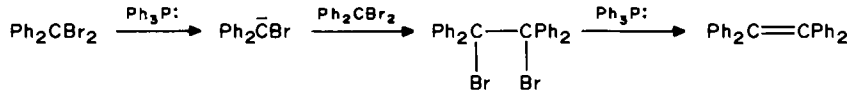
1,1-Dihalides undergo elimination with the formation of a new alkenic bond and the corresponding phosphine dihalide (Scheme 215)[636,637]. The reaction may involve a



R=Ph, X=Br; R—R=—N(CF$_2$)—(CF$_2$)$_2$—N(CF$_2$)—, X=Cl

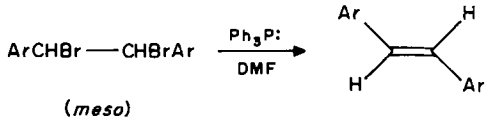
SCHEME 215

carbene intermediate[637] but could also proceed by the formation of a carbanion, followed by nucleophilic attack of the latter on a second molecule of dihalide, and then β-elimination (Scheme 216)[636].



SCHEME 216

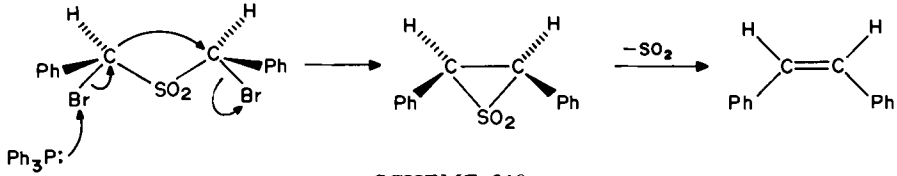
β-Eliminations from 1,2-dibromides (but not chlorides which undergo substitution) are brought about by the action of phosphide anions[638,639]. Tertiary phosphines give products of stereospecific anti-elimination (Scheme 217)[640,641]. Other examples of



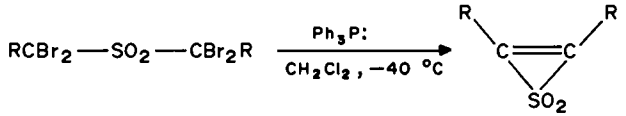
SCHEME 217

elimination from 1,2-dihalides include the formation of α-bromovinyl cyanide from 2,2,3-tribromopropionitrile[642], diphenylketene from diphenylbromoacetyl bromide[643] and the dechlorination of perchlorodiethyl ketone to give perchlorodivinyl ketone[644]. Selective dechlorination also occurs in the reaction of triphenylphosphine with perfluorochloro esters[645].

Elimination of bromine from α,α′-dibromosulphones gives either the corresponding thiirane dioxide or alkene with loss of sulphur dioxide (Scheme 218)[646]. The reaction



SCHEME 218



SCHEME 219

occurs stereospecifically with inversion at both centres. α,α,α′,α′-Tetrabromosulphones give the corresponding thiirene dioxides (Scheme 219) at −40 °C[647].

7. *Miscellaneous reactions*

Tertiary phosphines abstract halogens from a variety of inorganic halides, including the tetrahalides of tin and germanium (see Section IX.B.4)[621–623], tellurium tetrachloride (which is reduced to the element)[648], phosphorus(V) halides[649] and nitrogen trichloride[650].

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The Chemistry of Organophosphorus Compounds
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CHAPTER 12

Acid–base and hydrogen-bonding properties of phosphines

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I. INTRODUCTION

Phosphine shows only weakly acidic and weakly basic properties. Based on kinetic studies of proton–deuteron exchange in water, equilibrium constants for the dissociation of phosphine (equation 1) and for the protonation of phosphine by water (equation 2) have been estimated to be approximately 10^{-29} and 10^{-28}, respectively[1].

$$PH_3 + H_2O \rightleftharpoons PH_2^- + H_3O^+ \quad (1)$$

$$PH_3 + H_2O \rightleftharpoons PH_4^+ + OH^- \quad (2)$$

Substitution of hydrogen by organic groups in general increases the basicity substantially[2–5]. The effect results in part from inductive or mesomeric electron release, which increases electron density at phosphorus in the phosphine or stabilizes the corresponding phosphonium ion, but it is also dependent on steric factors and hybridizational changes that occur on protonation[6]. *Ab initio* molecular orbital calculations, used to study

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substituent effects of directly and remotely bonded groups, have shown that the electronic consequences of steric effects may be of comparable importance to direct electronic effects[7]. A wide range of basicities have been reported. Apart from the very low value for phosphine itself (ca -14), pK_a values are generally in the region of 0–5 for primary and secondary phosphines and 8–9 for simple trialkylphosphines[4], although values in excess of 11 are reported for tri-*tert*-butylphosphine[8] and tris(2,4,6-trimethoxyphenyl)phosphine[9,10], which thus have basicities comparable to that of piperidine.

The low proton acidity of phosphine (pK_a 29)[1] is reduced even further by alkyl substitution, although the replacement of hydrogen by aryl causes an increase in acidity, presumably by mesomeric stabilisation of the corresponding phosphide anions. Reported values of pK_a lie between 22 for diphenylphosphine and 37 for di-*tert*-butylphosphine[11].

II. ACIDITY OF PHOSPHINES

The acidity of phosphine is greater than that of ammonia but less than that of arsine, as shown *inter alia* by ^{1}H NMR studies of competition reactions between these hydrides and sodamide in liquid ammonia (equation 3)[12].

$$HA + NaNH_2 \rightleftharpoons A^- + NH_3 + Na^+ \qquad (3)$$

$$HA = PH_3 \text{ or } AsH_3$$

The greater acidity of phosphine compared with that of ammonia has also been demonstrated in the gas phase by ion cyclotron resonance spectroscopy, which showed the proton affinity of the phosphide ion, PH_2^-, to be approximately 40 kcal mol^{-1} less than that of the amide ion, NH_2^-[13,14].

Relative acidities and pK_a values for primary and secondary phosphines containing either alkyl or aryl substituents have been obtained from equilibrium data for the reactions of alkali metal phosphides with a number of hydrocarbons, alcohols and amines in tetrahydrofuran (equation 4)[11]. The following order of acidities was found:

$$R_2PM + R'H \rightleftharpoons R_2PH + R'M \qquad (4)$$

$$M = Li \text{ or } K;\ R' = \gtrless C,\ \gtrless N \text{ or } -O$$

$$Ph_2PH > PhPH_2 > PH_3 > C_6H_{11}PH_2 > Et_2PH > (C_6H_{11})_2PH > t\text{-}Bu_2PH$$

The decrease in acidity that accompanies increasing alkyl substitution (seen also in the lower acidity of methylphosphine compared with that of phosphine[12,15]), has been attributed to an increase in electron density at phosphorus as a result of the inductive effect of the alkyl substituents[11]. Aryl substitution, on the other hand, increases the acidity, possibly by stabilization of the phosphide anion through π-delocalization (**1**). Although

(1)

gas-phase acidities of organic derivatives of phosphine have not so far been determined, it is worth noting that for other classes of compound (e.g. alcohols and amines), an increase in alkyl substitution has in general been shown to increase acidity[16–18]. Alkyl substitution may stabilize both positive and negative ions in the gas phase by polarization interaction[19]. Other effects including solvation and ion pairing may therefore need to be considered in the solution chemistry of phosphines and phosphide anions. A further anomaly is evident in the higher acidity of alcohols compared with phosphine and its

derivatives as determined by metal–hydrogen exchange reactions in thf[11]; in the gas phase, phosphine was found to be more acidic than propanol, ethanol or methanol[13].

In accord with the proton acidities of phosphines in solution[11], an alkali metal phosphide can be prepared by interaction of the corresponding phosphine with an organometallic compound or other metal derivative only if the latter is obtained from a compound that is a weaker proton acid than the phosphine[20]. Phosphine and the aryl-substituted phosphines thus react with sodamide to give the corresponding phosphides (equation 5). Less acidic phosphines, on the other hand, may undergo ammonolysis; hydride ion is displaced from dimethylphosphine with the evolution of a molecular equivalent of hydrogen and formation of a phosphinoamine, possibly as shown in equations 6 and 7[15].

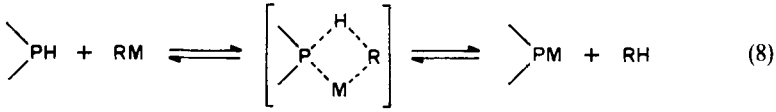
$$R^1R^2PH + NaNH_2 \longrightarrow R^1R^2P^-Na^+ + NH_3 \quad (5)$$

R^1 and/or R^2 = H or Ph

$$Me_2PH + NaNH_2 \xrightarrow{\text{liq. } NH_3} [Me_2PNHNa\cdot xNH_3] + H_2 \quad (6)$$

$$2[Me_2PNHNa\cdot xNH_3] + 2NH_4Br \longrightarrow Me_2PNHPMe_2 + 2NaBr + (3+x)NH_3 \quad (7)$$

Organometallic derivatives of lithium, magnesium, aluminium and zinc are generally useful for the preparation of phosphides by proton abstraction from primary or secondary phosphines. A four-centre reaction mechanism has been proposed (equation 8)[21,22].



(8)

Either one or both hydrogens of a primary phosphine can be replaced to give mono- or di-metallated derivatives. Since the second hydrogen is less acidic than the first, a double decomposition occurs between dimetallated derivatives and primary phosphines (equation 9)[11]. Direct replacement of acidic hydrogen by an alkali metal is also possible (equation 10). For phosphine (PH_3), pK_a values for the second and third dissociations have been estimated as 38 and 42 respectively; the third P—H bond shows a lower acidity than does benzene, so that reaction of phosphine with phenyllithium leads only to the formation of Li_2PH rather than Li_3P.

$$RPH_2 + M_2PR \longrightarrow 2MPHR \quad (9)$$

$$RPH_2 \text{ or } R_2PH \xrightarrow[\text{organic solvent}]{\text{alkali metal}} RPHM,\ RPM_2 \text{ or } R_2PM \quad (10)$$

Apart from the formation of phosphides as stable salts and their use in chemical synthesis[20], phosphide anions may occur as reactive intermediates, e.g. in the base-catalysed additions of phosphine and of primary or secondary phosphines to unsaturated compounds[23,24] (see Chapter 11).

III. BASICITY OF PHOSPHINES

A. Basicity in Solution

1. pK_a, enthalpies of protonation and linear free energy relationships

The basicity of phosphines in solution has been studied by numerous workers and is generally seen to increase as the degree of substitution by organic groupings increases[2–5]:

$$PH_3 \ll RPH_2 < R_2PH < R_3P \quad (R = \text{alkyl or aryl})$$

Determinations of pK_a have usually been based on the measurement of half-neutralization potentials in nitromethane[3,4,8,25-28] or chloroform–acetic acid[29], or on titration in aqueous ethanol[5,30-33].

The very low basicity of phosphine ($pK_a \sim -14$)[4] was recognized from early studies of proton–deuteron exchange in water[1] and has been confirmed by later measurements of the heat of proton transfer in fluorosulphonic acid[34]. Reasons for the dramatic increase in basicity that accompanies the introduction of an alkyl substituent in phosphine, compared with the much smaller effect in ammonia, have been discussed by various workers (see, e.g., ref. 6) and it now seems clear that the principal cause is related to solvation. Hydrogen bonding between phosphonium ions and water occurs to only a very small extent so that the stabilization afforded by the introduction of alkyl substituents is not offset by any significant loss of stabilization through hydrogen bonding[34]. This effect contrasts with that in the amine series in which the N—H protons form strong hydrogen bonds to water. The increase in stability of positively charged nitrogen that results from alkyl substitution is thus counterbalanced by a loss of hydrogen bonding to an extent that accounts for the well known 'anomalous' order of basicities for amines ($NH_3 < RNH_2 \approx R_2NH > R_3N$)[34-38]. The higher basicity of ammonia compared with that of phosphine may also be due to differences in the solvation energies of the corresponding 'onium ions (possibly in the region of 19 kcal mol^{-1})[6,39]. In addition, the rehybridization energy associated with protonation and formation of the tetrahedral 'onium ions will be greater for phosphine (bond angle 93°)[6,40] than for ammonia (bond angle 107°)[41]. *Ab initio* calculations[42,43] indicate that the lone-pair orbital of phosphine has much more s character ($sp^{0.8}$) than that of ammonia, which is essentially sp^3 hybridized[44].

The first systematic study of pK_a values for a range of primary, secondary and tertiary phosphines[4] showed separate parallel correlations, with some degree of scatter, with the sums of the Taft σ^* substituent[45] parameters for each of these three groups. The orders of basicity were found to be as follows:

(a) Tertiary phosphines ($pK_a = 7.85 - 2.67\sum\sigma^*$):

$$(c\text{-}C_6H_{11})_3P > Me_3P \approx Me_2PEt \approx MePEt_2 \approx Et_3P > n\text{-}Pr_3P > n\text{-}Bu_3P > n\text{-}Pe_3P > i\text{-}Bu_3P > PhPMe_2 \approx n\text{-}Bu_2PCH_2CH_2CN > Me_2PCH_2CH_2CN > n\text{-}Oct_2PCH_2CH_2CN \approx PhPEt_2 > MeP(CH_2CH_2CN)_2 > Ph_3P > (NCCH_2CH_2)_3P$$

(b) Secondary phosphines ($pK_a = 5.13 - 2.61\Sigma\sigma^*$):

$$(c\text{-}C_6H_{11})_2PH > n\text{-}Bu_2PH > n\text{-}Oct_2PH > i\text{-}Bu_2PH > Me_2PH > Ph_2PH > (NCCH_2CH_2)_2PH$$

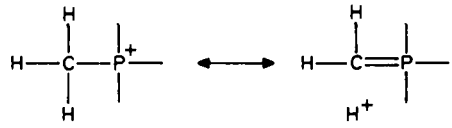
(c) Primary phosphines ($pK_a = 2.46 - 2.64\sum\sigma^*$):

$$n\text{-}OctPH_2 > i\text{-}BuPH_2$$

It was later shown that the points for all three groups lie on a single line[46,47] if the Taft substituent constants are replaced by Kabachnik's σ^{ph} parameters, derived for use with phosphorus compounds from the dissociation constants of acids of the type $R^1R^2P(O)OH$[48]:

$$pK_a = -3.45 - 3.423\sum\sigma^{ph} \quad (r = 0.950)$$

Steric factors do not appear to play more than a minor role in the determination of basicity, although some deviations occur for the larger alkyl groups, especially isobutyl[4,46]. The systematically higher pK_a values observed for the methyl phosphines were

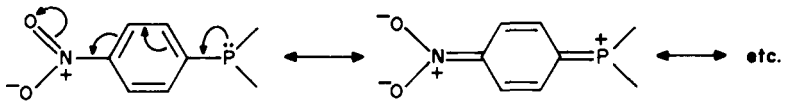


(2)

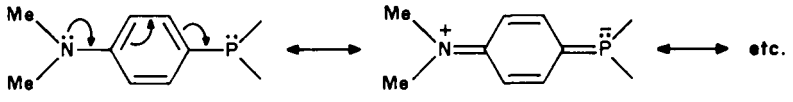
thought possibly to be associated with hyperconjugative interaction of the C—H σ-bonds with the phosphorus d orbitals (2)[46].

Within a homologous series of trialkyl phosphines, R_3P(R = Me, Et, *n*-Pr, *n*-Bu), a slight but distinct decline in basicity with increasing size of the alkyl group may be associated with steric hindrance to solvation[5]. A decrease in basicity is also observed on the replacement of alkyl by aryl[4,5] or by the introduction of alkyl groups that contain $-I$ substituents, e.g. CH_2CH_2CN[4] or $(CH_2)_nCOX$ (X = OR, NH_2 or OH)[31]. Carboxyphosphines have the betaine structure in aqueous solution[5].

Based on studies of various aryl phosphines, the evidence in most cases suggests that conjugative interaction between the aromatic ring and phosphorus is not a major factor in the determination of basicity. Steric effects of methyl substituents in the *ortho* position of the benzene ring also appear to be of less significance than inductive effects[30]. Delocalization of the phosphorus lone pair by conjugation with the benzene π-system in triphenylphosphine has been indicated by UV spectroscopy[49] and an increasing degree of 3p delocalization can be recognized with the introduction of strong electron acceptors (NO_2, CN, CHO, CO_2Me, CO_2H, $CONMe_2$ or $CONH_2$) into the aromatic ring (3)[50]. Conversely, delocalization of the ring electrons to the phosphorus 3d orbitals can be demonstrated if electron donors such as *p*-dimethylamino are present (4)[50,51]. pπ–dπ



(3)



(4)

delocalization from the benzene ring to positive phosphorus has also been invoked to account for the relatively high-field ^{31}P NMR chemical shifts of phenylphosphonium ions and their stabilization in the gas phase (see Sections III.A.2 and III.B). Phenyl-substituted phosphines, however, show only small deviations from the linear plots of log pK_a vs σ^* or σ^{ph}[4,46,47] and for a considerable range of substituted aryl phosphines (5, 6), good correlations have been obtained between pK_a values determined from measurements in

(5) (6)

nitromethane and the sums of the Hammett σ or Kabachnik σ^{ph} parameters. The following orders of basicity and correlations have been determined:

(a) For **5** (R = Et)[26,27]:

$$Me_2N > MeO > Me > H > MeO_2C \quad (pK_a = 6.30 - 2.56\sigma_p)$$

(b) For a series of mixed alkyl and aryl phosphines whose basicities were in the following order[25]:

$$Et_3P > PhPEt_2 > p\text{-}ClC_6H_4PEt_2 > Ph_3P$$

$$(pK_a = -4.606 - 4.0946\sigma^{ph}) \quad (r = -0.996)$$

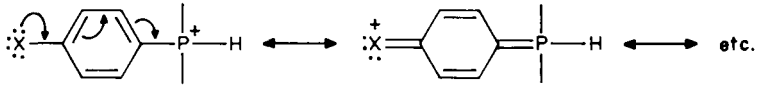
(c) For a wide range of tertiary phosphines with pK_a values varying from 11.4 to 1.03, as follows (R in R_3P)[8]:

$$t\text{-Bu} > c\text{-}C_6H_{11} > 4\text{-}Me_2NC_6H_4 > 4\text{-}MeOC_6H_4 > 4\text{-}MeC_6H_4 > 3\text{-}MeC_6H_4 > 2\text{-}MeC_6H_4 > H > 4\text{-}FC_6H_4 > 4\text{-}ClC_6H_4$$

$$(pK_a = -1.538 - 2.849\sigma^{ph}) \quad (r = -0.986)$$

The order of basicities for the 4-methylphenyl, phenyl and 4-chlorophenyl compounds is the same as that obtained on the basis of studies of equilibria between triarylphosphines and trityl chloride (equation 11)[52] and is supported by NMR studies of solutions of triarylphosphines and hydrogen bromide in dichloromethane, in which basicity was related to the ease with which the P—H proton could be observed[53]. Tris(*p*-chlorophenyl)phosphine (**6**, X = Cl) showed no significant deviation from the Hammett plot obtained in nitromethane[8], in contrast to an earlier observation based on studies in aqueous ethanol for **6** (X = MeO, Cl) and **5** (R = Ph or Et; X = Me_2N, MeO, H, F, Cl and Br)[32,33]. This unusual deviation, corresponding to an unexpectedly high basicity, and also the smaller deviations noted for **5** (X = Cl or Br) were attributed to a special mesomeric interaction with phosphorus in the case of *p*-halogenoaryl substituents (**7**), although it is not clear why a similar effect should not apply in the case of the *p*-methoxy derivative.

$$Ar_3P + Ph_3C^+ClO_4^- \rightleftharpoons Ar_3\overset{+}{P}CPh_3ClO_4^- \qquad (11)$$



(**7**)

It was subsequently shown[54] that the dimethylamino derivative within this series is protonated first at nitrogen, a factor not taken into account in the earlier studies, and that the protonation of compounds of the type $(p\text{-}XC_6H_4)_nPPh_{n-3}$ (X = H, Br, Cl, OMe, NMe_2) in aqueous ethanol does not follow the Hammett equation for reasons that were discussed. An excellent correlation was, however, obtained for results obtained in chloroform–acetic acid, showing again the relative unimportance of conjugation to phosphorus in the control of pK_a.

Enthalpies of protonation in fluorosulphonic acid have confirmed the large substituent effects of alkyl groups compared with those in the analogous oxygen and nitrogen bases[36]. For phosphine, cyclohexylphosphine, dicyclohexylphosphine and trimethylphosphine, the values of $-\Delta H_{HSO_3F}$ are 16.9, 29.9, 31.6 and 44.6 kcal mol^{-1}, respectively. For the following twelve tertiary phosphines, listed in order of increasing basicity:

$$(p\text{-}ClC_6H_4)_3P < (p\text{-}FC_6H_4)_3P < Ph_3P < (o\text{-}MeC_6H_4)_3P$$
$$< (p\text{-}MeC_6H_4)_3P < (p\text{-}MeOC_6H_4)_3P < MePh_2P$$
$$< Me_2PhP < Me_3P$$
$$< (c\text{-}C_6H_{11})_3P < Et_3P < t\text{-}Bu_3P$$

the heats of protonation ($-\Delta H_{HP}$/kcal mol^{-1}) show a good linear correlation with pK_a as determined from half-neutralization potentials in nitromethane:

$$-\Delta H_{HP} = 1.82\,pK_a + 16.3 \quad (r = 0.994)$$

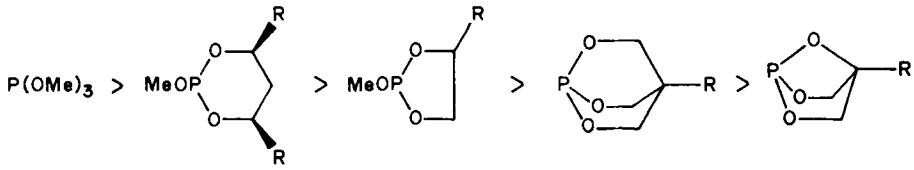
An excellent correlation is also obtained between Hammett parameters and enthalpies of protonation for the *para*-substituted triarylphosphines (p-$XC_6H_4)_3P$ with $-\Delta H_{HP}$ decreasing in the order X = MeO > Me > H > F > Cl. A much poorer correlation with σ^+ parameters suggests that the aromatic ring does not interact significantly with the d orbitals of phosphorus in the phosphonium ion[55], in agreement with a similar conclusion based on photoelectron spectroscopy[56].

2. *Spectroscopic studies*

A number of attempts have been made to correlate the basicities of phosphines and of other phosphorus(III) derivatives with NMR parameters for the protonated species. Studies have been made of the phosphine hydrobromides in dichloromethane[57] and of protonation in 100% sulphuric acid[58] or super-acid media such as FSO_3H or FSO_3H–SbF_5[59–61]. The change in chemical shift that occurs on protonation is dependent on structure, being downfield in most cases for trialkyl- or triaryl-phosphines (except for tri-*tert*-butylphosphine), but is significantly upfield if alkoxy or aryloxy groups are attached to phosphorus as in phosphorus(III) esters[58,60]. For the alkyl- and mixed alkyl–aryl-phosphines, the change that occurs on protonation increases in magnitude as the basicity of the phosphine increases in the order $Ph_2RP < PhR_2P < R_3P$[57], although it has not been possible to make correlations with changes in R within any one of these three groups.

^{31}P chemical shifts for various classes of phosphine[62–64] and for quaternary phosphonium ions[65,66] have been found to be related by simple linear equations to additive group contributions (σ^P constants) although these are not linearly related to Taft σ^* values[64]. A similar linear correlation is found between the sums of σ^P constants and ^{31}P chemical shifts for protonated trialkylphosphines in FSO_3H[59]. The deviation for triphenylphosphine, which shows a significantly higher chemical shift than this relationship would predict, has been attributed to π-delocalization of the ring electrons to phosphorus d orbitals. One-bond coupling constants J_{PH} for the protonated phosphines, R_3PH^+, decrease steadily as the steric bulk of the alkyl group increases from 497 Hz (R = Me) to 436 Hz (R = *t*-Bu). All values are significantly less than the coupling constant for the parent phosphonium ion, PH_4^+ (548 Hz). Such a decrease may be correlated with decreasing s character of the phosphorus orbital of the P—H bond[59,67] and corresponds to increasing basicity of the phosphine. The low value for tri-*tert*-butylphosphine (436 Hz) is in accord with its being one of the most basic phosphines known[8]. This may be expected as a consequence of the increase in C—P—C bond angle as the bulkiness of the substituent groups increases and a consequent increase of s character in the P—C bond. Alkoxy and phenoxy groups have a much larger effect on P—H coupling than can be explained on the basis of changes in hybridization and is probably associated with their strongly electron-withdrawing ($-I$) effect which increases the positive charge on phosphorus[58]. One-bond coupling constants lie mainly in the region 796–827 Hz for protonated trialkyl phosphites and rise to 870 Hz in the case of $(PhO)_3PH^+$. The very large upfield shifts shown by such esters on protonation have on the other hand been attributed to charge delocalization via pπ–dπ back-donation to phosphorus[60].

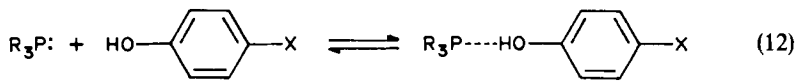
An interesting feature of cyclic and bicyclic phosphite esters is the effect of steric constraint on basicity as shown by protonation in FSO_3H at $-50\,^{\circ}C$[61,68]. A steady increase in J_{PH} from 826 to 928 Hz is observed, corresponding to a decrease in basicity, in the following order:



(8) (9) (10) (11) (12)

CNDO/2 calculations show a concomitant rise in positive charge on phosphorus and on the phosphorus-bound proton in the protonated species, but no trend in phosphorus hybridization. The observations are rationalized in terms of reduced repulsive interaction between the oxygen and phosphorus lone pairs in the more sterically constrained phosphites[69]. *Ab initio* calculations have shown that an oxygen lone pair that is antiperiplanar to the phosphorus lone pair raises the energy of the latter by 3.3 kcal mol^{-1} relative to a phosphite with no oxygen lone pair in this situation; on the other hand, on protonation of phosphorus the relative energy difference is reversed[70]. In addition, a 'hinge effect' has been proposed, as a possible explanation of the lower basicities of the more sterically constrained bicyclic phosphites[71]. In such systems, it is argued, the phosphorus lone pair will be more difficult to polarize because the O—P—O bond angles will be more difficult to open towards a tetrahedral configuration. Any widening must also tend to close the P—O—C angle from 120° and thus reduce π-delocalization from oxygen to phosphorus.

A similar order of basicities has been indicated by measurements of infrared shifts of the phenolic O—H stretching vibration resulting from hydrogen bonding with the phosphite esters (equation 12, R_3P = phosphite ester, X = H)[72]. Infrared studies of hydrogen



(12)

bonding between triarylphosphines and *p*-trifluoromethylphenol in carbon disulphide (equation 12, R = aryl, X = CF_3) have similarly been used to establish the following order for the effect of *para* substituents on the basicity of triarylphosphines[73]:

$$4\text{-MeO} \gg 4\text{-Me} > 4\text{-Cl} > 4\text{-H}$$

The results agree in part with the order of basicities obtained for these phosphines by determination of half-neutralization potentials in nitromethane[8], but the order for X = Cl and X = H is reversed. A possible explanation may be that hydrogen bonding of the phenol to substituent groups (MeO, Cl) increases the apparent basicity of the phosphine[8].

B. Gas-phase Basicities

The intrinsic basicities of molecules, unencumbered by solvent interactions, are obtainable from a study of proton transfer reactions (equation 13) in the gas phase and are measured in terms of proton affinity, *PA*. The relationship between the proton affinity of a

base, $PA(B)$, its homolytic bond dissociation energy, $D(B^+—H)$, and its ionization potential, $IP(B)$, is shown in the following equations:

$$B^1 + B^2H^+ \rightleftharpoons B^1H^+ + B^2 \tag{13}$$

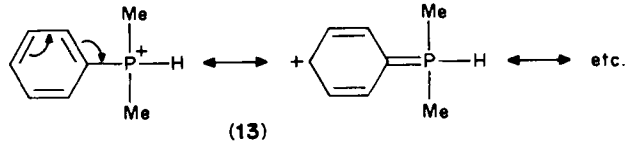
$$BH^+ \longrightarrow B: + H^+ \qquad \Delta H = PA(B) \tag{14}$$

$$BH^+ \longrightarrow B^{+\cdot} + H^\cdot \qquad \Delta H = D(B^+—H) \tag{15}$$

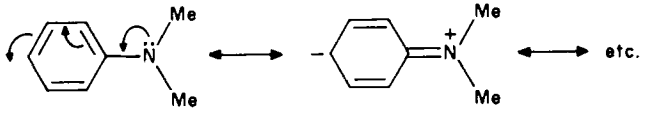
$$PA(B) - D(B^+—H) = IP(H^\cdot) - IP(B)$$

Based on ion-cyclotron resonance (ICR) spectroscopy[14], the proton affinities for phosphine, methylphosphine, dimethylphosphine and trimethylphosphine have been found to be 187.9, 206.9, 218.9 and 228.0 kcal mol^{-1}, respectively[74]. The value for phosphine is close to other reported values[75,76] and shows phosphine to be less basic than ammonia by ca 22 kcal mol^{-1}, a similar difference to that estimated from pK_a data for aqueous solution[6]. The increase in basicity for each methyl substitution is non-additive but is twice as large as that observed for methyl substitution in the amine series in the gas phase[77]. Another difference from the amines is the change in homolytic bond dissociation energy which decreases only slightly from 104 kcal mol^{-1} for PH_4^+ to 99.2 kcal mol^{-1} for Me_3PH^+, whereas the change for the amines is from 128.4 kcal mol^{-1} for NH_4^+ to 93.3 kcal mol^{-1} for Me_3NH^+. The relatively large effect of methyl substitution on the basicities of phosphines, compared with amines, may be related to differences in rehybridization energy on protonation but could also result from hyperconjugation between the methyl substituents and phosphorus d orbitals (**2**)[74].

The replacement of methyl by aryl brings about an increase in gas-phase basicity, as shown by the use of pulsed electron high ion source pressure mass spectrometry to measure the kinetics and equilibrium constants for exchange reactions between trimethylphosphine (B^1) and the various methyl phenyl derivatives (equation 13)[78]. For a constant $B^1(Me_3P)$, standard free energy changes for these equilibria in kcal mol^{-1} are -2.5 ($B^2 = Me_2PhP$), -3.2 ($B^2 = MePh_2P$) and -3.2 ($B^2 = Ph_3P$). Vertical ionization potentials, measured by photoelectron spectroscopy, decrease in the same order (i.e. from Me_3P to Ph_3P). The order of basicity is exactly the reverse of that found in solution[3–5], in which stabilization through solvation is presumably affected adversely as the more bulky phenyl groups are introduced. Conjugation of the π-electron system with empty d orbitals of phosphorus is thought to be an important stabilizing factor (**13**). The opposite effect of phenyl in the analogous amines is attributed to resonance stabilization of the neutral base (**14**) and to inductive destabilization of positive nitrogen by phenyl ($-I$) in the ammonium ion. Both of these influences are expected to be greater for nitrogen than for the larger phosphorus atom. A study of the proton affinities of some primary phosphines RPH_2 (R = Me, C_6H_{11} and Ph) leads to similar conclusions[79]. Calculations at the STO-3G,



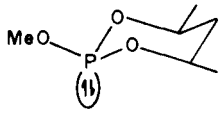
(**13**)



(**14**)

4–31G, STO–3G* and 4–1G* levels (the asterisks indicate with d orbitals) for PH_3, $MePH_2$ and $PhPH_2$ and for the protonated species predict proton transfer reaction energies in good agreement with experimental results. A shortening of the C—P bond is predicted for protonation of $MePH_2$ and particularly for $PhPH_2$, whilst a lengthening of the C—N bond is predicted for the corresponding nitrogen compounds. Stabilization of $PhPH_3^+$ is thought to occur mainly via π^* orbitals with some πd participation; hyperconjugative stabilization is indicated for $MePH_3^+$[79].

The order of proton affinities for a series of cyclic and bicyclic phosphites (**9**–**12**), determined by ICR spectroscopy[80], has been shown to be the same as the order of solution basicities determined previously (see above)[61]. In addition, a significant difference in proton affinity (2.6 kcal mol^{-1}) is observed between the stereoisomers of the six-membered ring phosphite (**9**, R = Me), the phosphorus lone pair being more basic in the axial position (**15**) than in the equatorial (**16**). The effect of steric constraint on basicity in cyclic



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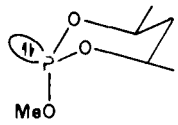

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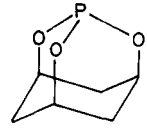


(17)

phosphites is discussed above (Section III.A.2). The proton affinity of phosphorus is thus decreased with increasing steric constraint and is paralleled by a corresponding increase in adiabatic ionization potential, indicating that the first ionization potential corresponds to ionization from the phosphorus lone pair orbital. For this series of phosphite esters and for a number of other phosphine derivatives, the overall order of proton affinities is as follows:

$$Me_3P > \mathbf{15} > \mathbf{16} > (MeO)_3P > \mathbf{9}(R = H) > Me_2PH > \mathbf{10}(R = H) \approx \mathbf{17} > \mathbf{11}(R = Me)$$
$$> \mathbf{11}(R = H) > MePH_2 > \mathbf{12}(R = Me) > \mathbf{12}(R = H) > PH_3 > PF_3$$

with values ranging from 228.2 to 196.5 kcal mol^{-1}. A good linear correlation of proton affinities with ionization potentials was obtained:

$$PA(B) = 0.853[459 - IP(B)]$$

allowing an estimate of proton affinity to be made for other phosphorus(III) derivatives whose ionization potentials are known. The closeness to unity of the coefficient relating PA(B) to IP(B) indicates that the homolytic bond dissociation energy is approximately constant for this series of compounds[80].

C. Salt Formation

Because of the low basicity of primary phosphines, their salts are unstable in water. Salt formation may occur in concentrated hydrohalic acids but hydrolysis occurs on dilution (equation 16)[81–83]. The salts of di- and tri-arylphosphines are also unstable in water, e.g. triphenylphosphine is precipitated if water is added to a solution in concentrated hydriodic acid[84]. More stable salts are obtained from di- or tri-alkylphosphines and are decomposed only by alkali[85].

$$RPH_3^+X^- + H_2O \longrightarrow RPH_2 + H_3O^+ + X^- \qquad (16)$$

R = alkyl or aryl

An infrared spectroscopic study of the products obtained from the reactions of triethylamine with anhydrous hydrogen halides in diethyl ether has confirmed their ionic structure (**18**) and has shown the presence of hydrogen bonding, $\overset{+}{P}—H\cdots X^-$, with increasing strength in the order I < Br < Cl[86]. An analogous hydrobromide and hydroiodide (**19**) are formed from triphenylphosphine but the only identifiable product from hydrogen chloride (equation 17) is the hydrogen dichloride salt (**20**). The latter dissociates slowly to the starting materials without a stable 1:1 intermediate being identifiable.

$$\underset{\textbf{(18)}}{Et_3PH^+\ X^-} \qquad \underset{\textbf{(19)}}{Ph_3PH^+\ X^-}$$

$$X = Cl,\ Br,\ or\ I \qquad X = Br\ or\ I$$

$$Ph_3P + 2HCl \rightleftharpoons \underset{\textbf{(20)}}{Ph_3PH^+HCl_2^-} \tag{17}$$

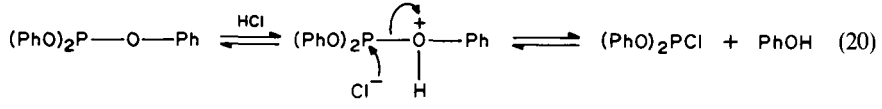
Hydrogen fluoride gives only liquid products with either triethyl- or triphenylphosphine, consisting of a polar 1:1 adduct (**21**), which is probably a strongly hydrogen-bonded complex, and an ionic hydrogen difluoride (**22**) (equation 18). Differences in basicity between the trialkyl- and triaryl-phosphines allow the former to be selectively removed from mixtures of both types by acid extraction[87].

$$R_3P + HF \rightleftharpoons \underset{\textbf{(21)}}{R_3PHF} \overset{HF}{\rightleftharpoons} \underset{\textbf{(22)}}{R_3PH^+HF_2^-} \tag{18}$$

D. Protonated Phosphines as Reactive Intermediates

The dealkylation of phosphorus(III) esters by hydrogen halides involves protonation of phosphorus. Phosphonium intermediates have been identified by ^{31}P NMR spectroscopy in solutions of trialkyl phosphites with hydrogen chloride at −60 to −80 °C[88–91]. Rapid exchange occurs at room temperature, presumably via a hydrogen-bonded intermediate (equation 19). The overall reaction kinetics for dealkylation are second order or higher in hydrogen chloride and it is likely that ionization of the H—Cl bond is assisted by the formation of a hydrogen dichloride ion or other higher aggregate. Phosphorus—oxygen cleavage may also occur, particularly in the case of phenyl esters. An O-protonated intermediate could be involved (equation 20) but has not been clearly identified. A mechanism involving the phosphonium intermediate in rate-determining P—O cleavage can also be envisaged (equation 21)[89].

$$(RO)_3P + HCl \rightleftharpoons (RO)_3P\cdots H—Cl \overset{HCl}{\rightleftharpoons} (RO)_3PH^+HCl_2^- \tag{19}$$



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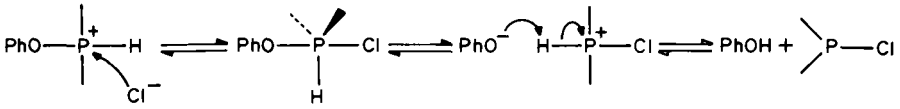

(21)

Tervalent phosphorus–nitrogen compounds are susceptible to P—N fission in acid conditions or in the presence of protic reagents[92]. Protonation at phosphorus has been demonstrated by ^{31}P NMR in acid-catalysed phosphorylations using tervalent phosphorus acid amides[93] but, as with P—O fission, the precise mechanism of cleavage is not certain. Either a *P*- or *N*-protonated species could be involved in the rate-determining step. The identification of a hydrophosphorane in two cases of P—N fission by alcohols or phenols suggested that a phosphonium intermediate was the immediate precursor[94].

IV. HYDROGEN-BONDING ABILITIES

Phosphines are able to engage in hydrogen bonding by interaction of the phosphorus lone pair with molecules containing acidic hydrogen. The effect of such hydrogen bonding on the O—H infrared stretching vibrations of phenols has been used as a measure of phosphine basicity (equation 12)[72,73] (see Section III.A.2). Hydrogen bonding to anhydrous hydrogen halides may also occur to a greater or lesser extent depending on the basicity of the phosphine and the ease of polarization of the hydrogen—halogen bond. Less basic phosphines (e.g. triphenylphosphine) or phosphite esters which do not form specific 1:1 salts with hydrogen chloride probably form a hydrogen-bonded complex as an intermediate en route to the phosphonium hydrogen dichloride (e.g. equation 19), and a similar sequence may occur in the reactions of tertiary phosphines with hydrogen fluoride (equation 18)[86,88].

There is no evidence that the P—H bond of primary or secondary phosphines can form hydrogen bonds to any significant extent. The P—H bond is relatively non-polar as a result of the similar electronegativities of these two elements. Studies of the P—H infrared stretching vibration for diphenylphosphine have shown no significant solvent effects[95]. There is some evidence for hydrogen bonding between the P—H proton and halide ion in phosphonium halides[86,96] and, weakly, between the P—H proton of dialkyl phosphonates and donor solvents such as acetone or pyridine[95]. The P—H bond is more polarized in these examples by the presence of a positive or partial positive charge on phosphorus.

V. BASICITY TOWARDS LEWIS ACIDS

Phosphines form complexes with a wide range of Lewis acids. The basicity of simple trialkylphosphines is generally less than that of the corresponding nitrogen bases towards class (a) acceptors but greater towards class (b) acceptors[97]. A measure of the relative basicities of phosphines can be obtained from calorimetric data, displacement reactions and relative volatilities[98,99]. Coordination to trimethylboron generally indicates a similar order of phosphine basicities to that observed for proton acids, e.g. $Me_3P > Me_2PH > MePH_2 > PH_3$ (the latter not forming a complex even at $-78\,^{\circ}C$)[99], although additional steric factors may be involved. Triethylphosphine is thus a very much weaker base than trimethylphosphine towards trimethylboron, being completely dissociated in the gas phase[100]. The extremely low basicity of trivinylphosphine towards this Lewis acid [$EtMe_2P > Me_3P > (CH_2{=}CH)Me_2P \gg Et_3P > (CH_2{=}CH)_3P$], might also be associated with delocalization of the phosphorus lone pair or with the $-I$ effect of vinyl[6]. Infrared stretching vibrations for the P—B bond of BF_3, BH_3, BD_3 and BMe_3 complexes[101], and for the B—H bond of BH_3 complexes[102], have been used to investigate the relative donor abilities of cyclic and bicyclic phosphites, and were found to correlate reasonably well with basicity orders determined by other means[56]. Data on the NMR spectroscopy, dipole moments, infrared spectroscopy, enthalpy of formation and displacement reactions of phosphine complexes with boron Lewis acids and other metallic acceptors have been reviewed[71].

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The Chemistry of Organophosphorus Compounds
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CHAPTER 13

Photochemistry of organophosphorus(III) compounds

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I. INTRODUCTION

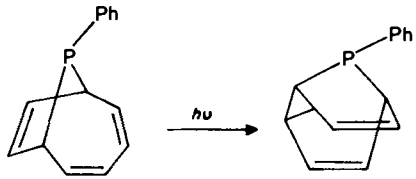
In recent years, the number of publications in the field of preparative photochemistry has increased considerably. Schönberg wrote one of the first systematic reviews on the topic in 1958, updated in 1968[1]. The most important publications are now regularly surveyed[2]. The photochemistry of organophosphorus(III) compounds[3] began with the investigations by Stiles et al.[4], who dealt with the photolysis of phosphine and its successively substituted compounds. Some selected results are now presented in an annual publication[5].

In this chapter, photochemical reactions of phosphorus(III) compounds are reviewed; the emphasis is on preparative aspects, reactions due to stabilizers, polymers or complexes are not included.

II. PHOSPHINES

A. Molecule Reactions

The photolytic decomposition of triarylphosphines has been described[6]. By photolysis of the bridged phosphine **1** in benzene through Pyrex glass, the tricyclic compound **2** is obtained (equation 1)[7]. The difference in the reaction mechanism compared with that for

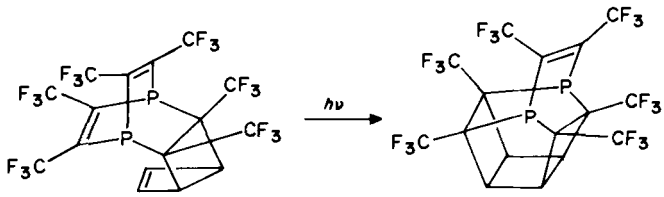


(1) (2) (1)

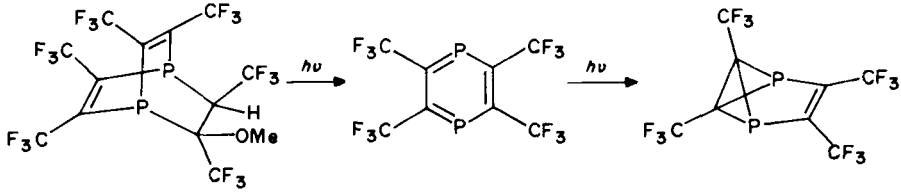
the corresponding oxides can be ascribed to different multiplicities (singlet and triplet, respectivly), leading to the formation of different products[7].

The cycloadduct of the diphospha analogue of barrelene and cyclobutadiene (**3**) reacts after photolysis in acetone exclusively in its *endo* configuration to give 2,5,7,10,11, 12-hexakis(trifluoromethyl)-1,6-diphosphahexacyclo[4.2.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$.$0^{7,10}$]dodec-11-ene (**4**) (equation 2)[8].

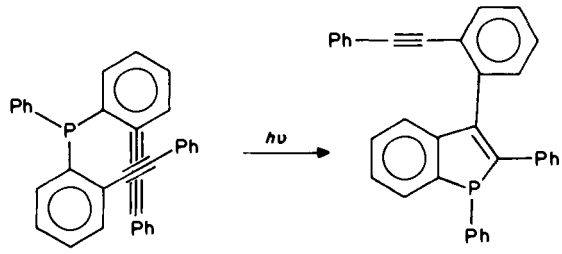
The methanol aduct (**5**) of diphosphabarrelene, however, gives 2,3,5,6-tetrakis-(trifluoromethyl)-1,4-diphosphabenzene (**6**) and on further irradiation a diphosphabenz-valene, 1,3,4,6-tetrakis(trifluoromethyl)-2,5-diphosphatricyclohex-4-ene (7) (equation 3)[9]. The first step can also be thermally induced. The product of the second step, an intramolecular [2 + 2]cycloaddition, was isolated as the first hetero analogue of tricyclo [2.2.2]octadiene. This confirms the stabilizing effect of the substituents and also the influence of the longer P—C bond[9].



(3) (4) (2)



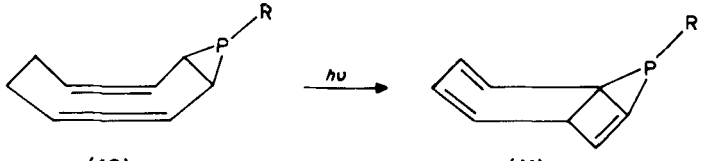
(5) (6) (7) (3)



(8) (9) (4)

By cyclization of *o,o*-bis(phenylethinyl)triphenylphosphine (8) in benzene under a nitrogen atmosphere a phosphaindole, 1,2-diphenyl-3-[(2-phenylethyinyl)-phenyl)]-λ^3-phosphindole (9) is obtained (equation 4)[10]. In contrast, the non-photocatalysed reaction leads via cyclization to the benzo-condensed phosphepin system. The UV-induced rearrangement of phosphanorbornadiene to phosphepine should be possible through the intermediate formation of quadricyclane from a [2 + 2]cycloaddition.

First experiments concering the disrotatory opening and other rearrangements in a stabilized quadricyclane system have been undertaken[11]. The phosphorbicyclus **10** on irradiation undergoes rearrangement to give the bridged *anti*-compound **11** in deutero-



(10) (11) (5)

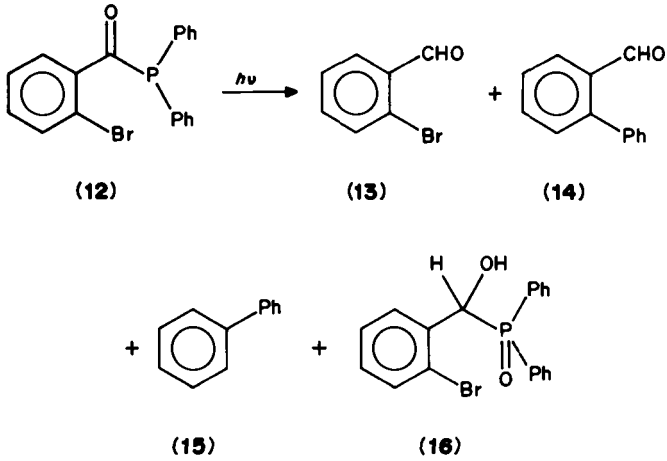
R = *t*-Bu, *c*-Hex, menthyl

benzene (equation 5)[12]. Similarly to the 1-substituted 2-vinylphosphiranes, 9-phosphabicyclo[6.1.0]nonatriene undergoes rearrangement after photolysis or catalysis by Ni^0. With the vinyl compounds all rearrangement products formed by differently initiated reactions are identical, whereas with the phosphirane **10** thermal and photochemical reactions yield *syn* and *anti* epimers, respectively. The epimers show a great difference in the chemical shifts of the corresponding ^{31}P NMR signals. The difference of $\Delta\delta P = 90$ ppm by far exceeds the value of 66.2 ppm found for the *syn* and *anti* substituted 7-phosphanorbornene[12].

Methylphosphine oxides are easily obtained by photochemical induced rearrangement of the hydroxymethylphosphines[13].

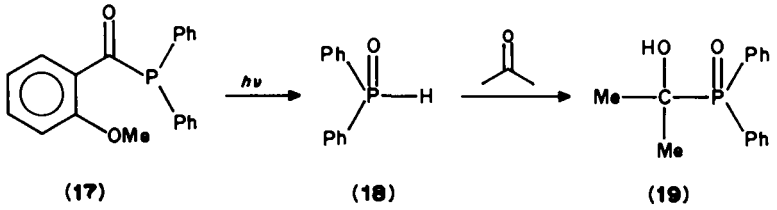
B. Photolysis of Acylphosphines

The photolysis of *o*-bromobenzoyldiphenylphosphine (**12**) yields 1-hydroxy-(*o*-bromobenzyl)diphenylphosphine oxide (**16**) by a rearrangement of a new kind[14]. Products due to both α-fission (**13**, **14**) and substitution (**14**, **15**) are formed (equation 6). The former reaction can be explained by a 1,2-transfer of the carbonyl oxygen to the phosphorus atom.



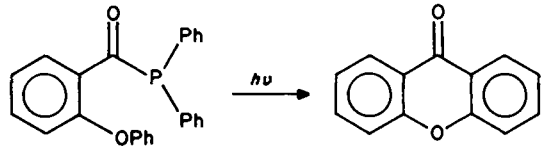
(6)

Aroyldiphenylphosphines bearing other *ortho*-substituents such as H, SMe and SO_2Me show similar reactions[15]. In addition to these reactions, the *o*-methoxy compound (**17**) undergoes a new kind of fission, forming diphenylphosphinic acid (**18**), which may be isolated by addition to carbonyl compounds (**19**) (equation 7)[16]. The structures of the α-hydroxyphosphane oxides **16** and **19** were confirmed by X-ray structure analysis.



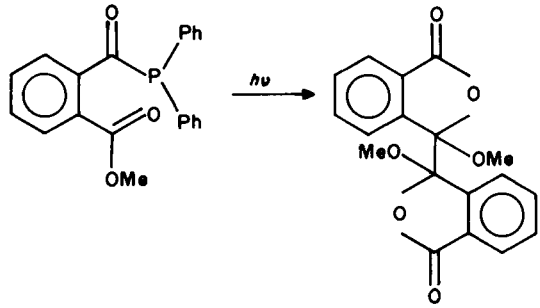
(7)

After irridation of aroyldiphenylphosphines with *ortho*-positioned π-functions, 1,2- and 1,4-addition products are obtained from the diphenylphosphinous acid formed by photochemical reaction with acetone or phenanthrenequinone. Aroyl radicals from the competing α-fission form five- and six-membered hetero- and carbo-cycles by neighbouring group interaction, e.g. xanthone (**20**), 3,3'-dimethoxy-3,3'-diphthalidyl (**21**) and the phenanthrene derivative **22** (equation 8–10)[17]. Experiments have been performed to



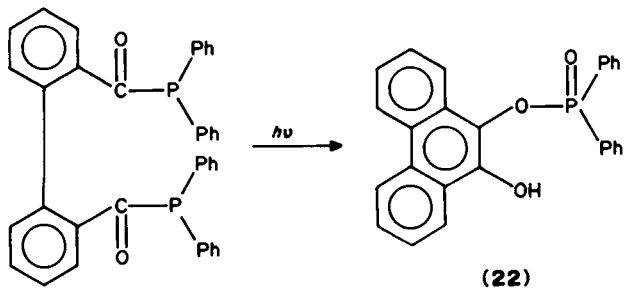
(8)

(20)



(9)

(21)



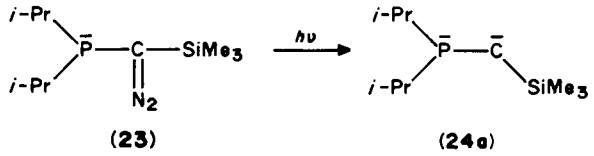
(10)

(22)

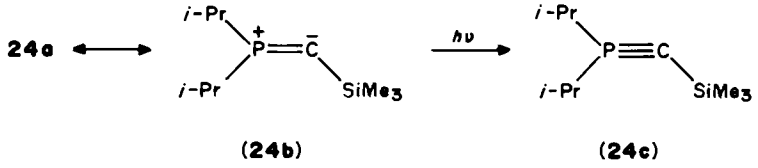
elucidate the reaction mechanism of the 1,2-oxygen transfer using ^{18}O-labelled compounds and an intermolecular six-ring mechanism was confirmed[18,19].

C. Photolysis of Diazophosphines

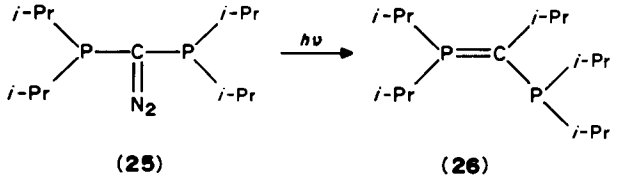
On irradiation of the α-diazophosphine **23**, a nitrogen molecule is abstracted and the corresponding α-phosphinocarbene **24a** is formed (equation 11). This is synthetically equivalent to the species **24b** and **24c** (equation 12)[20].



(11)

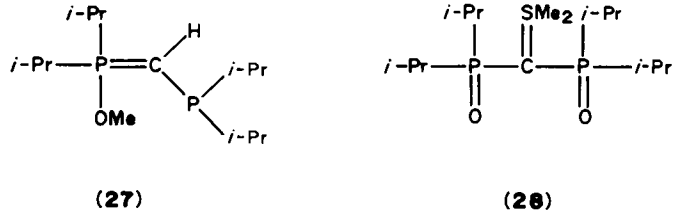


(12)

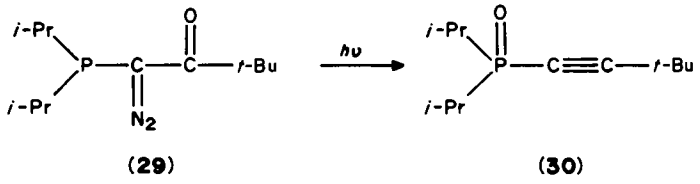


(13)

The bis(phosphino)diazomethane **25** reacts directly with loss of nitrogen via a carbene intermediate to give the phosphaalkene **26** (equation 13)[21]. However, in the presence of methanol or dmso compounds **27** and **28** are obtained. In contrast to the reaction of **25**, the



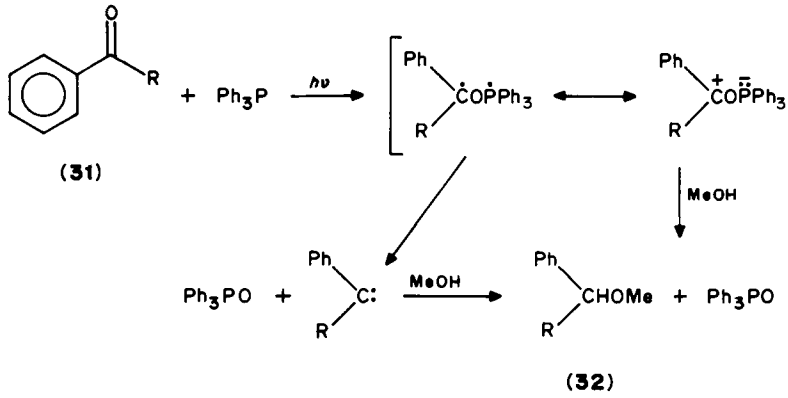
keto azo compound **29** does not undergo a 1,2-shift. However, (diisopropylphosphinyl)-*tert*-butylethyne (**30**) is formed via the carbene intermediate in a Wittig-like reaction (equation 14)[21]. These results compare very well with computations which predict only a small energy barrier for the rearrangement to the thermodynamically preferred phosphaalkene structure[22].



(14)

D. Reactions with Ketones

The UV irradiation of phenyl alkyl ketones (**31**), e.g. butyrophenone, valerophenone, γ-methylvalerophenone and acetophenone, in methanol and in the presence of triphenylphosphine yields a triphenylphosphine oxide together with the corresponding 1-phenyl-1-methoxyalkanes and Norrish II products. Kinetic investigations of these reactions confirmed that the ketone triplet state is quenched by the phosphine. Thereby the corresponding radical is obtained, which does not interact further with the triphenylphosphine[23]. With methanol, however, the corresponding products **32** can be prepared (equation 15).



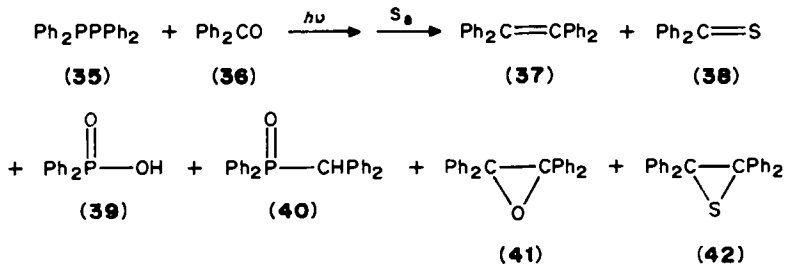
(15)

Benzophenone readily undergoes photolytic deoxygenation with triphenylphosphine. The phosphonium ylide (**33**) formed reacts in a Wittig reaction with acetaldehyde to give 1-methyl-2,2-diphenylethene (**34**) and triphenylphosphine oxide (equation 16)[24]. The formation of the ylide **33** was confirmed by IR spectroscopic investigations.

$$\underset{(33)}{Ph_3P{=}CPh_2} + MeCHO \longrightarrow \underset{(34)}{Ph_2C{=}CHMe} + Ph_3PO \qquad (16)$$

Generally, diaryl and aryl alkyl ketones with low π,π* triplet states react rapidly with triphenylphosphines to yield phosphonium ylides, whereas π,π* ketones, aldehydes and aliphatic ketones do not react at all[25].

The diphosphine **35**-like tetraphenyl- and tetraethyl-phosphines, react with benzophenone (**36**) under UV irradiation. Secondary products after further reaction with sulphur are tetraphenylethylene (**37**), thiobenzophenone (**38**), phosphinic acid (**39**), diphenylmethyldiphenylphosphine oxide (**40**), tetraphenyloxirane (**41**) and tetraphenyl-



(17)

thiirane (**42**) (equation 17). The reaction mechanism involves metathesis of the P—P bond with the π,π^* triplet of benzophenone[26].

E. Reactions with Unsaturated Compounds

The photochemical reaction of phosphine and its substituted analogues with unsaturated compounds leads to addition products[4,27]. In general, the reaction mechanism can be described by equations 18–20. The addition of the free phosphine radical to allene gives

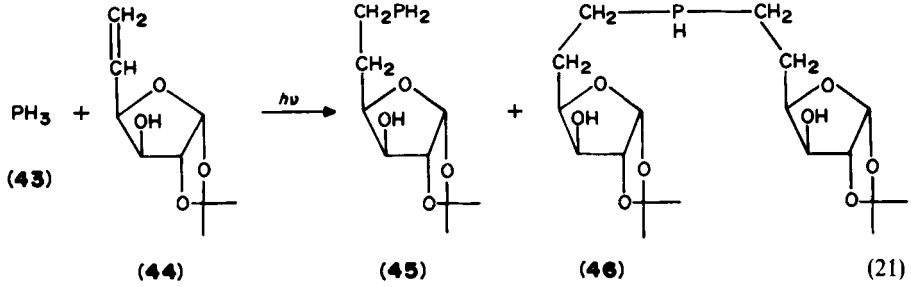
$$R_2PH \xrightarrow{h\nu} R_2P^{\cdot} + H^{\cdot} \tag{18}$$

$$R_2P^{\cdot} + CH_2{=}CH_2R \longrightarrow R_2PCH_2\dot{C}HR \tag{19}$$

$$R_2PCH_2\dot{C}HR + R_2PH \longrightarrow R_2PCH_2CH_2R + R_2P^{\cdot}, \text{ etc.} \tag{20}$$

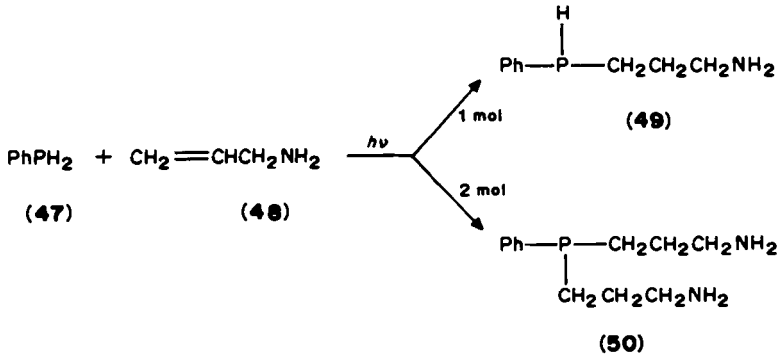
$R = H$, alkyl, substituted alkyl

the 1:1 product isopropenylphosphine in low yields[28]. Most of the product polymerizes. Secondary phosphines react with allyl alcohols after irradiation to form the corresponding 3-hydroxypropylphosphines[29]. The photocatalytic addition of phosphine (**43**) to 5,6-deoxy-1,2-*o*-isopropylidene-α-D-xylohex-5-enofuranose (**44**) leads to the corresponding primary (**45**) and secondary (**46**) phosphine (equation 21)[30]. This was shown by



(21)

transforming the oxidation products of a mixture of 5,6-dideoxy-1,2-*o*-isopropylidene-6-phosphine-α-D-xylohexafuranose (**45**) and bis-6-(5,6-dideoxy-1,2-*o*-isopropylidene-α-D-xylohexafuranose)phosphine (**46**) into the corresponding cyclohexylamine salts.

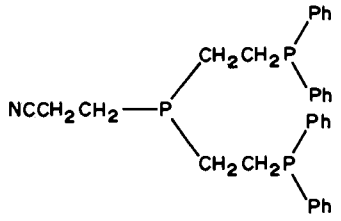


(22)

Phenylphosphine reacts analogously under the same conditions. The reaction of phenylphosphine (**47**) with 3-aminopropene (**48**) yields aminopropylphenylphosphine (**49**) and bis(aminopropyl)phenylphosphine (**50**), depending on the molar ratio (equation 22)[31]. The range of variability of the vinyl component is considerable, permitting the use of this group of compounds as polydentate phosphane ligands:

$$CH_2 = CHR$$
$$R = CH_2NH_2,\ CH_2N(CH_3)_2,\ OPh,\ Si(OEt)_3$$

It is also possible to work with the phospha components. For example, the reaction of propionitrilophosphine with diphenylvinylphosphine yields bis(diphenylphosphinoethyl) propionitrilophosphine (**51**)[31]. The reaction of diphenylphosphine (**52**) and triethoxy-



(**51**)

vinylsilane (**53**) gives triethoxysilylethyldiphenylphosphine (**54**) (equation 23)[31].

$$Ph_2PH + CH_2{=}CHSi(OCH_2Me)_3 \xrightarrow{h\nu} \begin{matrix} Ph \\ Ph \end{matrix}\!\!>\!PCH_2CH_2Si(OCH_2Me)_3 \qquad (23)$$

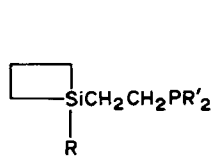
(**52**) (**53**) (**54**)

In general, the addition of secondary phosphines to alkenylsilanes, alkenylalkoxysilanes, alkenylchlorosilanes or polyalkenylpolysiloxanes under UV irradiation leads to organophosphorus-substituted silanes and polysiloxanes[32]. The reaction with diethylphosphine has been described for the following unsaturated silanes:

$Me_2Si(CH=CH_2)_2$ $(MeO)_2Si(CH_2CH=CH_2)_2$ $Cl_2(Ph)Si(CH=CH_2)$
$Me_2Si(CH_2CH=CH_2)_2$ $(EtO)Si(CH=CH_2)_3$ $Cl_2Si(CH=CH_2)_2$
$(CH_2{=}CH)_4Si$

Parallel to the addition to chlorovinylsilanes, a side reaction is observed in which the HCl formed under these conditions reacts with phosphine to give the corresponding phosphonium salt[32]. Diphenylphosphine yields the same products with chlorovinylsilane in benzene solution 32–34.

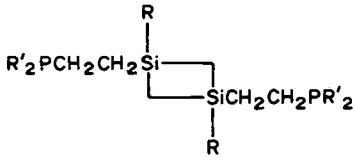
The synthesis of phosphinoethylenosila- (**55**) and -1,3-disila-cyclobutane (**56**) by



(**55**)

R′=Me,CF_3

R=Me,$CH_2{=}CH$,Ph,Cp,Et,PR'_2



(**56**)

photoaddition normally follows the anti-Markovnikov rule. If, however, trifluoromethyl is used instead of methyl as the phosphine substituent, the proportion of Markovnikov product is increased[35].

Primary polyfluoroalkyl-phosphines are formed in the reaction of phosphine with fluoroalkenes; for example, hexafluoropropylphosphine is obtained from phosphine and hexafluoropropene[36]. Dimethyl- and bis(trifluoromethyl)-phosphines correspondingly react with olefins following a free-radical mechanism. The phosphine radicals $R_2P^{\bullet}$ are considered to form stable intermediates by attack on the olefinic double bond[37]. Irradiation of but-2-ene (**57**) and bis(trifluoromethyl)phosphine (**58**) generate 1-methylpropylbis(trifluoromethyl)phosphine (**59**) (equation 24).

$$\underset{\textbf{(57)}}{\text{MeCH=CHMe}} + \underset{\textbf{(58)}}{(CF_3)_2PH} \xrightarrow{h\nu} \underset{\textbf{(59)}}{(CF_3)_2P\overset{\overset{\text{Me}}{|}}{\text{CHEt}}} \tag{24}$$

Trialkylphosphines add to olefins under photochemical conditions. After prolonged irradiation, ethylbis(trifluoromethyl)phosphine (**60**) and ethylene (**61**) yield ethyltrifluoromethyl-3,3,3-trifluoropropyl phosphine (**62**) (equation 25)[38].

$$\underset{\textbf{(60)}}{(CF_3)_2PEt} + \underset{\textbf{(61)}}{CH_2=CH_2} \xrightarrow{h\nu} \underset{\textbf{(62)}}{CF_3-\overset{\overset{\text{Et}}{|}}{\text{P}}-CH_2CH_2CF_3} \tag{25}$$

The formation of the radical is believed to be caused by abstraction of a trifluoromethyl group. Experiments have been performed to determine the mechanism of the addition reaction between olefins and phosphine. Either a radical or an ionic mechanism was considered[39]. Bis(trifluoromethyl)phosphine adds to trifluoroethylene to give 1,2,2-trifluoroethylbis(trifluoromethyl)phosphine (**63**)[40].

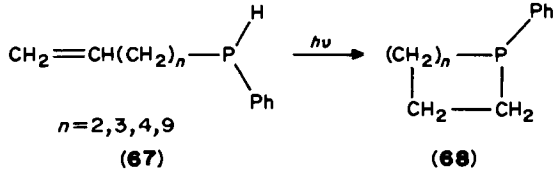
$$\underset{\textbf{(63)}}{(CF_3)_2PCF=CF_2}$$

Diphosphines, such as tetramethyldiphosphine and tetrakis(trifluoromethyl)-diphosphine, react with alkenes (C_2H_4, C_2F_4, CH_2=CHF, C_3H_6, *cis*- and *trans*-MeCH=CHMe, $CH_2=CF_2$) to give the corresponding diphosphanoethanes[41]. On irradiation, tris(trifluoromethyl)phosphine (**64**) reacts with ethylene (**65**) with insertion to give bis(trifluoromethyl)-3,3,3-trifluoropropylphosphine (**66**) (equation 26). With vinyl fluoride, vinyliden fluoride and propene the reaction proceeds with greater regioselectivity and the yield of 1:1 adduct is low.

$$\underset{\textbf{(64)}}{(CF_3)_3P} + \underset{\textbf{(65)}}{CH_2=CH_2} \xrightarrow{h\nu} \underset{\textbf{(66)}}{(F_3C)_2PCH_2CH_2CF_3} \tag{26}$$

In these reactions, and also with vinyl chloride, but-1-ene and hexafluoropropene, mostly the educts are recovered unchanged. But-2-yne and hexafluorobut-2-yne do not react, unlike propyne, which yields [1,1,1-trifluoro-3-bis(trifluoromethyl)phosphino] *cis*-but-2-yne[42].

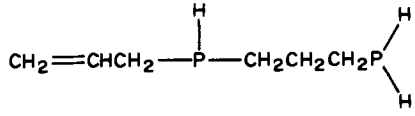
The cyclic phosphines **68** with five-, six-, or seven-membered rings are obtained by irradiation of secondary phosphines (**67**) with a terminal double bond in the alkenyl group by means of an intramolecular addition (equation 27)[43,44]. If, however, the phenyl group is



(27)

(67) (68)

replaced with a hydrogen atom, an intermolecular anti-Markovnikov addition takes place and the head–tail dimer **69** is obtained[45].

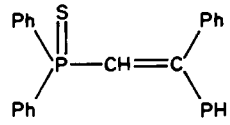


(69)

In contrast to UV irradiation, a new bicyclic diphosphine is formed on initiating the reaction with aibn[45]. 1,1,1,4,4,4-Hexafluorobutyne leads to the formation of 1:1 adducts using bis(trifluoromethyl)phosphine, tetraphenyldiphosphine or diethylphosphine; 2:1 adducts are obtained using bis(trifluoromethyl)phosphine. With dimethylchlorophosphine and tetramethyldiphosphine, however, no addition takes place. Triphenylphosphine enhances the polymerization of butyne even at 42.2 °C[46]. The synthesis of dialkenylbromophosphines is feasible by photoinitiated reaction of alkenyldibromophosphines and alkynes[47].

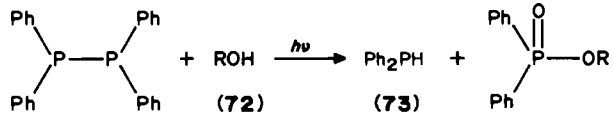
F. Reactions with Other Compounds

Tetraphenyldiphosphine reacts under UV irradiation with triplet carbon atoms from diphenylethylene. After sulphurization, 2,2-diphenylethenyl(diphenyl)phosphine sulphite (**70**) is obtained[48].



(70)

The photoinduced oxidation of trisubstituted phosphine leads to the corresponding oxides using oxygen at low temperatures[49]. After irradiation of tetraphenyldiphosphine (**71**) in an alcohol (**72**), diphenylphosphine (**73**) and the corresponding alkyldiphenylphosphinates (**74**)[50] are obtained (equation 28). Use of (−)-octan-2-ol

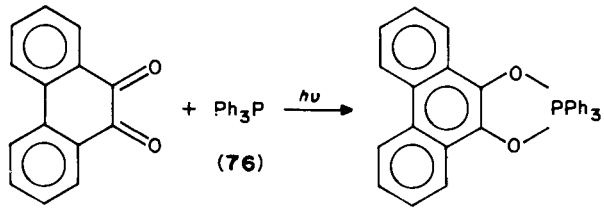


(28)

(71) (72) (73) (74)

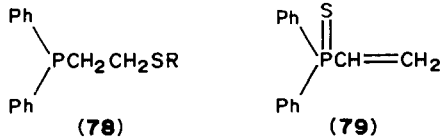
R=Me, Et, *i*-Pr, 2-C_8H_{17}, $PhCH_2$

results in a mixture of octane-2-yldiphenyl-phosphinite and -phosphinate[51]. 9,10-Phenanthroquinone (**75**) reacts with triphenylphosphine (**76**) under UV irradiation to give 2,2,2-triphenyl-1,3,2-dioxaphospholene (**77**) (equation 29). The latter is obtained in its

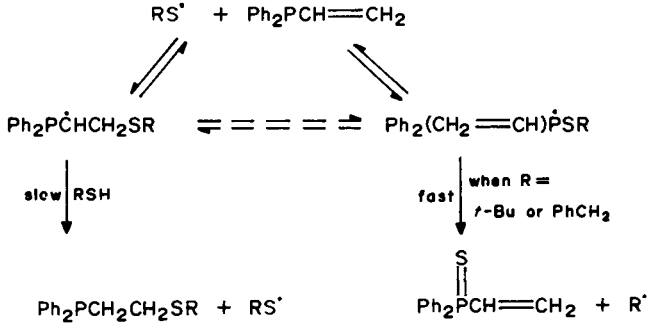


(29)

dipolar form by adding water. This reaction is not feasible using benzil, biacetyl or *dl*-camphor-quinone, but it is possible with acenaphthene- and 1,2-naphthene-quinone[52]. Phenyl- and diphenyl-phosphine is easily added to the olefinic double bond of 2-vinyl-1, 3-dioxa-6-aza-2-silacyclooctane[53]. Depending on the substituted group R, thiols react with diphenylvinylphosphine to yield either the Markovnikov product (**78**) or the



sulphide (**79**)[54]. An equilibrium can be described between the two radical intermediates (equation 30)[55].



(30)

The irradiation of benzyldiselenide (**80**) and triphenylphosphine (**81**) in acetonitrile yields dibenzylselenide (**82**), dibenzyl (**83**) and triphenylphosphine selenide (**84**) (equation 31). The main process is the fission of the Se—Se bond, leading to radicals which react in a chain mechanism to form the products[56,57]. If, in the diselenide, the phenyl group is substituted by 9-anthryl, two isomeric forms of phosphorus- and selenium-free polycycles are obtained in addition to the formation of triphenylphosphine selenide[58,59].

$$\underset{\textbf{(80)}}{PhCH_2SeSeCH_2Ph} + \underset{\textbf{(81)}}{Ph_3P} \longrightarrow \underset{\textbf{(82)}}{PhCH_2SCH_2Ph} + \underset{\textbf{(83)}}{PhCH_2CH_2Ph} + \underset{\textbf{(84)}}{Ph_3PSe} \qquad (31)$$

The reaction between organoditellurides and tertiary phosphines leads to an intermediate triorganyl phosphinetelluride. The latter splits off Te yielding the original phosphine[60]. The tendency for photofission of the Me—C bond increases in the sequence $R_2S_2 < R_2Se_2 < R_2Te_2$, where the occurrence of Me—Me bond fission decreases.

G. Formation of Phosphonium Compounds

At room temperature triphenylphosphine does not react with tribromomethane. After irradiation with UV light, however, triphenyldibromomethylphosphonium bromide is obtained[61]. Aryl iodides (**85**) form triphenylarylphosphonium iodide (**87**) in the presence of triphenylphosphine (**86**) (equation 32)[62]. Using tributylphosphine gives tributylphenylphosphonium iodide. In both cases the product yield is not changed on addition of aibn[62]. If the phosphonium salt is formed by photolysis of the aryl iodide followed by reaction of the aryl radical with the phosphine, the competing reaction should be the addition of iodine to the phosphine. Thus, for example, after hydrolysis formation of the corresponding phosphine oxide is also expected to occur[63,64]. The irradiation of a triarylphosphine in the presence of an alcohol such as methanol, iso-propanol or dioxane yields the tetraarylphosphonium salt in addition to diaryphosphine and arylphosphine[65,66].

$$\underset{\textbf{(85)}}{ArI} + \underset{\textbf{(86)}}{Ph_3P} \xrightarrow{h\nu} \underset{\textbf{(87)}}{Ph_3(Ar)P^+\ I^-} \tag{32}$$

Ar = *p*-tolyl, *p*-anisyl, *p*-diphenylyl, *p*-hydroxyphenyl

Irradiation of an equimolar mixture of the triphenylphosphine (**88**) and different diaryliodonium fluoroborates (**89**) leads to the corresponding tetraarylphosphonium tetrafluoroborates (**90**) (equation 33)[67,68]. The reaction also takes place in the presence of visible light[69].

$$\underset{\textbf{(88)}}{Ph_3P} + \underset{\textbf{(89)}}{Ar_2IBF_4} \xrightarrow{h\nu} \underset{\textbf{(90)}}{Ar\overset{+}{P}Ph_3\overset{-}{B}F_4} \tag{33}$$

Ar = Ph, *p*-MeOPh, *p*-ClPh, *m*-NO_2Ph, *o*-NO_2Ph, *m*-EtO_2CPh

H. Radiolyses

After radiolysis in a 2-kCi gama cell 200 (Co^{60}) a solution of triphenylphosphine in benzene yields pentane, cyclohexane, hexane (four isomers), hexene and *n*-heptane[70]. On raising the phosphine concentration the hexane yield increases at the expense of cyclohexane and *n*-heptane. An increase in benzene concentration after irradiation results from the mechanism in equation 34–36.

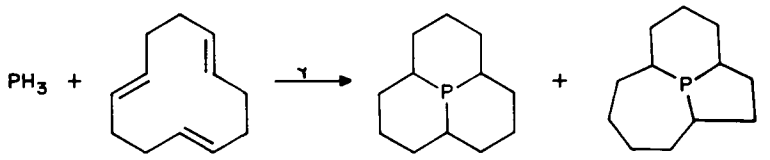
$$2Ph_3P \xrightarrow{\gamma} 2Ph^{\cdot} + 2Ph_2P^{\cdot} \tag{34}$$

$$2Ph_2P^{\cdot} \longrightarrow Ph_2P{=}PPh_2 \tag{35}$$

$$2Ph^{\cdot} + 2H^{\cdot} \longrightarrow 2PhH \tag{36}$$

Experiments using pulse radiolysis in cyclohexane have been undertaken with diphenylchlorophosphine, diphenylmethylphosphine and triphenylphosphine. For example, dppm–cyclohexane mixtures generate diphenylphosphine, diphenylcyclohexylphosphine, tetraphenyldiphosphine, hydrogen, methane, ethane, ethylene, phosphorus oligomers and solid phosphorus compounds, but dicyclohexyl is not formed[71,72]. Irradiation of phosphine (**91**) and 1,5,9-cyclododecatriene (90% all-*trans*) (**92**) with an 8000

Ci ^{60}Co source leads to 13-phosphatricyclo[7.3.1.0^{5,13}]tridecane (**93**) and 13-phosphatricyclo[6.4.1.0^{4,13}]tridecane (**94**) (equation 37)[73].



(91) (92) (93) (94) (37)

From triphenylphosphine and methanol in an oxygen-free solution, Ph_3PCH_2OH is obtained, which decays to give phosphine, ethylene glycol and formaldehyde as successive products. In oxygen-containing solutions phosphine oxide is formed[74]. γ-Irradiation of triphenyl phosphine and aryl halides such as chlorobenzene or 1,4-dibromobenzene yields tetraarylphosphonium salts[75]. Tributylphosphines reacts in a similar way and the following compounds could be isolated by radiolysis[76,77]:

$[PPh_4]F$	$[Ph_3P(p\text{-Tol})]Br$
$[PPh_4]Cl$	$[Ph_3P(p\text{-Tol})]Cl$
$[PPh_4]Br$	$[Ph_3P(Naph)]Cl$
$[PPh_4]I$	$[Ph_3P(Naph)]Br$
$[Ph_3P(p\text{-ClPh})]Cl$	$[Ph_3P(Thioph)]Br$
$[Ph_3P(p\text{-BrPh})]Br$	$[Bu_3PPh]Br$
$[Ph_3P(p\text{-IPh})]I$	$[Bu_3PPh]I$
$[Ph_3P(p\text{-Tol})]Cl$	$[Ph_3P(o\text{-ClPh})]I$

The experiments show that addition of benzene, cyclohexane and cyclohexene increase the yields by energy transfer from the solvent to the reactant. Because all three solvents exhibit similar effects, very specific processes have to be considered. A transfer of activation energy can be excluded since the three molecules show completely different excited states. The ionization potential of triphenylphosphine lies below that of the solvent molecules, So a charge-transfer process is the probable explanation. The free electron should be captured by the aryl halide[77].

I. Reactions of H-phosphines

Experiments on the SiF_4-sensitized decomposition of phosphine after photolysis have been undertaken[78]. A CO_2 TEA (transverse excited atmospheric pressure) laser served as the source of IR radiation. PH_3–SiH_4 mixtures were also analyzed[79]. After photolysis at 265 nm, phosphine reacts to give hydrogen molecules and diphosphine, which decomposes in turn to red phosphorus[80]. Similar results have been found using a UV wavelength of 147 nm[81]. In the presence of NH_3, the reaction leads to aminophosphines[82]. Flash photolysis of phosphine yields directly red phosphorus and molecular hydrogen[83]. A mixture with oxygen reacts to give several oxidation products[84,85]. After photosensitization, phosphine readily undergoes H–D exchange (equation 38)[86]. The equilibrium

$$PH_3 + HD \rightleftharpoons PH_2D + H_2 \tag{38}$$

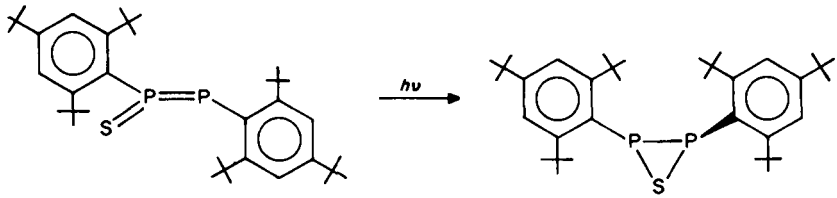
constant varies from 1.37 to 1.05 at 0 °C and 700 °C, respectively. Photo-oxidation of phosphine with phosphine-d_3 proceeds on a comparable time scale regarding the individual steps[87].

J. Miscellaneous

^{31}P CIDNP experiments showed that photochemical homolysis of triphenyl phosphine starts from a triplet state to yield dehydrobenzene after fission of an *ortho*-hydrogen atom from a phenyl radical[88]. The 254-nm photo-oxidation of triphenylphosphine, diphenylmethylphosphine and phenyldimethylphosphine proceeds by a free-radical chain mechanism, $n \rightarrow \pi^*$ excitation taking place at about 260 nm[89]. In the presence of tertiary phosphines, photochemical deoxygenation of aminoxides[90] is possible in addition to the synthesis of thiols[91]. Concerning the formation of phosphine radicals, various workers have reported two-step photo-oxidation of triphenylphosphine[92,93], quenching of excited states[94–99] and ESR studies[100–121].

III. PHOSPHENES

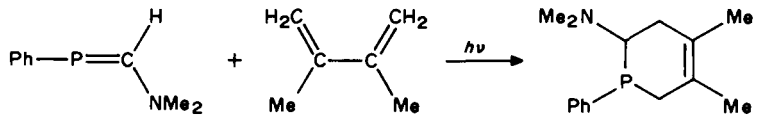
The stable *trans*-1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene 1-sulphide (**95**) obtained by sulphuration of diphosphene rearranges after photolysis to give the stable product (*E*)-2,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (**96**) (equation 39)[122]. This iso-



(**95**) (**96**) (39)

merization also takes place in the solid state. The 514.5-nm photolysis of a toluene solution of *trans*-1,2-bis(2,4,6-tri-*tert*-butyl)diphosphene with an Ar laser leads to the unstable *cis*-isomer which was identified spectroscopically[123]. An X-ray structure analysis of the metal complex stabilized product proved the $E \rightarrow Z$ photoisomerization. *Ab initio* calculations pointed to a relatively high energy barrier for the isomerization of diphosphenes. Rotational states are preferred to inversional states. The rotational barrier is possibly lowered by either steric or electronic effects[124].

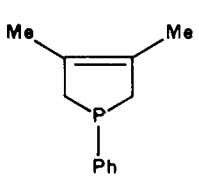
The phosphaalkene **97** reacts with 2,3-dimethylbutadiene (**98**) by [2 + 4]cycloaddition to give the phosphorine **99** (equation 40). On the other hand, UV irradiation of



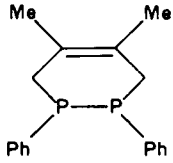
(**97**) (**98**) (**99**) (40)

the phosphaalkene **97** in acetonitrile in the absence of any trapping agent leads to a mixture of pentaphenylcyclopentaphosphine, tetraphenylcyclotetraphosphine and 1,2-bis(dimethylamino)ethylene. Phenylphosphinides and dimethylamino carbenes are presumed to be intermediates. The phosphaalkene which contain a methyl group instead

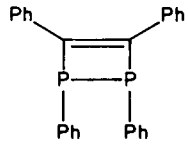
of hydrogen does not react by [2 + 4] cycloaddition, but rather the phospholene **100** and the diphosphorine **101** are obtained. In the presence of tolane the diphosphetane **102** is found[125].



(100)

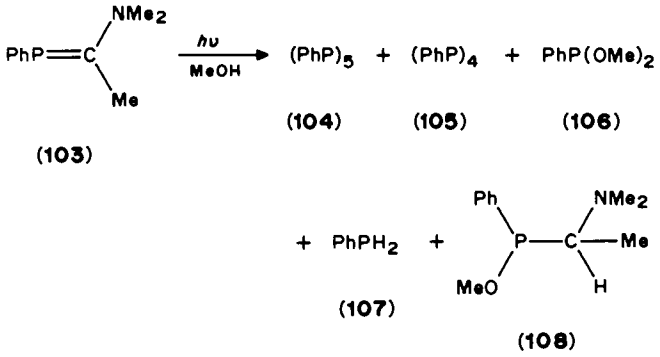


(101)



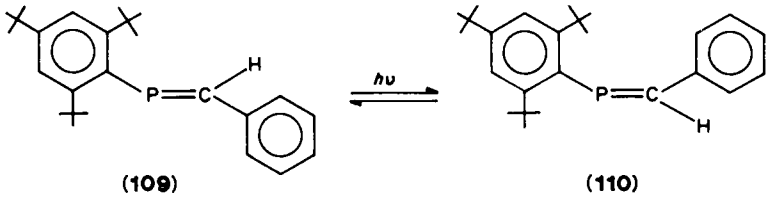
(102)

If the photolysis of (*N*,*N*-dimethylaminomethyl)methylenephosphine (**103**) is undertaken in methanolic solution, pentaphenylcyclopentaphosphine (**104**) and tetraphenylcyclotetraphosphine (**105**) are obtained, in addition to phenyldimethoxyphosphine (**106**), phenylphosphine (**107**) and the two diastereomers of the methanol adduct (**108**) (equation 41)[126].



(103) (104) (105) (106) (107) (108) (41)

(*E*)-*P*-α-(*tert*-butyldimethylsilyloxy) benzylidene-(2,4,6-tri-*tert*-butylphenyl) phosphine rearranges after irradiation with a medium-pressure Hg lamp at 0 °C and under an Ar atmosphere to the corresponding *Z*-isomer; both forms are reasonably stable[127]. (*E*)-benzilidene-*P*-2,4,6-tri-*tert*-butylphenylphosphine (**109**) exists in equilibrium with its *Z*-isomer (**110**) when irradiated with UV light (equation 42)[128].

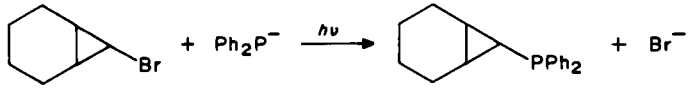


(109) (110) (42)

IV. PHOSPHIDES

The reaction of *m*- and *p*-iodo- and -bromo-toluenes with potassium diphenylphosphide leads to the corresponding diphenyltolylphosphines with either thermal or photochemical

initiation. The experimental findings agree with the assumption of a nucleophilic substitution following an $S_{RN}1$ mechanism[129]. 7-Bromonorcarane (**111**) reacts by the same mechanism with the phosphide **112** in liquid ammonia to give (7-norcaranyl)diphenylphosphine (**113**) (equation 43). The latter can be readily isolated as

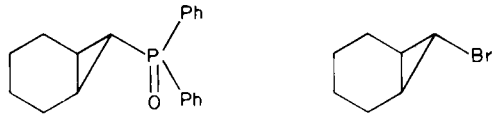


(43)

(111) (112) (113)

the phosphine oxide. The photoreaction is inhibited by di-*tert*-butyl nitroxide and 1,4-dinitrobenzene[130].

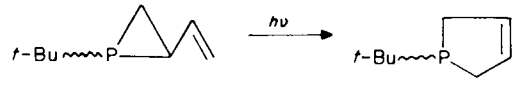
The same reaction sequence is exhibited by geminal dibromocyclo propanes, e.g. dibromonorcarane. In this case, after irradiation and reaction with hydrogen peroxide, the phosphine oxide **114** and the monobromide **115** are obtained; the isomeric form of **115** is not found[131].



(114) (115)

V. PHOSPHIRANES

Pure, non-oligomerized phosphorus tricycles are rare. The 2-vinylphosphirane **116**, synthesized from an organo-dichlorophosphine and Mg–butadiene, gives 1-*tert*-butyl-3-phospholene (**117**) on irradiation with an HPK-burner (Philips) in pentane solution (equation 44). In this case there is only one reaction path, whereas side-products are



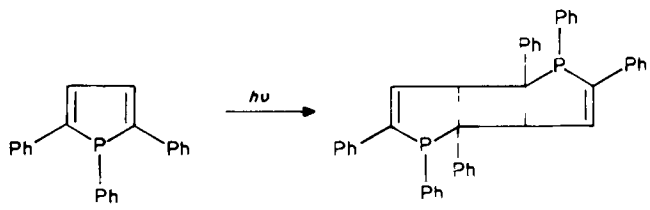
(44)

(116) (117)

obtained in the reaction of the cyclohexyl and the methyl compounds, which also lead to 3-phospholenes[132]. 9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene reacts by 1,5-sigmatropic rearrangement after thermal and photochemical initiation to give the *syn* and *anti* isomers of 9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene, respectively[12].

VI. PHOSPHOLES

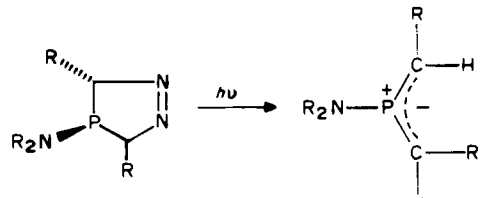
The UV irradiation of 1,2,5-triphenylphosphole (**118**) through Pyrex in a solution of tetrahydrofuran–diethyl ether yields the dimer (**119**) (equation 45). Exclusively the 'head-to-tail' adduct is found[133]. There has been one report concerning the mechanism of the photoinduced rearrangement of 1-phenyl-*cis*-3a,7a-dehydrophosphindole to 1-phenylphospha-2,4,6,8-*cis*,*cis*,*cis*,*trans*-cyclononatetraene[134]. The dihydrodiaza-



(45)

(118) (119)

phosphole **120** decays under irradiation to give molecular nitrogen and bismethylene-phosphorane (**121**). On heating, the corresponding phosphirane is obtained in a con-rotatorical cyclization. Formation of λ^3-azaphosphiridine, however, is not found[135].

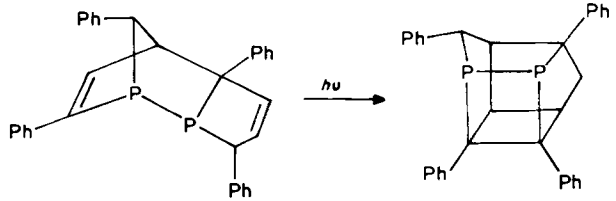


(46)

(120) (121)

R=SiMe$_3$

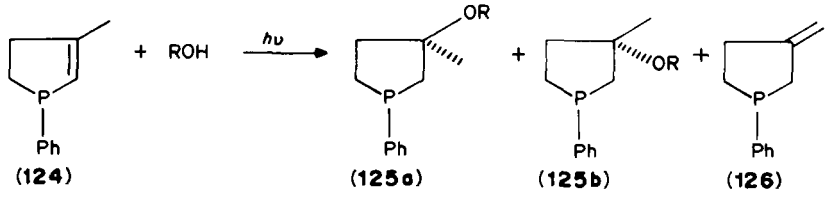
Photolysis of the [4 + 2] *endo*-dimer 3,6,9,10-tetraphenyl-1,2-diphosphatricyclo-[5.2.1.0^{2,6}]deca-3,8-diene (**122**) yields the cage compound 3,6,9,10-tetraphenyl-1,2-diphosphapentacyclo[5.2.1.0^{2,6}.0^{3,9}.0^{4,8}]decane (**123**) (equation 47)[136]. The mechanism



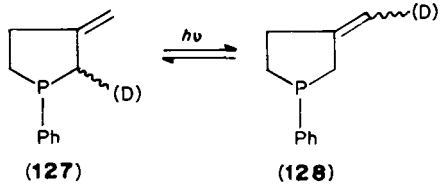
(47)

(122) (123)

can be rationalized in terms of a [2 + 2] intramolecular cycloaddition of the two double bonds[137]. UV irradiation of 3-methyl-2-phospholene (**124**) and methanol in xylene solution causes migration of the double bond to yield the *exo*-methylene derivative **126** in addition to the two isomeric 3-methoxy compounds (**125**) (equation 48). 3-Methyl-3-phospholene does not show this reaction under the same conditions[138]. The regioselectivity of the methoxy group attacking only the $C_{(3)}$ position is also proved by the photolysis of unsubstituted 2-phospholene. Here only the two isomeric 3-methoxy compounds are obtained, irrespective of the nature of the alcohol[139]. The existence of a photochemical equilibrium between the two *exo*-methylene compounds **127** and **128** after irradiation in methanol-*d* (equation 49) confirms the mechanism described above. If 1-phenyl-2-phospholene is methyl-substituted in the 2- or 2,3-positions no reactions occurs[139].



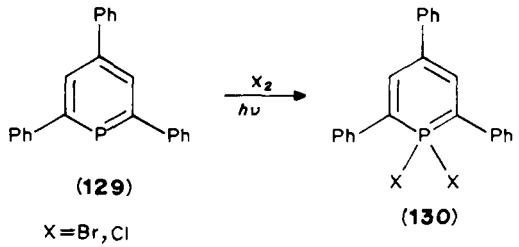
(48)



(49)

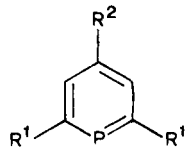
VII. PHOSPHORINS

1,1-Dihalo-λ^5-phosphorins are easily obtained by irradiation from λ^3-phosphorins and molecular halogens. For example, 2,4,6-triphenyl-λ^3-phosphorin (**129**) reacts with equimolar amounts of bromine or chlorine to give the dibromide and dichloride, respectively (**130**) (equation 50)[140].



(50)

2,4,6-Triphenylphosphorin does not react with bromine or chlorine at room temperature. After irradiation, however, the halogens readily add to the phosphorus atom. The reaction can be followed by taking samples after finite time intervals and adding an excess of methanol. By this means from the 1,1-dihalides the strongly fluorescent 1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorin is formed quantitatively. It can be detected by thin-layer chromatography and thus distinguished from the starting compound. With this method a whole series of dihalogen phosphorins (**131**) could be prepared. The more electrons the λ^3-

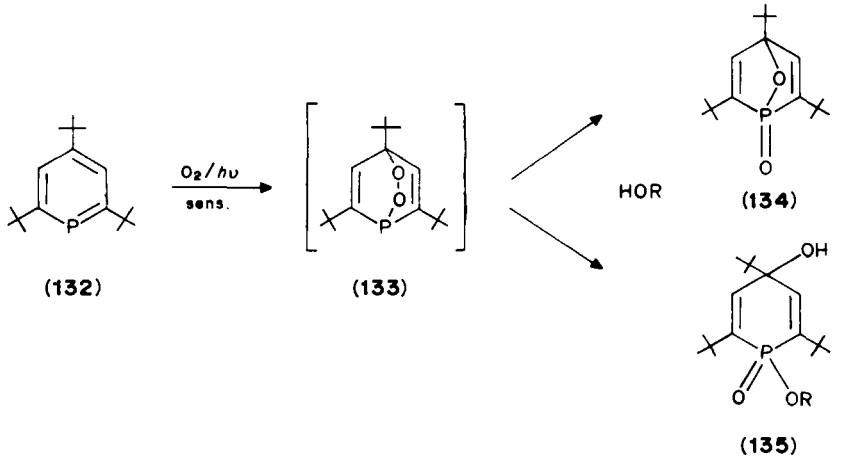


R^1, R^2=Ph, *p*-MeOPh, *p*-FPh, *p*-ClPh, Me, *t*-Bu, CH_2Ph

(131)

phosphorin carries, the faster is the rate of the halogenation reaction. In this reaction and also in the thermally induced variation, a 1-halo-λ^4-phosphorin radical is considered to be the intermediate. The first step could be the formation of a donor–acceptor addition product, which rearranges slowly to yield the dihalogenated form[141].

After irradiation of 2,4,6-tri-*tert*-butylphosphorin (**132**) in anhydrous cyclohexane, the endoperoxide **133** is obtained by eosin-sensitized oxidation with molecular oxygen via a 1,4-addition mechanism (equation 51). The primary product was not isolated but detected

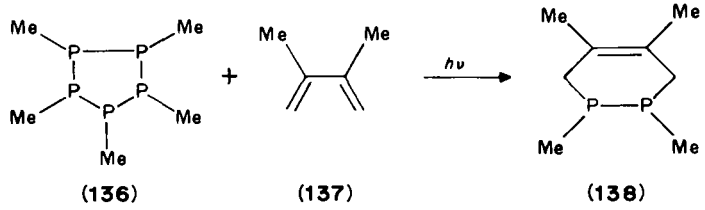


(51)

by identification of the subsequent products **134** and **135**[142]. 2,4,6-Triphenylphosphorin reacts after photo-oxygenation to give a number of hardly separable products[143].

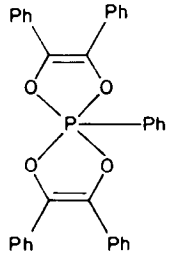
VIII. CYCLOPOLYPHOSPHINES

On irradiation or heating of cyclopolyphosphines, insertion into disulphide bonds takes place[144] in addition to the formation of 1,1′-spirobis(phosphadioxole)[144] and exchange of chain members in cyclopolyphosphines[145]. Phosphinidene is assumed to be an intermediate. The photoreaction between pentamethylpentaphosphine (**136**) and 2,3-dimethylbutadiene (**137**) yields 1,2,4,5-tetramethyltetrahydro-1,2-diphosphorin (**138**) (equation 52)[146].



(52)

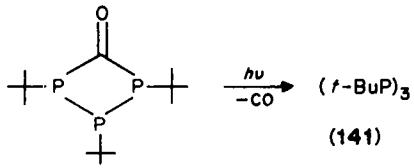
Pentaphenylpentaphosphine generates phenylphosphinidene on photoirradiation, which forms 2,3,5,7,8-pentaphenyl-1,3,6,9-tetraoxa-5-phosphaspiro[4.4]nonadiene (**139**) with benzil[147].



(139)

The following reaction paths have been discussed for the reaction of cyclopolyphosphines with dienes[147]: synchronous or two-step addition of fragments RP and R_2P_2 to the diene; addition of a chain-like diradical to the diene and cyclization after homolysis of a P—P bond; and addition of the trimeric R_3P_3 molecule to the diene yielding a carbon–phosphorus diradical, followed by cyclization to a five- or six-membered ring to liberate R_2P_2 or RP, which may react further.

On irradiation with sunlight, 1,2,3-tri-*tert*-butyl-1,2,3-triphosphetan-4-one eliminates carbon monoxide and forms 1,2,3-tri-*tert*-butylcyclotriphosphine (**141**) (equation 53)[148].



(140) (141) (53)

A similar light-induced co-extrusion is shown by the corresponding five-membered ring molecules[149].

IX. HALOPHOSPHINES

A. Reactions with Unsaturated Compounds

The UV irradiation of a mixture of propene and phosphorus tribromide yields 2-bromo-1-methylethylphosphorus dibromide with traces of the isomeric 2-bromopropylphosphorus dibromide. After thermal initiation, the yield of the latter grows considerably. The main reaction path is shown in equation 54–57.

$$PBr_3 \xrightarrow{h\nu} Br^{\bullet} + {}^{\bullet}PBr_2 \tag{54}$$

$$Br^{\bullet} + MeCH{=}CH_2 \longrightarrow MeC^{\bullet}HCH_2Br \tag{55}$$

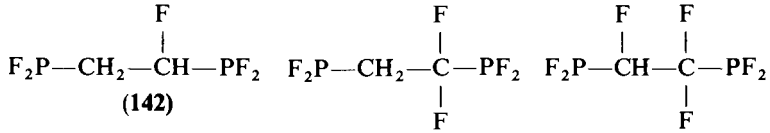
$$MeC^{\bullet}HCH_2Br + PBr_3 \rightleftharpoons MeCH(P^{\bullet}Br_3)CH_2Br \tag{56}$$

$$MeCH(P^{\bullet}Br_3)CH_2Br + MeCH{=}CH_2 \longrightarrow MeCH(PBr_2)CH_2Br + MeC^{\bullet}HCH_2Br \tag{57}$$

In the same way 1:1 adducts are obtained by reaction of phosphorus tribromide with ethylene, hept-2-ene, oct-1-ene and cyclohexene[150]. The photochemical initiation of the

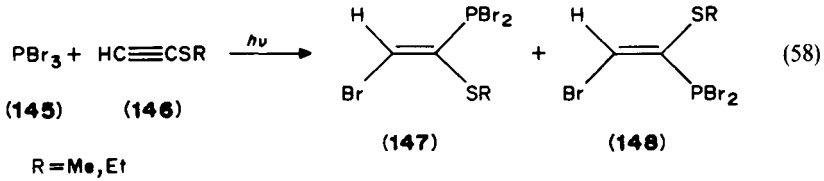
radical chain addition of phosphorus trichloride to olefinic double bonds is more effective than the peroxide-induced reaction. Both isobutene and vinylcyclohexene react easily[151]. In a similar way, phosphorus halides add to allyl halides[152], acetylenic hydrocarbons[153], styrene and phenylacetylene[154]. Whereas reaction of phosphorus tribromide with iodobenzene readily forms dibromophenylphosphine,[155] with benzene only minor amounts of this product are obtained[156].

The photoreaction of tetrafluorodiphosphine with ethylene leads to the bidentate ligand 1,2-bis(difluorophosphino)ethane,[157] via the equilibrium of the diphosphine and the difluorophosphine radical[158,159]. Similarly, the reaction proceeds with some unsubstituted olefins such as propene, but-2-ene and cyclohexene and with some perfluoroalkenes such as tetrafluoroethylene and hexafluoropropene[160]. Partially fluorinated alkenes permit the synthesis of 1,2-bis(difluorophosphino)-1-fluoroethane (**142**), 1,2-bis(difluorophosphino)1,1-difluoroethane (**143**) and 1,2-bis(difluorophosphino)-1,1,2-trifluoroethane (**144**)[161].



(142) (143) (144)

By photochemical reaction of phosphorus tribromide (**145**) with alkyl ethinyl sulphides (**146**), the *E*- and *Z*-isomers **147** and **148** are obtained (equation 58)[162]. Alkoxyethynes

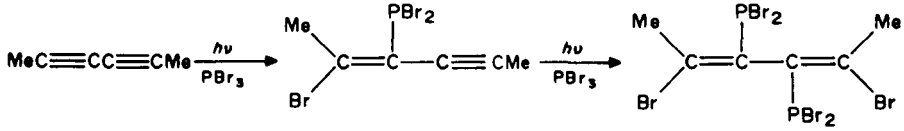


(145) (146) (147) (148)

R = Me, Et

(58)

preferentially generate the *E*-isomers[163]. In the presence of phosphorus tribromide the trichlorides react with alkynes to form mainly the pure trichloro compound, a mixed halide being produced in only minor amounts[164]. Hexa-2,4-diyne (**149**) adds phosphorus tribromide in a two-step photolysis reaction, primarily to give the enyne compound (**150**) then the hexadiene (**151**) (equation 59)[165].



(149) (150) (151)

(59)

B. Radiolyses

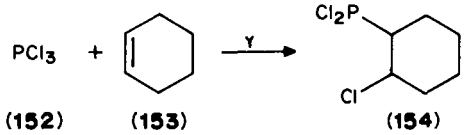
γ-Irradiation of phosphorus trichloride and hydrocarbons leads to successive substitution of the halide groups by organic groups[166]. Depending on the intensity of the ^{60}Co

source, different product compositions can be obtained. With cyclohexane the following products were formed[167]:

$C_6H_{11}PCl$	$ClC_6H_{10}PCl_2$
$(C_6H_{11})_2$	$(C_6H_{11}PCl)_2$
$C_6H_{11}Cl$	$C_6H_{10}(PCl_2)_2$
P_2Cl_4	$(C_6H_{11})_2PCl$

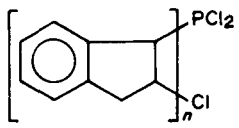
Experiments have been published showing the dependence of this type of reaction on the absorbed radiation dose[168]. In addition to other organophosphorus compounds, chlorodiphenylphosphine in hexane has been investigated by pulse radiolysis technique[169]. Using lower temperatures, phosphorus trichloride reacts with cyclohexane to yield 1-chlorocyclohexylphosphorus dichloride. At higher temperatures cyclohexylphosphorus dichloride and cyclohexenyl chloride are formed in equal amounts. Both reaction paths follow a radical chain mechanism. The quantum yield lies in the range 10^2–10^3 depending on the temperature applied. Using different terminal olefins normally only one isomer is obtained, which carries the PCl_2 group in the terminal position; only with isobutene both isomers are formed. Under these conditions only low yields of PCl_2–Cl addition products are found using chlorinated olefins; styrene, however, polymerizes readily[170,171]. Polymerization of isobutene is feasible at lower temperatures in the liquid state[172]. In an autoclave (chloroisobutyl)dichlorophosphine is obtained in addition to some isobutenyldichlorophosphine and alkyl chlorides[173].

γ-Irradiation of phosphorus trichloride (**152**) and cyclohexene (**153**) at 100 °C and 3–4 rad s^{-1} leads to high yields of (2-chlorocyclohexyl)dichlorophosphine (**154**) (equation 60). Identical behaviour is shown by cyclopentene, hex-1-ene, hept-1-ene and



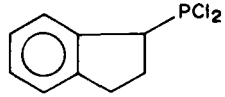
(**152**) (**153**) (**154**) (60)

hept-3-ene, whereas with alkylphosphorus dichlorides only products of radical recombination reactions are obtained[174]. Addition of tetrachloromethane, benzene or water has a positive influence on this reaction, iron(III) salts partially and copper(I) and copper(II) ions fully inhibit the reaction[175]. The addition of phosphorus trichlorides to ethylene at 20–100 °C and 10–50 atm yields a mixture of telomeric compounds (**155**), at 100–200 °C and 10–100 atm, however, the Kharasch product (**156**) is obtained[176]. The activation energy of the radical-induced addition of PCl_3 to hept-1-ene has been determined to be 6 $\pm$ 0.6 kcal mol^{-1}[177]. α-Methyl styrene forms a polymer of relatively low molecular weight after irradiation at 20 °C, the rate of polymerization being extremely slow. In the presence of PCl_3 the rate is markedly enhanced and addition products are not found[178]. Phosphorus trichloride and propene or 2-methylbutene form mixtures of isomers in the gas phase[179]. Irradiation of PCl_3 and indene leads to the telomer **155**. Using the phosphine in high excess, other telomers and small amounts of the monomers **156** and **157** are obtained[180].

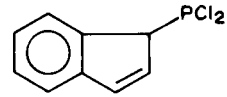


$n = 5, 3, 2$

(**155**)



(**156**)



(**157**)

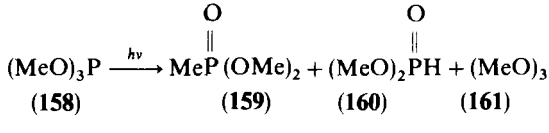
C. Miscellaneous

EPR studies have been published dealing with the intermediates from reactions of phosphorus halides[181–184].

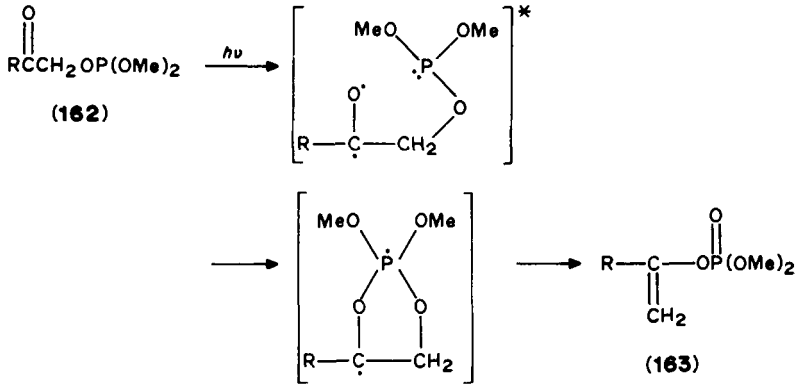
X. PHOSPHITES

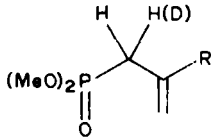
A. Molecule Reactions

Photolysis of trimethyl phosphite (**158**) at 20 °C in the absence of solvents yields dimethyl methylphosphonate (**159**), dimethyl phosphite (**160**) and trimethyl phosphate (**161**) in addition to some unreacted starting material (equation 61). The reactions of triethyl, triisopropyl and tri-*n*-butyl phosphite follow the same scheme[185]. The dialkyl alkylphosphonate is the main product in all cases, proving that a photochemical Arbusov rearrangement takes place. Irradiation of α-ketophosphites (**162**) leads via an intramolecular photoreaction to vinylphosphates (**163**) (equation 62): again dimethyl phosphite is another main product[186]. Experiments were carried out to elucidate the reaction mechanism with deuterated dimethyl allylphosphites. Again an intramolecular reaction leads to the rearrangement product allylphosphate (**164**)[187]. Rearrangement of the unsubstituted allyl product in benzene takes place regiospecifically. After gas-phase irradiation of trimethyl phosphite with a CO_2 laser in the presence or absence of air, phosphate, methane, ethane, methanol, ethanol and P-polymers are formed[188].



(61)

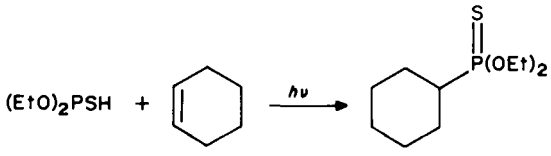




(62)

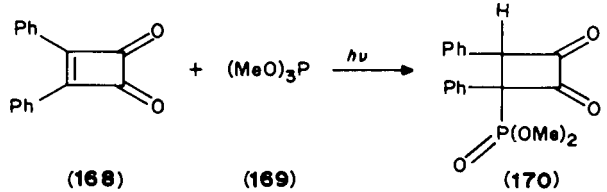
B. Reactions with Unsaturated Compounds

The UV irradiation of equimolar mixtures of dialkyl hydrogenthiophosphites and olefins yields dialkyl alkylthiophosphonates. After formation of a thiophosphite radical an anti-Markovnikov addition leads to the product. Polymers formed by side reactions are assumed to be the result of radical transfer reactions. In this way diethyl hydrogenthiophosphite (**165**) and cyclohexene (**166**) form diethyl hexylthiophosphonate (**167**) (equation 63)[189].

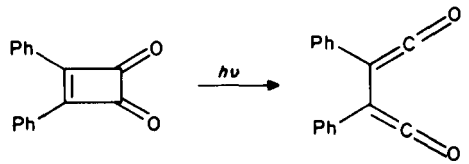


(165) (166) (167) (63)

Multifunctional unsaturated compounds such as bialkyl, haloolefins and vinyl ethers react in the same manner[190]. Diphenyl cyclobutadiene (**168**) in benzene or tetrahydrofuran reacts with trimethyl phosphite (**169**) under irradiation to give the adduct **170** in quantitative yield (equation 64). This observation can be explained by addition of the dialkyl phosphite radical formed to the cyclobutenedione or to the diketene (**171**) eventually being formed (equation 65)[191]. Diketene reacts with isonitrile to give a five-membered ring but does not react with phosphite[191]. After irradiation of dibutyl phosphite and *N*,*N*-dibutyloctamide, *N*,*N*-dibutylphosphinooctadecanamide is obtained[192,193].

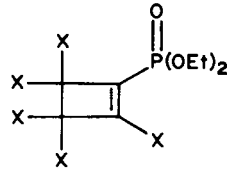


(168) (169) (170) (64)



(168) (171) (65)

Photoinduced addition reactions of dialkyl phosphites to polyfluorocyclobutenes such as perfluoro-, 1,2-dichlorotetrafluoro-, 1-chloro-2,3,3,4,4-pentafluoro-, 1,3,3,4,4-pentafluoro- or 1-chloro-3,3,4,4-tetrafluoro-cyclobutene yield dehydrogenated 1:1 adducts. In this way polyfluorocyclobutenyl phosphonates (**172**) are formed rather than the direct adducts[194].



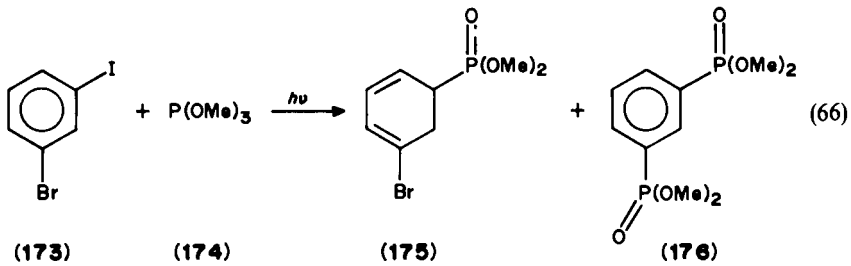
X=F, Cl

(172)

C. Reactions with Aryl and Alkyl Halides

The photoinitiated arylation of phosphites is of considerable importance in the field of UV-induced reactions of this species[195,196]. For example, photolysis of iodo- and bromobenzene in the presence of trialkyl phosphite readily yields dialkyl phenylphosphonates and phenylene bisphosphonates if the benzene is disubstituted with halide[197,198].

3-Bromoiodobenzene (**173**) and trimethyl phosphite (**174**) react to form dimethyl (3-bromophenyl)phosphonate (**175**) and tetramethylphenylen bisphosphonate (**176**) (equation 66). Whereas monosubstituted bromobenzene leads to low yields, disubstitution leads to substantially increased yields. The effect of activation depends on the substitution pattern[198,199]. The mechanism of the reaction between iodobenzene and triphenyl phosphite involves the attack of a phenyl radical on the phosphite molecule forming a phosphoranyl radical. It follows a one-electron transfer from the latter to an iodine atom. A quasi-phosphonium salt is formed which reacts immediately to give a dialkyl phenylphosphonate and an alkyl iodide[200].



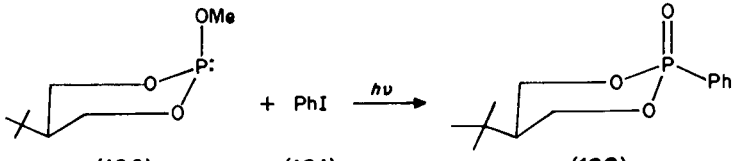
(173) (174) (175) (176) (66)

Investigations included reactions of aryl halides with other substituents. Products obtained thereby were dimethyl 2,6-dimethyl phenyl-, dimethyl 3,5-dimethoxyphenyl-, dimethyl 1-naphthyl-, dimethyl 2-thienyl- and dimethyl 2-furyl-phosphonate[201]. The photolysis of iodobenzene at 60 °C in a mixture of trimethyl phosphite and dimethyl- or diethyl-phosphite yields rate constants in accordance with those obtained from the thermal decay of phenylazotriphenylmethane. From this observation conclusions were drawn concerning the mechanism of the photo-initiated Arbusov reaction[202].

Thermal reaction of triethyl phosphite (**177**) and iodotrifluoromethane (**178**) does not lead to a product whereas the photoreaction yields diethyl trifluoromethylphosphonate (**179**) (equation 67)[203]. Diethyl pentafluorophenylphosphonate is obtained in a similar manner. In contrast to oxidation with N_2O_2, the UV irradiation of eq-5-*tert*-butyl-ax-2-methoxy-1,3-dioxane (**180**) in the presence of iodobenzene (**181**) yields the *trans*-isomer (**182**) as the main product (equation 68)[204].

$$(EtO)_3P + CF_3I \xrightarrow{h\nu} (EtO)_2P(O)CF_3 \quad (67)$$

(177) (178) (179)



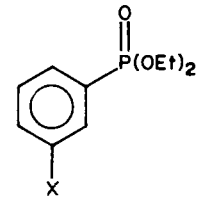
(180) (181) (182) (68)

An important intermediate in the formation of 1,2-bis(methylphosphino)-, 1,2-bis(dimethylphosphino)-and 1,2-bis(2-propylphosphino)-benzene is 1,2-bis(methoxyphosphoryl)benzene, which is feasible from reaction between 1,2-dichlorobenzene and trimethyl phosphite[205]. Triethyl phosphite and tetrachloromethane only react to a limited extent to give a mixture of diethyl trichloromethylphosphonate, tetraethyl dichloromethyldiphosphonate and hexaethyl chloromethyltriphosphonate[206]. Triisobutyl phosphite (**183**) and trifluoroiodomethane (**184**) react after irradiation to form diiso-butyl trifluoromethylphosphonate (**185**) (equation 69)[207].

$$(i\text{-BuO})_3P + CF_3I \xrightarrow{h\nu} F_3C{-}P(O)(O\text{-}i\text{-Bu})_2 \quad (69)$$

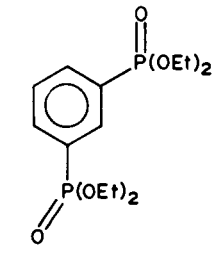
(183) (184) (185)

After irradiation in liquid ammonia, potassium dialkylphosphites react with aryl iodides to form dialkyl arylphosphonates, presumably by an $S_{RN}1$ mechanism[208]. Kinetic and mechanistic studies have been performed on this reaction[209]. The reaction of *m*-bromoiodobenzene and *m*-chloroiodobenzene with diethylphosphite anion leads to monosubstituted products (**186**) where only the iodine has been replaced, and further to disubstituted products (**187**). The quantitative proportions of products depend on the concentrations of the substrates[210–212]. The *ortho* compounds show analogous behaviour[213]. Use of dibromomethane leads via a Michaelis–Becker reaction to methylenebisphosphonates[214,215]. Potassium *O,O*-diethylphosphite (**188**) reacts with iodobenzene (**189**) after irradiation to form *O,O*-diethyl phenylthiophosphonate (**190**) nearly quantitatively (equation 70). The corresponding diamide form *N,N,N',N'*-tetramethylphenylphosphondiamide (**191**)[216]. Using bromobenzene instead of iodobenzene markedly decreases the reaction rate.

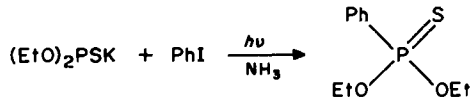


X=Br, Cl, F

(186)

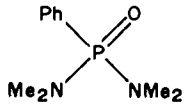


(187)



(70)

(188) (189) (190)

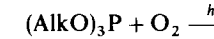


(191)

D. Reactions with Oxygen

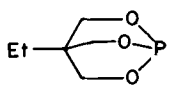
Trialkyl phosphites are well known reagents for deoxygenation reactions, e.g. for oxiranes, diaroyl peroxides, *N*-oxides and nitroso compounds, which form the corresponding trialkylphosphates. A direct synthesis is possible under UV irradiation in the presence of oxygen. In this way the corresponding phosphates are generated from tri(2-chloropropyl)phosphite, triethyl phosphite, benzyldiethyl phosphite, triallyl phosphite, tri(2-chloroethyl) phosphite and triisobutyl phosphite[217]. The exothermic photo-oxidation of tertiary phosphites using dry air or oxygen follows a free-radical mechanism, indicated by the fact that hydroquinone inhibits the reaction[218,219]. This could be confirmed for many trialkyl phosphites, with the exception of triphenyl and phenyldi(2-ethylhexyl) phosphite. Dialkyl phosphites, however, cannot be photo-oxygenated[220].

While trialkyl phosphites (**192**) are readily oxygenated to the phosphates (**193**) (equation 71), the reaction with cyclic phosphites is more complex.[221] The reaction of the bicyclic compound **194** is facile, whereas the monocyclic compounds **195** and **196** give only small yields. Kinetic studies on the dye-sensitized (rose bengal, methylene blue) photo-oxidation of trialkyl phosphites have been published. The course of the reaction was demonstrated by a Stern–Volmer plot of the β-carotene quenching[222,223].



(71)

(192) (193)



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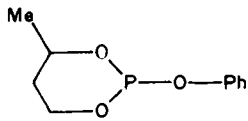
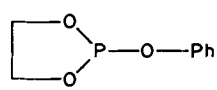


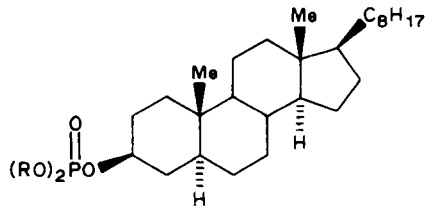
(195)



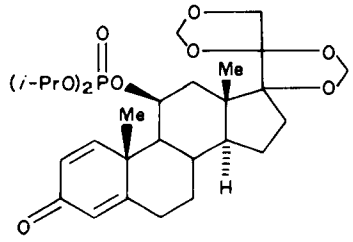
(196)

E. Reactions with Other Compounds

Under UV irradiation in the presence of trialkyl phosphites (R = *i*-Pr, Me, Et, *t*-$BuCH_2$, CF_3CH_2, $PhCH_2$), 5α-cholestan-3β-ol- nitrite can be transformed into the corresponding phosphate (**197**). The selectivity of this carefully performed phosphorelation may be demonstrated by the synthesis of the sterically hindered species **198**[224].



(197)



(198)

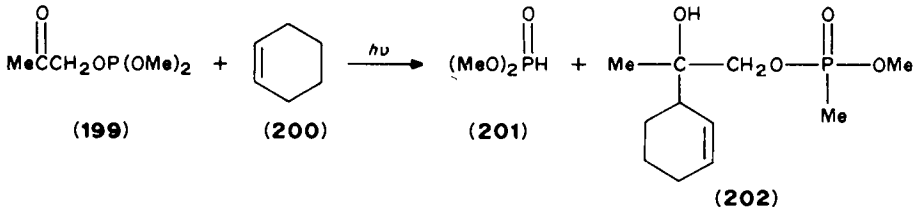
In contrast to the thermally induced reaction, the photoreaction of isobutyl disulphide with triethyl phosphite leads nearly quantitatively to the sulphide and some thionophosphate[225]. Analogously thiols are desulphurized[226]. The reaction mechanism can be understood primarily in terms of the attack of an alkyl radical on the S—H bond (equation 72–74)[227].

$$RS^{\cdot} + P(OEt)_3 \longrightarrow RS\dot{P}(OEt)_3 \tag{72}$$

$$RS\dot{P}(OEt)_3 \longrightarrow R^{\cdot} + SP(OEt)_3 \tag{73}$$

$$R^{\cdot} + HSR \longrightarrow RH + RS^{\cdot} \tag{74}$$

Photolysis of dimethyl(propan-2-onyl) phosphite (**199**) in cyclohexene (**200**) yields some phosphorous acid (**201**) and the β-hydroxy compound **202**, the latter being generated from an intermediate via a photo-Arbusov reaction[186].



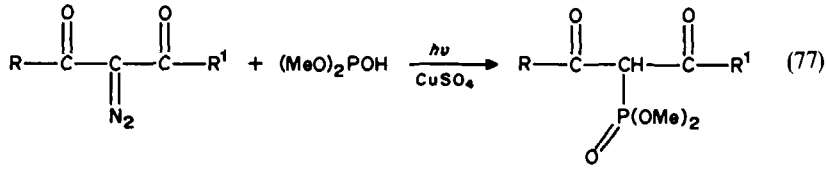
(199) (200) (201) (202)

(75)

Triethyl phosphite undergoes isomerization to diethyl phosphite and diethyl ethylphosphonate when photolyzed in the presence of acetonitrile[228]. Photolysis of chloroacetone and triethyl phosphite leads to vinyl phosphate, keto phosphonate, triethyl phosphate, diethyl ethylphosphonate, chloroethane and biacetonyl. The reaction between the first two products depends on the kind of substitution in the acetone starting material[229]. Using bromotrichloromethane (**203**), triethyl phosphite (**204**) and butanethiol (**205**) good yields of *S*-butyl diethylphosphorothioate are obtained (**206**) (equation 76). Changing the halide substitution decreases the yield of the product[230]. The photoreaction of bis(*m*-carboran-9-yl)- and bis(*p*-carboran-2-yl)-mercury with trimethyl phosphite leads to dimethyl β-carboranylphosphonates[231]. The phosphoranyl radical formed initially adds

(203) (204) (205) (206) (76)

readily to the oxygen atom of 3,6-di-*tert*-butyl-*o*-benzoquinone[232]. After reaction of a diazo-1,3,-dione (**207**) with dimethyl phosphite (**208**) in the presence of copper sulphate, 2-phospho-substituted 1,3-dicarbonyl compounds (**209**) are obtained (equation 77). The corresponding thiono compounds are accessible in the same way[233].



(77)

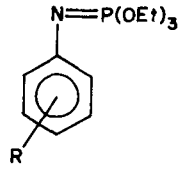
(**207**) (**208**) (**209**)

$R = R^1 = MeO, Me, Ph$

$R = MeO, R^1 = Me$

$RR^1 = CH_2CMe_2CH_2$

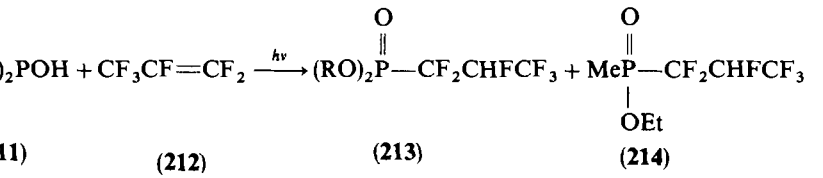
The photochemical deoxygenation of aromatic nitro compounds with triethyl phosphite[234] leads to the formation of triethyl phosphate and triethyl *N*-arylphosphorimidate (**210**)[235]. Depending on the substitution pattern, the product ratio can change. *Ortho*-alkyl-substituted nitrobenzenes generate pyridines or azepines via rearrangement of the initial nitrene species[236].



(**210**)

F. Radiolyses

Irradiation of triethyl phosphite with ^{60}Co γ-radiation yields ethanol, diethyl phosphite, triethyl phosphate and diethyl ethylphosphonate[237]. Pulse radiolysis in methanol leads to phosphoranyl radicals[238]. After reaction of dialkyl phosphites (**211**) with hexafluoropropene (**212**), a phosphonate (**213**) and phosphinate (**214**) are obtained[239]. The best yields are obtained working in the range of 20–35 Mrad.



(**211**) (**212**) (**213**) (**214**)

R = Me, Et, *i*-Pr (78)

Radiolysis of dimethyl, diethyl and diisopropyl phosphite in the presence of vinyl acetate leads to the 1:1 or the 1:2 adduct, whereas trimethyl phosphite adds to allyl acetate

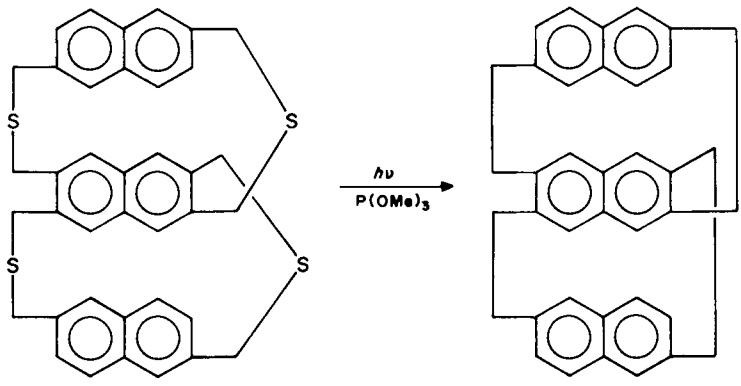
only in a 1:1 relation[240]. The ^{60}Co-initiated addition of dibutyl phosphite to the terminal or internal double bonds of the monounsaturated amines of fatty acids yields the respective dibutylphosphonamides. Typical products are *N*,*N*-dibutyl-9(10)-dibutylphosphonooctadecanamide, *N*-(9(10)-dibutylphosphonooctadecanoyl)-2,6-dimethylmorpholine and *N*-(9(10)-dibutylphosphonooctadecanoyl)-*N'*-methylpiperazine[241].

Studies on the radiochemically induced Michaelis–Arbusov reaction have been performed using trialkyl phosphites and phenyl halides. By this method the following phosphonates were obtained: dimethyl phenyl-, diethyl phenyl-, diisopropyl phenyl-, dimethyl *p*-chlorophenyl-, dimethyl *p*-toluyl-, dimethyl *m*-chlorophenyl- and dimethyl 2-thiophenyl-phosphonate. The *G* values for the radiation of phenylphosphonates derived from aryl halides and trialkyl phosphites are comparable to those of the tetraphenylphosphonium salts from triphenylphosphines and halobenzenes. The yields based on chloroiodo- or iodo-benzene are much higher than those for the formation of phosphonium iodide. Presumably the Michaelis–Arbusov reaction proceeds as a chain reaction. This is not the case, however, if halogen-substituted pyridines are used[77,242]. Phosphite radicals generated by γ-radiolysis react with disulphides such as lipoic acid or penicillic amine with electron transfer. The amino radical **215** is also capable of reducing tetranitromethane (**216**) splitting off one NO_2 molecule to form the anion **217** and metaphosphoric acid (**218**) (equation 79)

$$\underset{\textbf{(215)}}{HPO_3^{\cdot -}} + \underset{\textbf{(216)}}{C(NO_2)_4} \xrightarrow[-NO_2]{} \underset{\textbf{(217)}}{C(NO_3)_3^-} + \underset{\textbf{(218)}}{HPO_3} \qquad (79)$$

G. Miscellaneous

Phosphites take part in many photochemical processes acting as promoter or catalysts. The photochemical desulphurization of tetrathia[3.3]naphthalenophane (**219**) with triethyl phosphite generates the triple-layered [2.2]naphthalenophane **220** (equation 80)[244].

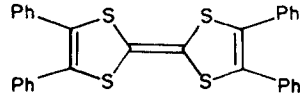


(80)

(219) **(220)**

Aliphatic phosphites show a promoting effect on the radical addition of hydrogen sulphide to propene. The impact of various parameters such as solvents, interactions and products and the mechanism have been extensively described[245–248]. UV irradiation of 4,5-diphenyl-1,3-dithiol-2-thione in the presence of triethyl phosphite and acetonitrile

leads to the formation of tetraphenyltetrathiofulvalene (**221**). The photochemically induced electron transfer of the phosphite to the thionodithiol accelerates the coupling[249]. The photohydroxylation of aromatic compounds with oxygen is also feasible in the presence of trialkyl phosphites using substrates such as benzene, halobenzenes, toluene and anisole[250]. The formation and reactions of phosphoranyl radicals[251-255], quenching of exited states[94] and ESR studies[256-265] of radicals generated from phosphites have also been described.



(**221**)

XI. PHOSPHINITES

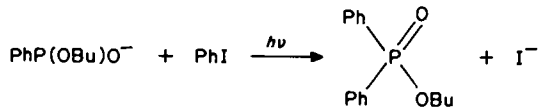
The reaction of dialkylphosphinous acid with cyclohexane in the presence of chlorine as a radical initiator leads to the formation of a cyclohexyldialkylphosphine oxide under UV irradiation[266]. The anion of diphenylphosphinous acid (**222**) acts as a nucleophilic phosphanion and forms triphenylphosphine oxide (**224**) by reaction with phenyl iodide (**223**) or bromide in ammonia (equation 81)[216].

$$\underset{\textbf{(222)}}{Ph_2PO^-} + \underset{\textbf{(223)}}{PhI} \xrightarrow{h\nu} \underset{\textbf{(224)}}{Ph_3PO} + I^- \qquad (81)$$

The photoreaction of diethylphosphinous acid with pentamethylvinylcyclotrisiloxane and heptamethylvinylcyclotetrasiloxane proceeds with ring cleavage to linear siloxane groups. Addition reactions to the vinyl groups are observed simultaneously[267].

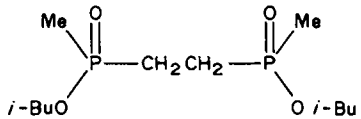
XII. PHOSPHONITES

The anion of the *O*-butylphenylphosphonous acid (**225**) reacts under UV irradiation with bromo- and iodo-benzene (**226**) by an $S_{RN}1$ mechanism to give butyl diphenylphosphinate (**227**) in high yields (equation 82). The reaction rate is considerably slower when dmso is used as a solvent instead of ammonia[216].



(**225**) (**226**) (**227**) (82)

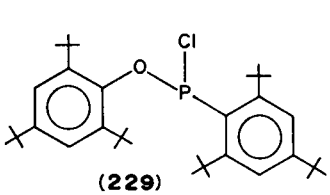
Methanephosphonous isobutyrate reacts with acetylene under an inert gas atmosphere to give ethane-1,2-di(methylphosphinoic isobutyrate) (**228**). Analogously, the following



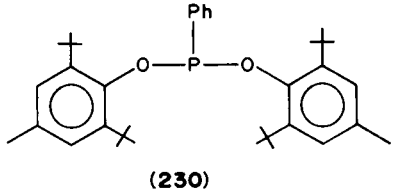
(**228**)

esters can be used: methyl, ethyl, propyl, *n*-butyl, isobutyl and 2-chloroethyl esters, and ethanephosphonous acid dodecyl, propanephosphonous acid hexadecyl, benzenephosphonous acid isobutyl, ethylbenzenephosphonous acid isobutyl, benzylphosphonous acid isobutyl, phenylethylphosphonous acid isobutyl, and naphthalenephosphonous acid isobutyl esters[268].

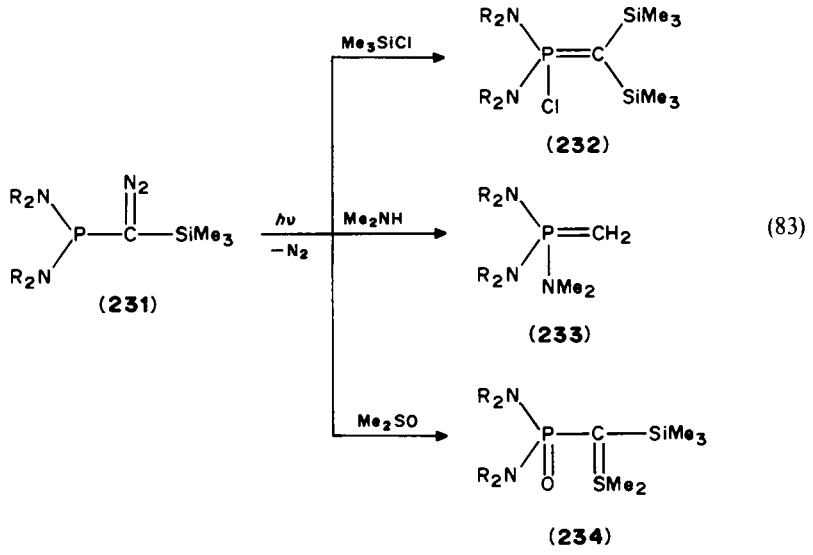
The hypophosphite anion reacts in a way similar to the well known desulphurization with the corresponding P(III)-compounds. For instance, cystine is reduced to cysteine after UV irradiation. The mechanism is based on the attack of a thiyl radical by the enolic form of $H_2PO_2^-$[269]. Under γ-irradiation the alkylphosphines react with perfluoropropene[239]. Reduction and/or photolysis of bis(2,4,6-tri-*tert*-butylphenyl)phosphonous acid chloride (**229**) and *O,O*-bis(4-methyl-2,6-di-*tert*-butylphenyl)phenylphosphonite (**230**) leads to the formation of RP and RO radicals, respectively[251]. A diamide of the phosphonous acid, (trimethylsilyl)[bis(diisopropylamino)phosphino]diazomethane (**231**), in the presence of trimethylchlorosilane or dimethylamine or dimethyl sulphoxide, gives the products **232**–**234** (equation 83)[270].



(229)



(230)

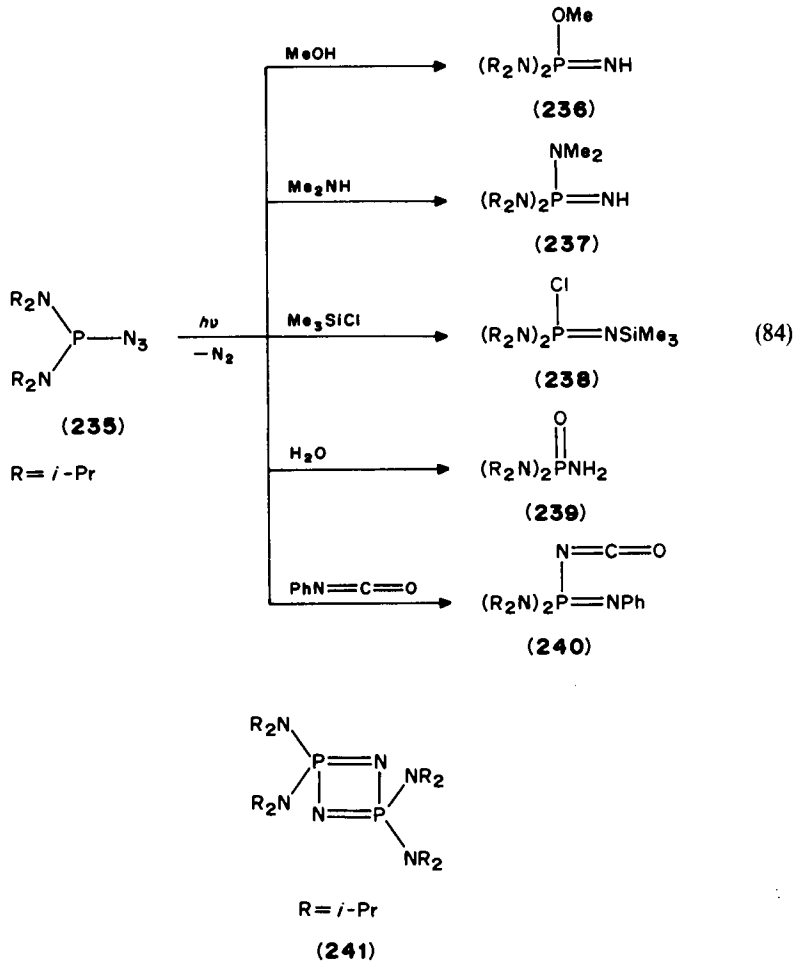


(83)

XIII. AZIDOPHOSPHINES

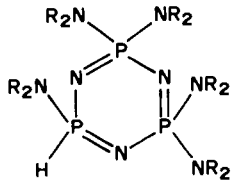
On photolysis of azidobis(diisopropylamino)phosphine (**235**), several adducts (**236**–**240**) are formed, presumably derived from the intermediate nitrilo-λ^5-phosphine (equation 84). The stabilization of the intermediate is confirmed by the fact that no Curtius rearrange-

ment is observed, in contrast to the reaction with tetra- or penta-coordinated phosphorus azides[271]. At lower temperatures the nitrilophosphine dimerizes and formation of diazadiphosphete (**241**) is detected[272]. By steric effects the isopropylamino group causes the possible Staudinger reaction to be suppressed, which could lead to $[(R_2N)_2PN)_n$[273,274]. On the other hand, its low migration ability prevents the formation of a tricoordinated λ^5-phosphine, $R_2NP(=NR_2)$[275,276].



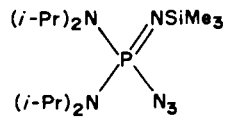
(84)

The trimer hydridopentaminocyclotriphosphazene (**242**) is obtained after photolysis of the azide **235** in deuterobenzene, whereas the corresponding hexamine is not formed[277]. Trimethylsilylazide reacts with the azide **235** in a photoinitiated Staudinger reaction to give the iminophosphinazide **243**, which is not generated by thermal initiation[277]. Formation of an intermediate nitrilophosphine is confirmed by the fact that a 1,2-addition reaction takes place and by *ab initio* calculations which show a relationship between nitrenes and nitriles stemming from delocalization of the solitary electron pairs $n_\pi(P) \rightarrow p_\pi(N)$ and $n_\pi(N) \rightarrow d_\pi(P)$[278].



R=*i*-Pr

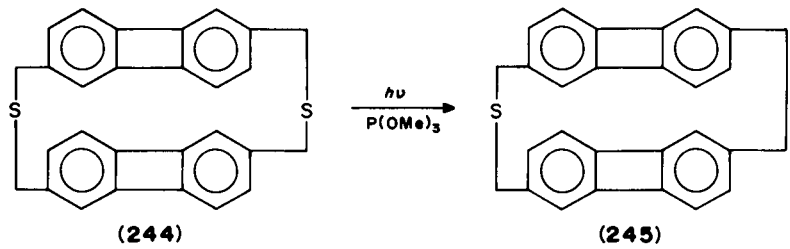
(242)



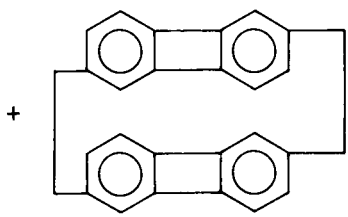
(243)

XIV. MISCELLANEOUS

In addition to the desulphurization of thianaphthalenophane (**219**)[244] a number of examples of this type of reaction are known. 2,13-Dithia[3.3](2,6)biphenylenophane (**214**), generated from the reaction of 2,6-bis(bromomethyl)biphenylene with the disodium salt of 2,6-dimercaptobiphenylene, is desulphurized after photolysis in the presence of trimethyl phosphite to give monothiabiphenylenophane (**245**) and biphenylenophane (**246**) (equation 85)[279]. The biphenylenonaphthalenophanes are obtained in the same way[279].



(244) (245) (85)

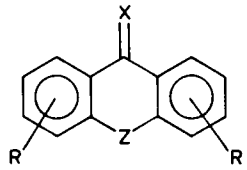


(246)

Cyclophanes are also formed by photolytical deselenation and ring contraction using hexamethylphosphorous triamide. The proudct yields are higher when photolytically induced deselenation is used than by using the Stevens rearrangement which employs hydrogenation and flash pyrolysis of diselenocyclophanes. They also exceed those obtained by photodesulphurization of the corresponding thia derivatives[280–283] or those using thermal desulphonation of cyclic disulphones[284].

In addition to the photochemically induced monodesulphurization of cystine by hypophosphite[269,285], these methods have been employed for other disulphidic bonded peptides such as insulin, glutathione, lysozyme and plasma albumin[286]. The photoinduced

chain reaction of phosphonate and hydrogen peroxide is initiated by interaction of the products from water radiolysis with hydrogen peroxide and phosphorus(III)[287]. The chain propagation reaction consists of two steps and termination is induced by recombination or disproportionation of the radicals. The photoaddition of hydrogen sulphide to alkenes is (among others) catalyzed by tricyclic phosphorus(III) compounds such as **247**. Further, the reaction of dodec-1-ene with hydrogen sulphide to give dodecanethiol is performed in a mixture of xanthone and tributyl phosphite[91]. The photochemical reduction of uranyl ions is obtained using triphenylphosphine or the corresponding compounds of arsenic, antimony and bismuth[288–291]. Kinetic studies were performed on tri-*p*-tolylphosphine[292], 1,2-ethylenebis(diphenylphosphine) and but-1,4-enebis(diphenylphosphine)[293].



X=O, S, R

Z=PR, P(OR)

R=H, halo, alkoxy, alkyl, aryl

(247)

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CHAPTER **14**

Free-radical reactions of organophosphorus(III)

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I. BACKGROUND

A number of reactions occur when free radicals are generated in the presence of tricovalent phosphorus compounds, as illustrated by reactions 1–3. The subject has been reviewed several times[1]. The last comprehensive summary articles appeared in 1979[1a] and 1983[1b] (coverage through early 1981) at the peak of activity in the area. A more specialized review was published in 1982[2]. The emphasis in those reviews was on the phosphoranyl radicals, **1–3**, which are indeed intermediates in many such reactions. The 1983 review contained a compilation of ESR data for most of the great number of radicals of this type characterized by ESR. This chapter is not intended to repeat in an exhaustive way

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what has been compiled previously. Instead, an overview of the factors controlling the products of the overall reactions will be given, including a limited discussion of rates of specific reactions. Reactions in which the intact phosphoranyl radical is trapped will then receive some coverage. A look at the highlights of the structures and permutational processes of phosphoranyl radicals and the stereochemical aspects of reactions in which they are involved will follow. Next, some photochemical processes in which phosphoranyl 1,3-biradical species may be intermediates will be discussed. Finally, useful applications of the reactions of free radicals with tricovalent phosphorus derivatives to the development of antioxidants and in synthesis will be highlighted. More thorough coverage will be given throughout to recent work.

A great deal of direct and indirect evidence can be cited for the intermediacy of phosphoranyl radicals in these processes[1]. However, it is by no means sure that they lie on the major reaction pathway in all cases. For example, when R′ · is fairly stable, reaction 2 may well be a concerted process. These reactions are, however, most easily discussed in terms of **1**–**3** and similar intermediates, and we shall do so throughout this chapter.

Oxidation:

$$RO^{\cdot} + P(OEt)_3 \longrightarrow \underset{\textbf{(1)}}{RO\dot{P}(OEt)_3} \longrightarrow R^{\cdot} + O{=}P(OEt)_3 \qquad (1)$$

Substitution:

$$RO^{\cdot} + R'P(OEt)_2 \longrightarrow \underset{\textbf{(2)}}{RO\dot{P}(OEt)_2R'} \longrightarrow ROP(OEt)_2 + R''^{\cdot} \qquad (2)$$

Free-radical Arbuzov:

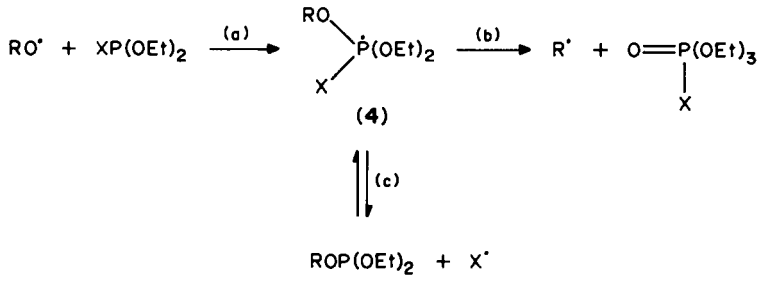
$$Ph^{\cdot} + P(OEt)_3 \longrightarrow \underset{\textbf{(3)}}{Ph\dot{P}(OEt)_3} \longrightarrow PhP(O)(OEt)_2 + Et^{\cdot} \qquad (3)$$

Although reactions 1–3 are very representative of the processes available to free radicals and tricovalent phosphorus molecules, not all potential combinations of radicals and phosphorus-containing reactants lead to net reaction. In fact, the formation of isolable product is dependent on the structures of both the reactant radical and the phosphorus-containing partner.

Tricovalent phosphorus compounds also undergo loss of an electron to yield radical ions, $Z_3P^{+\cdot}$, which themselves undergo reactions, particularly additions to nucleophiles. Reduction can give $Z_3P^{-\cdot}$. These redox topics will not be reviewed here.

II. ENERGETICS, RATES AND OVERALL REACTIVITY

Another view of processes 1–3 is given by the reactions in equation 4. Reactions 4a involves an alkoxy radical which forms a very strong bond to phosphorus in the



(4)

intermediate phosphoranyl radical. The process is irreversible, rate determining and nearly diffusion controlled. Variations in the competion between steps 4b and 4c, and thereby the relative amounts of oxidation and substitution, are determined primarily by changes in the relative stabilities of R$^{\bullet}$ and X$^{\bullet}$[1,2].

As indicated, reaction 4c is sometimes reversible, and the reaction of X$^{\bullet}$ with $ROP(OEt)_2$ can potentially lead to the free-radical Arbuzov process (reaction 3). With X$^{\bullet}$ = Ph$^{\bullet}$, the Ph—P bond is relatively strong, and addition (reaction 4c) is then irreversible. Correspondingly, no substitution accompanies reaction 4b when X = Ph, i.e. no $ROP(OEt)_2$ is formed[3]. Other radicals for which addition is rapid and probably irreversible include RS$^{\bullet}$[4], $Me_3SiO^{\bullet}$[5], BzO$^{\bullet}$[6], F$^{\bullet}$[7], $(EtO)_2P(O)O^{\bullet}$[8], $X_3P^{+\bullet}$[9] and perhaps $(Me_3Si)_2N^{\bullet}$[10]. Evidence for the reversibility of addition of RS$^{\bullet}$ to $(RO)_3P$ has been presented[11]. However, it is difficult to see how the reaction can be so rapid (see below), and presumably exothermic, and still be reversible. Examples of relatively clean substitution reactions include are shown in equation 5[12,13]. When X = Cl about equal amounts of substitution and oxidation occur. With X = OR and Ph, only oxidation results. The difference between X = RO, Ph and Cl and the remainder of X can be seen by comparing the *average* bond strengths (*D*) for the series of corresponding PX_3. Thus, $D(PX_3)$ decreases in the order $P(OR)_3 > PCl_3 \approx PPh_3 > P(OPh)_3 > P(NMe_2)_3 > PR_3$. (Compilations and discussions of bond energies have appeared elsewhere; see Chapter 5 and refs 1a and 1f.)

$$t\text{-BuO}^{\bullet} + (EtO)_2PX \longrightarrow t\text{-BuOP(OEt)}_2 + X^{\bullet} \qquad (5)$$

$$X = Me, Et, t\text{-Bu, benzyl, } n\text{-Bu}_2N, PhO, OP(OEt)_2$$

The ordering of these bond energies can also be used to rationalize the fact that whereas Ph$^{\bullet}$, which adds irreversibly to $P(OR)_3$, gives an efficient formation of phenylphosphonate (reaction 3). Me$^{\bullet}$[3], Et$^{\bullet}$[13] and $Me_2N^{\bullet}$[3b,14] add to tricovalent phosphorus reversibly and only give a product when a benzyloxy group, which undergoes β-scission relatively rapidly, is present (reaction 6). This is in spite of the fact that free-radical Arbuzov processes are 40–50 kcal mol^{-1} exothermic overall[15–17]. Indeed, ESR evidence[13] for the reversible formation of $MeP^{\bullet}(OEt)_3$, but not Et$^{\bullet}$ when Me$^{\bullet}$ is generated in the presence of the phosphite, has been presented. The idea that $(Me_3Si)_2N^{\bullet}$[10], $(EtO)_2P(O)O^{\bullet}$[8] and BzO$^{\bullet}$[6] also add to phosphorus irreversibly is based on the fact that all three give Arbuzov reactions (ESR evidence) in which radicals no more stable than Et$^{\bullet}$ or *t*-Bu$^{\bullet}$ are formed on C—O β-scission.

$$PhCH_2OP(OEt)_2 + X^{\bullet} \rightleftharpoons PhCH_2\overset{\bullet}{\underset{X}{P}}(OEt)_2 \longrightarrow \underset{X}{O=P(OEt)_2} + PhCH_2^{\bullet} \qquad (6)$$

Not unexpectedly, then, the use of $PhCH_2O^{\bullet}$ in reaction 4 results in an increased proportion of oxidation. The β-scission/α-scission ratio (observed oxidation/substitution ratio) with benzyloxy radical as reactant decreases in the order X = PhO > n-Bu_2N > Me > Et > *t*-Bu > $PhCH_2$ as is consistent with an increasing rate of α-scission[12]. In general, the ease of β-scission decreases in the order $PhCH_2O > CH_2{=}CHCH_2O > t$-BuO > *i*-PrO > *sec*-BuO > *c*-C_5H_{10} > EtO > MeO[12,13,18–22]. In keeping with the relative weakness of the C—S bond, reaction of RS$^{\bullet}$ with a series of $XP(OEt)_2$ gives almost entirely sulfur transfer (oxidation) when the P—X bond is relatively strong[12]. However, on reaction of a series of alkylphosphonites, $RP(OEt)_2$, with different R'S$^{\bullet}$, both oxidation [$RP(S)(OEt)_2$] and substitution [$R'SP(OEt)_2$] products result in ratios which are predictable from the relative stabilities of R$^{\bullet}$ and R'$^{\bullet}$[23]. Illustrative of the greater amount of oxidation using thiyl rather than alkoxyl radicals is the finding that although with $EtP(OEt)_2$ even $PhCH_2O^{\bullet}$ gives nearly complete Et$^{\bullet}$ displacement, *i*-PrS$^{\bullet}$ yields about two thirds oxidation.

The above ordering of average bond strengths is also useful in understanding the ease with which reaction 7 occurs. Thus X$^{\cdot}$ which form stronger bonds to phosphorus readily displace those Z more weakly bonded. For the series RO, PhO, R_2N, R, any group Z in the series can be displaced by any one to the left of it functioning as X$^{\cdot}$[14].

$$X^{\cdot} + ZP(OEt)_2 \rightleftharpoons \begin{matrix} X \\ \diagdown \\ \dot{P}(OEt)_2 \\ \diagup \\ Z \end{matrix} \longrightarrow XP(OEt)_2 + Z^{\cdot} \qquad (7)$$

The irreversible and reversible bond formations discussed constitute two cases of reactivities of free radicals. A third case involves radicals too stable or weakly bonding to tricovalent phosphorus to be reactive under any circumstances. For example, $PhCH_2^{\cdot}$, *t*-Bu$^{\cdot}$ and *i*-Pr$^{\cdot}$ do not undergo reactions 6 and 7[3b,14] (see, however, the next paragraph).

These three kinds of reactivities are depicted diagrammatically in Figure 1. Placing all the phosphoranyl radical intermediates at the same energy is, of course, an oversimplification. In fact, modification in the structure of the phosphorus-containing reactant can strongly affect the reactivity of a given radical. For instance, both $Me_2N^{\cdot}$ and Et$^{\cdot}$ give Arbuzov reactions with $PhP(OEt)_2$ but not with $(EtO)_3P$[3b,14], and even relatively stable, sterically

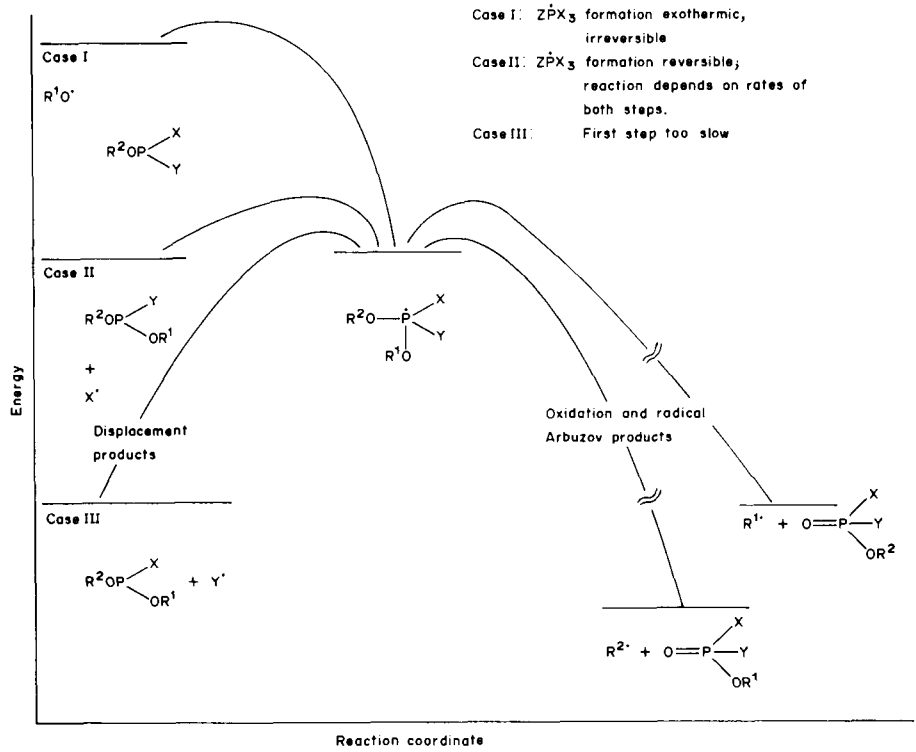


FIGURE 1. Effect of thermodynamics of phosphoranyl radical formation on overall reactivity. Reprinted with permission from *Acc. Chem. Res.*, **15**, 117 (1982). Copyright (1982) American Chemical Society.

bulky *t*-Bu$^{\bullet}$ and *i*-Pr$^{\bullet}$ do the same with Ph_2POEt[24,25]. As will be noted later, both of the intermediate phosphoranyl radicals in these reactions are probably ligand-π radicals with the odd electron in the phenyl ring system. They may be more stable than $R\dot{P}(OEt)_3$ or $Me_2N\dot{P}(OEt)_3$ and may even be formed irreversibly.

Several estimates of the thermodynamics of phosphoranyl radical formation have been made on the basis of average bond strengths, product studies and ESR-derived equilibrium data. By combining the measured enthalpy change of equation 8[26] with the approximately 17 kcal mol^{-1} exothermicity of the displacement of Me$^{\bullet}$ from $MeP(OR)_2$ by RO$^{\bullet}$, the addition of *t*-BuO$^{\bullet}$ to $MeP(OR)_2$ can be estimated to be at least 20 kcal mol^{-1} exothermic[3b,26]. Similarly, it was possible to estimate that the addition of Ph$^{\bullet}$ to $(RO)_3P$ is 10–15 kcal mol^{-1} exothermic[3b]. Photoacoustic measurements have shown[27] reaction 9 to be favored enthalpically by 13.6 ± 3.8 kcal mol^{-1}[27]. This technique also gave[27] a heat of reaction for process 10 of 24 ± 2 kcal mol^{-1}. Thus, the addition of alkoxy radicals is uniformly exothermic. The reaction with Ph_3P, perhaps surprisingly, does not seem to be more favorable than that with *n*-Bu_3P even though the former yields the potentially more stable, ligand-π type as mentioned above. One measurement of this type was made in the gas phase. The addition of fluorine atoms to PF_3 was estimated[7] to be exothermic by 92 kcal mol^{-1}.

$$Me^{\bullet} + P(OR)_3 \rightleftharpoons Me\dot{P}(OR)_3 \qquad (8)$$

$$\Delta H^{\circ} = -7 \text{ kcal mol}^{-1},\ R = i\text{-Pr}$$

$$t\text{-BuO}^{\bullet} + Ph_3P \longrightarrow [t\text{-BuPPh}_3]^{\bullet} \qquad (9)$$

$$\Delta H^{\circ} = -13.6 \pm 3.8 \text{ kcal mol}^{-1}$$

$$t\text{-BuO}^{\bullet} + n\text{-Bu}_3P \longrightarrow t\text{-BuO}^{\bullet}P(\text{Bu-}n)_3 \qquad (10)$$

$$\Delta H^{\circ} = -24 \pm 2 \text{ kcal mol}^{-1}$$

The irreversibility of the reactions of RO$^{\bullet}$ with phosphite triesters was demonstrated chemically early in the research on such systems when it was shown that ^{13}C-labeled *t*-BuO$^{\bullet}$ failed to be incorporated into $(t\text{-BuO})_3P$ (equation 11)[28].

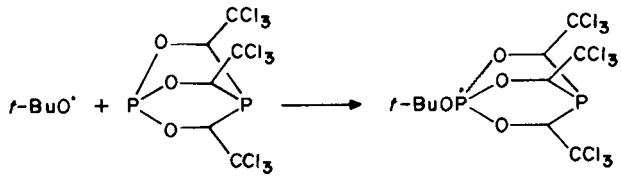
$$t\text{-Bu*O}^{\bullet} + P(\text{OBu-}t)_3 \rightleftharpoons t\text{-Bu*O}\dot{P}(\text{OBu-}t)_3 \rightleftharpoons t\text{-BuO}^{\bullet} + t\text{-Bu*OP(OBu-}t)_2 \qquad (11)$$

The equilibrium of equation 8 responds to the steric size of R[26]. Although polar effects on the very rapid reactions of *t*-BuO$^{\bullet}$ with a series of $ArP(OEt)_2$ could not be detected[3b], the less reactive *t*-BuOO$^{\bullet}$ oxidized a series of PX_3 with rate constants correlated by σ^* ($\rho^* = -0.75$)[29].

It has been reported[30] that the ESR signal strength of phosphoranyl radicals formed on photolysis of *t*-BuOOBu-*t* in the presence of trialkyl and methyldialkyl phosphites is very sensitive to the steric size of the alkoxy groups and gives no signal at all in some cases. A stereoelectronic effect on the degree of hindrance exhibited by a heteroatom-containing side-chain also was noted. By contrast, a series of dimethylalkyl phosphites showed no variation in signal intensities. These results were supported by product studies in some instances. It is surprising that irreversible reactions so nearly diffusion controlled in rate should exhibit important steric effects.

An unusual test of selectivity was provided by reaction 12 in which the *tert*-butoxy radical added to the phosphite moeity rather than to the phosphine functionality[31]. A similar selectivity was seen on reaction of the same substrate with the carboranyl radical generated on photolysis of $(C_2H_{11}B_{10})_2B$[32].

Figure 1 and Figure 2 (taken from ref. 2) make it clear that the reverse of β-scission is thermodynamically and kinetically unfavorable. The overall oxidation reactions are over 50 kcal mol^{-1} exothermic. If the formation of the phosphoranyl radical on addition of RO$^{\bullet}$



(12)

is 25 kcal mol^{-1} exothermic, then the reverse of β-scission must be at least 25 kcal mol^{-1} endothermic. Interestingly, evidence has been presented which was interpreted initially in terms of process 13[33]. This is totally inconsistent with known energetics. More recently, a lower energy phosphoranyl radical-like transition state, rather than an actual intermedi-

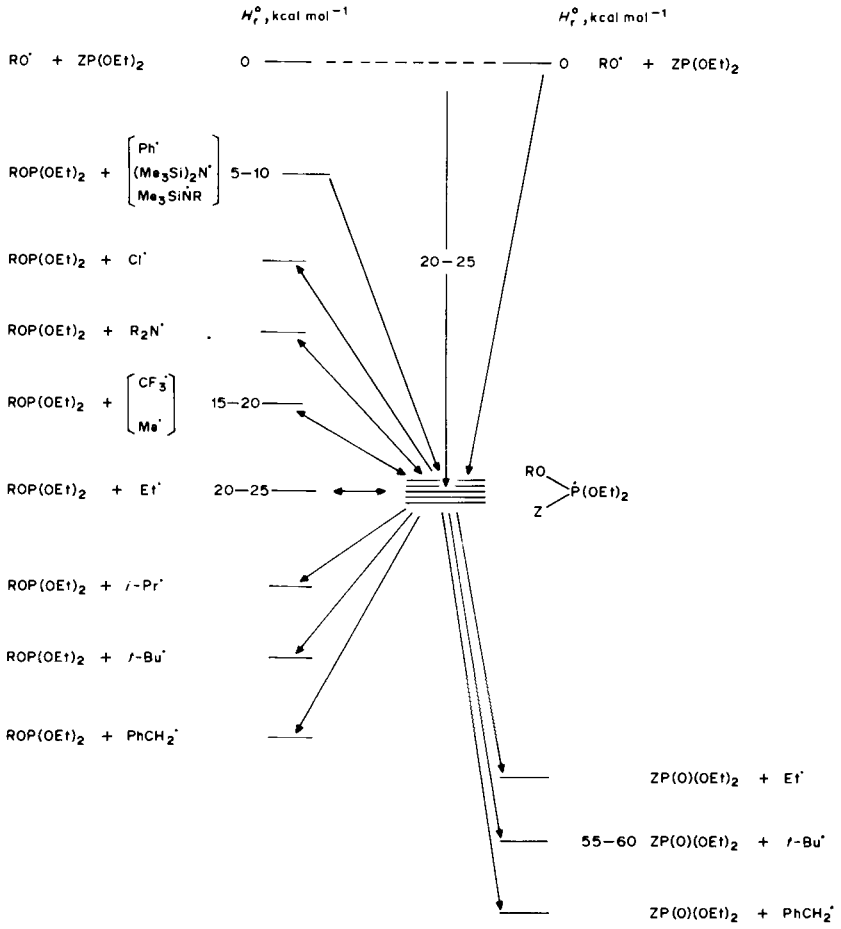


FIGURE 2. Estimated heats of reactions of various phosphoranyl radical processes. Reprinted with permission from *Acc. Chem. Res.*, **15**, 117 (1982). Copyright (1982) American Chemical Society.

ate, has been assigned to these processes[34].

$$R^{\cdot} + O{=}P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \longrightarrow ROP(=O)(OR')_2 + R'^{\cdot} \quad (13)$$

Further evidence has been provided[35] that the reaction of CCl_4 with triethyl phosphite has a major component which is ionic, by way of $[Cl_3C]^-[ClP(OEt)_3]^+$, and a minor one involving addition of $Cl_3C^{\cdot}$ to phosphorus, which was increased by UV light or the addition of azobisisobutyronitrile (aibn). A single electron-transfer mechanism for $Cl_3C^{\cdot}$ formation was ruled out.

III. SOME SELECTED RATE CONSTANTS

A. Radicals with PZ_3

Second-order rate constants, k_p ($1\ mol^{-1}\ s^{-1}$), have been measured for the irreversible reaction of individual radicals and representative PZ_3. Values in the range 8.1×10^8–5.1×10^9 were found for the oxidative additions of $RO^{\cdot}$ to $(EtO)_3P$, Ph_3P, Et_3P and $PhP(OMe)_2$ at room temperature[3b,36]. Laser flash photolysis measurements[36a] of the reactions of $RO^{\cdot}$ with $(EtO)_3P$ and $PhP(OEt)_2$ confirmed the earlier rate constants determined by ESR. For the reaction of $Ph^{\cdot}$ with $(MeO)_3P$, k_p is 3.5×10^8 at 45 °C[3b,37]. A recent estimate puts k_p for $RS^{\cdot} + (EtO)_3P$ at 3.1×10^8 at 25 °C[38]. The addition of t-$BuOO^{\cdot}$ to $(MeO)_3P$ has a k_p at 178 K of only $11\ mol^{-1}\ s^{-1}$ [29].

B. α-and β-Scission

A large number of ESR and laser flash plotolysis–transient optical spectroscopic experiments have yielded rate constants for α- and β-scission. Kinetic parameters for key processes are given in Table 1. The principle that both processes are aided by the formation of a relatively stable radical is evident. Ethyl radical is less readily formed on β-scission than is *tert*-butyl (cases 1 and 2). The same effect can be seen in cases 8 and 9 and also 12 and 13 giving α-scission. The much greater rate of α-scission compared with β-scission in general is evident when both processes could emanate from the same phosphoranyl radical. Evidently the transition state for β-scission is characterized by a large degree of C—O bond cleavage but does not benefit from the stability which would result if P=O bond formation were well advanced.

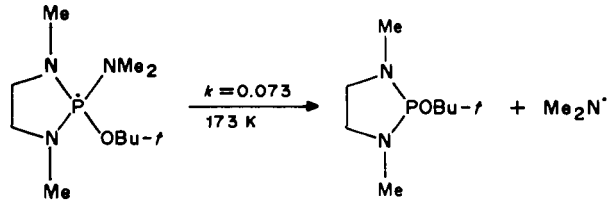
The most recent technique applied to these systems is laser flash photolysis–ESR (case 1b), in which decay of t-$BuOP(OEt)_3$ is observed under conditions such that radical–radical reactions are unimportant[39]. The rate constant determined at 293 K agrees well with that determined by optical monitoring of the radicals (case 1a), but the activation parameters differ slightly.

Both α- and β-scission are slowed when the group which would undergo scission is part of a five-membered ring. Thus reactions 15[26] and 17[26] are retarded in their five-membered ring counterparts, which undergo processes 14[41] and 16[26,42] instead. Attachment of a *tert*-butoxy group to phosphorus contained in a five-membered ring also slows the formation of *tert*-butyl radicals by a factor of four at 213 K compared with t-$BuOP(OEt)_3$ (case 1b, Table 1).

Even alkyl substitution on the five-membered ring fails to bring about β-scission except at higher temperatures[43]. Thus **6**, formed from the hydridophosphorane on reaction with t-$BuO^{\cdot}$, gives no evidence of β-scission at 45 °C. However, at 130 °C a chain reaction ensues (equation 18) to give a stable, ring-opened trialkyl phosphate from a chain-transfer

TABLE 1. Rates of selected α- and β-scission processes

Case	*Radical*	Scission *process*	*log A* (s^{-1})	E_a (*kcal mol*$^{-1}$)	k(s^{-1})(temp., K)	Ref.
1a	t-BuO$\dot{P}$(OEt)$_3$	β	11.5 ± 0.5	8.2 ± 0.5	3.4×10^5 (300)	36a
1b	t-BuO$\dot{P}$(OEt)$_3$	β	12.9 ± 0.5	10.0 ± 0.5	2.8×10^5 (293)	39
2	(EtO)$_4$P$^{\cdot}$	β	12.9	13.0	0.4 (213)	13
3	[t-BuOPPh(OEt)$_2$]$^{\cdot}$	β	12.4	8.5	1.5×10^6 (300)	36a
4	[t-BuOPPh$_2$OMe]$^{\cdot}$	β	12.0	8.6	5.2×10^5 (300)	36a
5	[t-BuOPPh$_3$]$^{\cdot}$	β	11.7	12.1	7.8×10^2 (300)	36b
6	(t-BuO)$_2$POCH$_2$CH$_2$O	β			5.5×10^5 (303)	36a
7	t-BuO(Me$_3$SiO)$\dot{P}$OCH$_2$CH$_2$O	β	10.8	8.5	4.0×10^4 (300)	36a
8	t-BuO$\dot{P}$Me$_3$	α			32.3 (173)	26
9	t-BuO$\dot{P}$(Bu-n)$_3$	α	12.7	5.8	2.9×10^8 (300)	36a
					2.3×10^5 (173)	36a
10	(t-BuO)$_2\dot{P}$(NMe$_2$)$_2$	α	14.2 ± 0.5	10.8 ± 0.5	3.4 (173)	26
11	t-BuO$\dot{P}$(OEt)$_2$Et	α			630 (173)	58c
12	(t-BuO)$_2\dot{P}$(Et)$_2$	α	11.5	11	0.0082 (173)	40
13	(t-BuO)$_2\dot{P}$(CH$_2$CH=CH$_2$)$_2$	α	10.7	6.7	180 (173)	40



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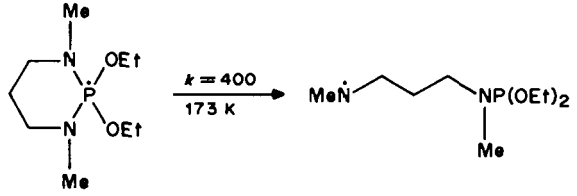

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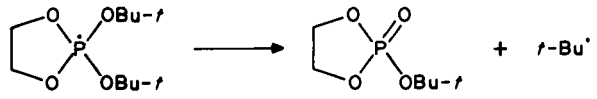

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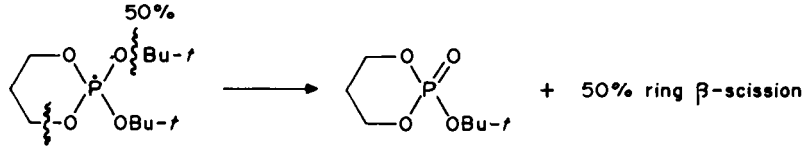
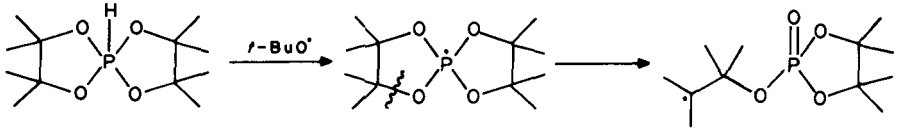


(17)

50% 50% + t-Bu·

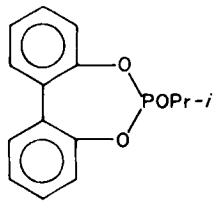
reaction of **7** with the hydridophosphorane[44]. The stabilizing effect of a five-membered ring is useful if reactions of the intact phosphoranyl radical are of interest.



(18)

(6) **(7)**

Consistent with the above is the remarkable retarding effect on α-scission of placement of the oxygen of an incipient phenoxy radical in a ring[45]. Phosphite **8** undergoes exclusive oxidation to the phosphate on reaction with *t*-BuO· at 50 °C (no ring-opening α-scission). If *i*-Pr is replaced, however, by a 2,6-di-*tert*-butyl-4-methylphenyl group, the latter is displaced. Phosphite **10** gives an α/β scission ratio of 2:1. For **9** and **11** the α/β ratios are 1:2 and 1:4.



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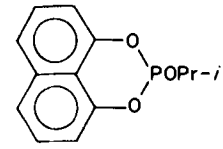
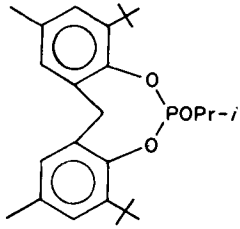


(9)

Phenyl substituents may retard α-scission since (*n*-PrPhMePOBu-*t*)· undergoes exclusive β-scission[46]. The measured rates of β-scission do not appear to be increased by phenyl substituents (see Table 1). The decomposition of case 5 is in fact slower than, for example, cases 1 and 2.



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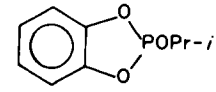
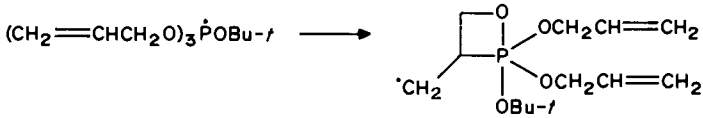


(11)

IV. OTHER REACTIONS OF PHOSPHORANYL RADICALS

In addition to scission, phosphoranyl radicals formed via oxidative addition or from pentacovalent phosphorus precursors can undergo reactions in which they are trapped as intact entities. Much of the evidence for these processes is spectroscopic. Thus, at relatively low temperatures, rate constants for self-reaction of *t*-BuOP(OR)$_3$ and other phosphoranyl radicals have been determined[47]. An intriguing possibility is that P(V)–P(V) dimers are formed, but no product studies have been reported. Reversible dimerization of certain ligand π radicals has been noted[48]. However, they were not generated by oxidative addition but rather on abstraction of the hydrogen of a precursor hydridophosphorane. Spirocyclic and bicyclic phosphoranyl radicals, also from hydridophosphoranes, add to olefins[43,49] and carry out displacement on disulfides[50]. Certain phosphoranyl radicals also have been trapped by abstraction of chlorine from CCl_4[51] and by addition to *t*-BuNO[20] and to 5,5-dimethyl-1-pyrroline 1-oxide[52]. ESR evidence for the formation of a phosphoranylperoxy radical, $(EtO)_4POO^{\cdot}$, in the presence of oxygen has been presented[53]. This assignment has been disputed, however[54].

Intramolecular cyclizations involving phosphoranyl radicals formed on oxidative addition have been verified by ESR. Four-membered ring formation appears to be favored (reaction 19), although a five-membered ring can be generated (reaction 20)[20]. Other radicals from cyclization which have been characterized include **12** and **13**. Triazenylph-



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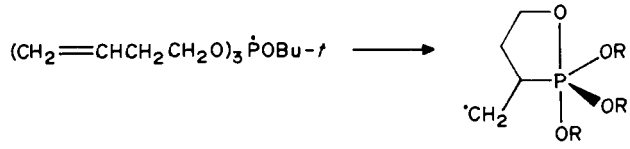

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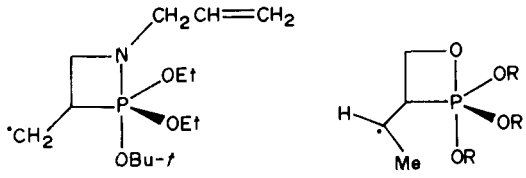
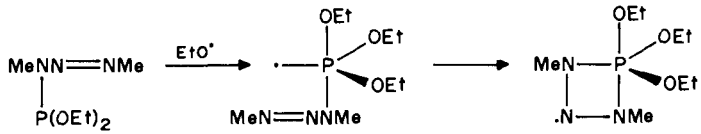


(12) (13)

osphoranyl radicals also undergo cyclization (reaction 21)[55]. The product radical from reaction 12 was reported to be trapped by orthoquinones to give adducts such as **14**[31]. Finally, results consistent with the trapping of phosphoranyl radicals by oxidative electron transfer have been published. Reaction 23b involves one of several metallic species proposed as potential oxidants in the reaction system:[56]



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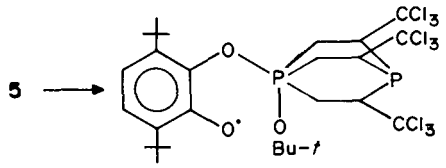


(14)

(22)

$$R^{\cdot} + PPh_3 \longrightarrow [RPPh_3]^{\cdot} \qquad (23a)$$

$$[RPPh_3]^{\cdot} + [CpW(CO)_3]_2 \longrightarrow R\overset{+}{P}Ph_3 + CpW(CO)_3^- + CpW(CO)_3^{\cdot} \qquad (23b)$$

Reactions 19–23 all involve phosphoranyl radicals formed on oxidative addition of a free radical to tricovalent phosphorus. Except for reaction 23, all evidence for these processes was inferred from ESR measurements alone. It may be possible to design reactions which capitalize on these concepts to give useful chemistry including the syntheses of molecules of unusual structure.

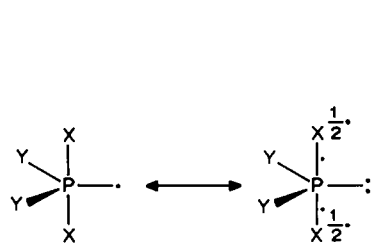
V. PHOSPHORANYL RADICAL STRUCTURE AND STEREOCHEMISTRY

Although the primary interest of non-specialists in this area of research may be in the factors which influence reaction pathway and the applications of these systems in synthesis

and elsewhere, it would still be a mistake not to include aspects of the great amount of work which has been done on the structural and stereochemical properties of the phosphoranyl radical intermediates involved in the majority of the reactions of free radicals with tricovalent phosphorus derivatives. ESR measurements, studies of overall reaction stereochemistry and theory have worked in complementary fashion in this area.

A. Structural and Geometric Types

Most of the early work[1] was concerned with phosphoranyl radicals with very large isotropic hyperfine phosphorus splittings (600–1300 G). The obviously high degree of spin density on phosphorus led to the assignment of structure by analogy to truly pentacovalent phosphoranes with the odd electron in an approximately sp^2-hybridized equatorial orbital (**15**). Consistent with a near-trigonal bipyramidal structure were the non-equivalencies of otherwise identical ligands[57]. A modification of this thinking was required by isotropic studies with H apical[58] and in anisotropic spectra of radicals with apical F[59] and Cl[60] substituents which showed a high proportion of spin density delocalized onto the apical substituents with consequent large apical phosphorus hyperfine splittings. Valence bond theory allows for this by inclusion of canonical from **16**, which features a two-electron, three-centered apical bonding system. In molecular orbital terms, orbital mixing to give a SOMO with antibonding character as displayed in **17**[59] accommodates well the observed spin density distribution. Structure **15**, however, reasonably approximates these species, especially their geometries, and is used throughout this chapter.



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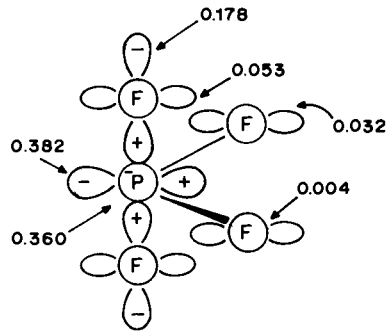
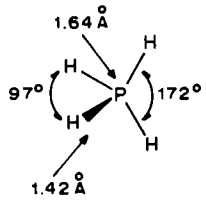


(17)[59]

As with truly pentacovalent phosphoranes, the relative preferences of substituents for apical and equatorial positions are expressed in terms of apicophilicities. To a first approximation apicophilicities follow group electronegativies, but orders are modified by the identities of the other substituents on phosphorus and the placement of phosphorus in a ring. Recent studies, to be discussed below, point to other factors, including apical bond strengths. Comparisons of several series of phosphoranyl radicals have led to apicophilicity orders. Thus, for non-cyclic compounds one order is[61] $Cl > CF_3 > RO >$ and another is[62] $Me_3Si(PhCH_2)N > RO$ and also[62] $(RO)_2P(O)NMe > RO$ and CF_3O, $(CF_3)_3CO$, FCO_2, FSO_3, $> F$[63]. For cyclic compounds[5], *t*-BuO > EtO > C_4H_4N (pyrrolyl) > $Me_3SiO >$ $(Me_3Si)_2N$ and[8] CF_3, $(EtO)_2P(O)O > RO$. For both cyclic and acyclic cases, the following is usually found[6]: F, Cl, $RCO_2 > RC(O)NR$, $OCN > RO$, $R_2N > H > R$. RO often does have greater apicophilicity than R_2N, but the order can be reversed, and they certainly have more nearly the same apicophilicities than they do in phosphoranes. A five-membered ring with O or N bonded to phosphorus

is more stable attached equatorial/apical than diequatorial[1a,b,e], and the same is true for six-membered rings, at least those containing two nitrogens[26]. In cyclic compounds, ring O is always more apicophilic than ring N. Since the bond angles about phosphorus are predicted by theory[64] to be collapsed somewhat towards the vacant equatorial position, i.e. towards local T_d symmetry (structures **18** and **19**), the difference in energy between equatorial/apical and diequatorial ring attachment may be less than it is with truly pentacovalent analogs.



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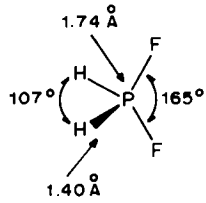

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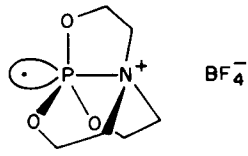
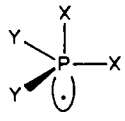


(20)

The majority of phosphoranyl radicals have been assigned trigonal bipyramidal structures with the vacant position (odd electron) equatorial (TBP-e) on the basis of INDO, CNDO, Hückel, MS_α and *ab initio* calculations[64]. Energy-optimized structures from the most recent *ab initio* methods for two species are given by **18** and **19** (4–31G basis set, d polarization functions on phosphorus and sulfur, unrestricted Hartree–Focke)[65]. Local C_{3v} symmetry, trigonal bipyramidal radicals with the unpaired electron apical (TBP-a) (**21**), are higher in energy, as indicated by both experiment and theory[64,66,67]. Another local C_{3v} structure is a σ^* species, **22**, of more nearly tetrahedral geometry with the odd electron in the P–Y antibonding orbital. An example is $[Ph_3PCl]^\cdot$ (**23**).[68]

ESR data for a tricyclic species of restricted geometry have been interpreted by one group as evidence for the geometry shown in **20**, that of a TBP-a species[69]. This claim has been challenged by a second group which proposes that the data are better interpreted as being those of σ^* radical which also would have local C_{3v} geometry but a different SOMO (see below)[67,70]. The isotropic phosphorus to 'apical' nitrogen hyperfine splitting of 22 G was pointed out as being nearly the same as for an apical N in a TBP-e structure[67,70], unlike what is expected for an apical N in a TBP-a radical[69]. The evidence that there is a high degree of spin density on nitrogen in species **20** is then *not consistent* with a TBP-a radical but rather supports the σ^* structure.[67,70]



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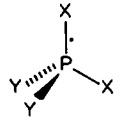

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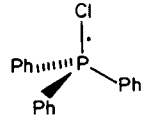

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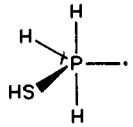
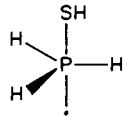


(24)

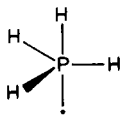
Ab initio calculations on $H_4P^{\cdot 65}$, $HS\dot{P}H_3$[65] and $FH_3P^{\cdot 66}$ (4-31G basis set) indicate a lower energy for the TBP-a structure compared with the σ^* alternative. On the other hand, there are ESR studies of phosphoranyl radicals in addition to **23** for which the σ^* configuration is even more stable than the TBP-e configuration (see below for some recent examples).

Recently, UHF 4-31G calculations[65] including d polarization orbitals showed $(PH_3SH)^\cdot$ to have a TBP-e minimum energy structure with SH equatorial (**24**). A TBP-a

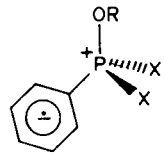
structure (apical SH) (**25**) was calculated to be 11.0 kcal mol^{-1} higher in energy as a point of inflection. For $PH_4^{\bullet}$ the TBP-a form (**26**) was calculated to be a 'top hill' structure 18.7 kcal mol^{-1} above the stable minimum, TBP-e form. All tetrahedral structures, said to approximate σ^* configurations, were dissociative. The relative energies and stabilities of TBP-a and σ^* radicals are of special interest since Roberts has proposed that σ^* radicals may serve as potential intermediates or transition states for permutational exchange of apical and equatorial ligands and also the intermediates through which α- and perhaps also β-scission take place (see below)[42,70,86].



(**25**)



(**26**)

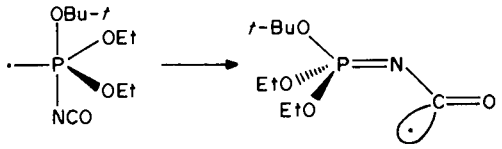


(**27**)

There is complete agreement based on both experimental data[71] and theory at the *ab initio*[72] and MNDO–SCF[73] levels that symmetrical radicals such as $[(RO)_3PP(OR)_3]^{+\bullet}$ are σ^* species. Further, theory suggests[72] that for $Z_3PX^{+\bullet}$, the greater the energy of single electron transfer between the $Z_3P^{+\bullet}$ and X groups, the more likely it is that the cation radical will be a TBP-e species. Hence $X_3P^{+\bullet} + X_3P$ leads to a stable σ^* radical.

Another type of phosphoranyl radical structure is illustrated by **27**, which is termed a ligand-π radical. These radicals have small phosphorus hyperfine splittings (9–45 G)[62,74,75]. They are probably not very different in energy from their TBP-e counterparts. Thus, configuration **27** is formed when X = RO. A TBP-e structure is populated, however, for X = H, MeS, Cl or CF_3CH_2O[74], substituents which do not readily stabilize a positive charge on phosphorus. Other examples of ligand-π radicals include[74] $[CH_2{=}CHPX_2Y]^{+\bullet}$ and various tri- and tetra-aryl phosphoranyl radicals[1a,e].

A final class of phosphoranyl radicals has the odd electron completely delocalized through ylide-like bonding. These are termed ligand-σ radicals. An example is **28**, which was observed by ESR to be formed on rearrangement of an initially formed TBP-e precursor (equation 24)[76].



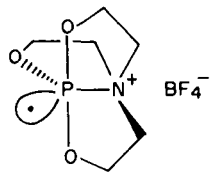
(24)

(**28**)

B. Recent Experimental Structural Studies

A number of significant new examples of radicals of the above types have been reported since the subject was last reviewed. Related to the disputed structure **20**, it was reported from single-crystal ESR measurements that the TBP-e permutamer of **20**, structure **29**, was formed at 77 K from the hydridophosphorane, whereas **20** resulted at 193 K[69b,c]. Radical **29** was not converted into **20** on annealing **29** at 193 K. Another radical formed by

reduction of a thiophosphate precursor was said to have the TBP geometry structure **30**[69c]. Strong criticism of this assignment also has appeared.[67,70] At this point it is not certain that a phosphoranyl radical of truly TBP-a geometry has been characterized. In fairness, it should be remembered that both the TBP-a and σ^* structures have local C_{3v} geometries and differ, although not insignificantly, only in bond angles about phosphorus and in the nature of the SOMO. In fact they probably do not differ greatly in energy, and structures intermediate between the two may be encountered.



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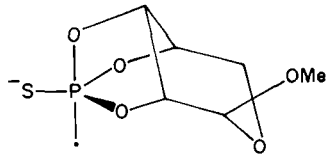

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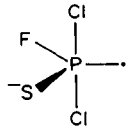
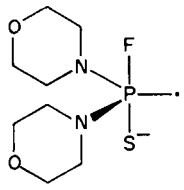


(31)

More evidence for the formation of observable σ^* radicals has been presented, often from electron capture by $X_3P{=}Z$[77-79]. The frozen-matrix-isolated TBP-e radical **31** was formed at 77 K on X-irradiation of $Cl_2P(S)F$[77]. Similarly, TBP-e **32** resulted, but the dipyrrolidinochlorophosphine sulfide gave the σ^* radical, **33**[78]. It also is notable that in **31** the chlorines rather than the fluorine are apical. This is contrary to the above ordering which gave equal apicophilicities to these substituents. Clearly, electronegativity alone does not determine apicophilicity.



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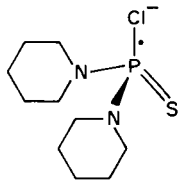

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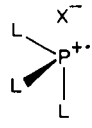


(34)

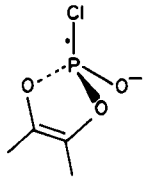
In fact, it has been proposed[70] that charge transfer from phosphorus to an apical ligand will be an important stabilizing factor (**34**). The apicophilicity of A for a hypothetical radical, $[ABPL_2]^{\cdot}$, has been estimated quantitatively by use of equation 25, which predicts apicophilicity to increase as the value of α_A decreases. In this equation $IP(BPL_2)$ is the ionization potential for BPL_2, EA the electron affinity of A$^{\cdot}$ and D(PA) the average bond strength estimated from that for PA_3. Indeed, this treatment predicts a greater apicophilicity for Cl than for F, as seen with **31**.

$$\alpha_A = IP(BPL_2) - EA(A^{\cdot}) + D(PA) \tag{25}$$

Related arguments have been used to predict when a σ^* species would be of lower energy than its TBP-e alternative[70]. When the value of α_A in a species $[APL_3]^{\cdot}$ is much smaller than that of the other three ligands (greater apicophilicity), a σ^* radical with a σ^*(P–A) orbitil will be favored. The difference between **32** and **33** can thereby be explained (see related ideas above concerning $[Z_3PA]^{+\cdot}$ species[72]). Whereas many phosphoranyl radical structure appear to follow the predictions based on α, $[Ph_3PBr]^{\cdot}$ is more distorted in structure toward TBP than is Ph_3PCl, even though σ_{Br} is smaller than α_{Cl}. Matrix effects

were suggested to be dominant in the bromo case[70]. However, an argument that distortion towards TBP-e geometry for $[Ph_3PBr]^{\cdot}$ is to be expected based on calculations for $[Z_3PA]^{+\cdot}$ has also been advanced[72].

Indeed, clear evidence for the effect of medium on structure has been noted[79a]. In a crystalline matrix the radical of σ^* structure **35** is formed. In a frozen solution, however, its structure was shown to be TBP-e (**36**). Radical **36** may have been generated from **35**. The expected relatively small energy difference between various geometries of phosphoranyl radicals is substantiated by this result.



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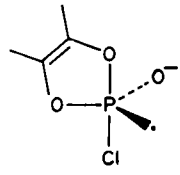
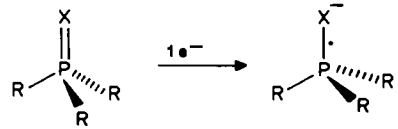


(36)

From the above argument concerning apicophilicity and ESR data, both $[Me_3PSR]^{\cdot}$ and $[Ph_3PSR]^{\cdot}$ were assigned probable σ^* structures with σ^*(P–S) orbitals containing the odd electron[70]. This assignment was questioned, however, in the publication[65] containing the calculations reported above for $[H_3PSH]^{\cdot}$ (**24**).

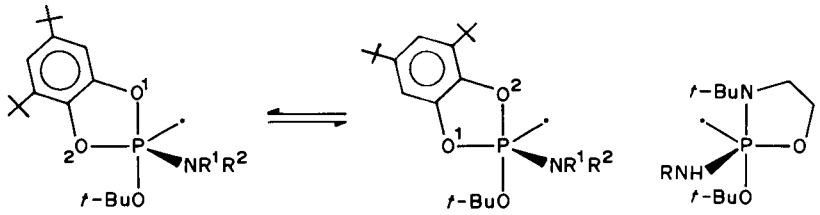
Radicals formed on electron capture by $R_2P(S)P(S)R_2$ (R = Me, Et, Ph) were assigned, as a result of single-crystal ESR studies and *ab initio* calculations, structures with the odd electron in an antibonding orbital symmetrically distributed over the two phosphorus atoms[79b]. Because it did not possess rotational symmetry, this radical was not designated as a σ^* species. When the disulfide contains two chiral phosphorus centers, MePhP(S)P(S)MePh, the starting diastereomer geometry determines the electron distribution[79c]. Kinetic factors were suggested to be responsible for the unsymmetrical electron distribution in the product of capture by the *meso* compound and symmetrical distribution in the radical formed from the racemic diastereomer.

X-irradiation of single-crystal trialkylphosphine sulfides and selenides led to electron-capture products of yet another essentially σ^* radical with C_3 or slightly C_s geometry depending on the geometry of the precursor[79d]. However, the P=S or P=Se bond captures the electron, unlike what occurs in formation of **32** and **33** (equation 26).



X = S, Se (26)

A most interesting series of radicals generated from *o*-phenylene phosphoramidites have been studied by ESR. They exist in two forms, **37** and **38**, which are slowly interconverted (equation 27)[80]. The presence of the five-membered ring so stabilizes them against ring α-scission to form a phenoxy-like radical that amino (α-scission) and *t*-butyl radicals (β-scission) are observed instead. The competition between α- and β-scission is influenced by the nature of the amino group. For the cases $R^1 = H$, R^2 = alkyl, β-scission is observed, whereas α-scission is the rule for $R^1 = R^2$ = alkyl. At low temperatures, a bimolecular loss of signal was seen.

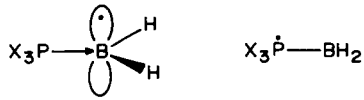


(27)

(37) (38) (39)

When radical **39** is generated, only one stereoisomer is noted[81], perhaps because of steric repulsions between the *tert*-butoxy and NHR groups when the *tert*-butyl is equatorial. For the case R = *t*-Bu, a normal ESR spectrum was noted, but introduction of a chiral R group (*sec*-Bu or $MeCHCO_2Et$) led to the appearance of the superimposed spectra of two diastereomers with hyperfine coupling constants differing by about 6 G.

Interestingly, the low-temperature ESR spectrum of the π radical $[t\text{-BuOPPh}_3]^{\cdot}$ showed the odd electron to be confined to one ring[70]. At higher temperatures all three rings became magnetically equivalent.



(40) (41)

Reaction of *tert*-butoxy radicals with $X_3P \rightarrow BH_3$ gave the radical $[X_3PBH_2]^{\cdot}$, shown by ESR measurements to have the structure **40** (X = MeO, CF_3CH_2O, Me_2N, Et, *n*-Bu, *t*-Bu, Ph)[82], which is really a ligand-π phosphoranyl radical and evidently is more stable than the alternative TBP form, **41**. These so-called phosphine–boryl radicals readily abstract bromine atoms from alkyl halides. When $R_2PH \rightarrow BH_3$ reacts with *t*-butoxy radicals, however, the radical from the P—H moiety is abstracted (equation 28)[83]. The phosphinyl–borane radical generated adds to allenes and isocyanides, like the phosphine–boryl radical, and abstracts bromine from alkyl bromides.

$$t\text{-BuO}^{\cdot} + R_2PH \rightarrow BH_3 \longrightarrow R_2\dot{P} \rightarrow BH_3 \qquad (28)$$

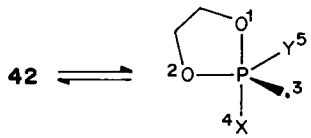
C. Permutational Isomerization

It became evident some time ago from variable-temperature ESR measurements that the ligands on TBP-e phosphoranyl radicals can undergo very rapid, intramolecular exchange between apical and equatorial positions (see **37**⇌**38** in equation 27). Several questions have been asked about these processes: how fast are they?; what is the stereochemical mode of the exchange?; by what mechanism (pathway) does permutation occur? The permutation mode classifies a rearrangement with respect to numbers and types of substituents (axial or equatorial) participating in the exchange and the stereochemistry of the process without any regard to pathway.

Variable-temperature ESR measurements have shown that for a variety of $RO\dot{P}X_3$ (X = H[64a], Me[26], F[84]), the first-order k_{ex} is 10^6–$10^7\ s^{-1}$ at about 200 K. $\Delta G^{\neq}$ of exchange for $EtO\dot{P}F_3$[84] is 7.2 kcal mol^{-1}. For *t*-$BuO\dot{P}Me_3$[26] E_a is 3.6 kcal $mole^{-1}$, and for *t*-$BuO\dot{P}H_3$[64a,85], $\Delta G^{\neq}$ is 5.3 kcal mol^{-1}. For another non-cyclic case, $C_4H_4NP(OEt)_3$[5], E_a is 4.4 kcal mol^{-1} (C_4H_4N = 1-pyrrolyl). It is intrinsically impossible to define the mode of apical/equatorial ligand exchange for the above acyclic cases.

Particularly fruitful ESR studies have involved cyclic radicals illustrated by **42**. Since pentacovalent phosphoranes undergo ligand exchange by a mode one (MI) process, a natural assumption would be that phosphoranyl radicals should do likewise, especially since the vacant position in the TBP-e structure is an equatorial odd electron which one would be tempted to treat as the pivot group. Such a process is illustrated by the equilibrium **42**⇌**43**, a pairwise exchange of apical and equatorial substituents (equation 29). The odd electron remains equatorial. However, variable-temperature ESR work[6,8,41,42,86] focusing on hyperfine splittings between phosphorus and the CH_2 hydrogens excludes the M1 exchange and is only understood via an M4 (*exo*) exchange, **42**⇌**44** (equation 30). These processes also are rapid with $k_{ex} = 10^7$–10^9 s^{-1} at about 200 K and E_a in the range 2–5 kcal mol^{-1}[41,42,86].

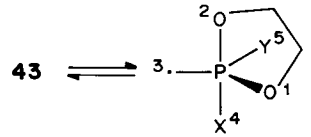
(42) (43) (29)



42 (30)

(44)

The M4 (ring) exchange, wherein O(1) and O(2) of **42** together with the odd electron are involved (**43**⇌**45**, equation 31), generally occurs more slowly and only when X = Y. Measured E_a values are 6–8 kcal mol^{-1} and k_{ex} 10^6–10^8 s^{-1} at 273 K[6,8]. Five-membered rings evidently do not readily accommodate the geometry changes required for M4(ring) exchange, which may involve an intermediate or barrier state that is TBP-a or σ^* (**46**) and requires the ring oxygens to be in equatorial (basal) positions and the O—P—O ring angle to be expanded.

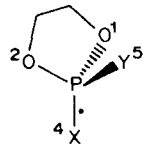


43 (31)

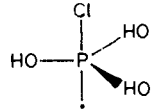
(45)

A very significant investigation of the effect of the nature of Y on the rate of M4(ring) exchange has been reported[70]. For Y = RO and X = MeS, HS or Cl, k_{ex} for the M4(ring) process at 273 K was 10^9 s^{-1} or greater. This effect was rationalized in terms of the influence of the nature of X on the difference in energy between **43** and the proposed σ^* intermediate (**46**) for M4(ring) exchange with the odd electron in the P—X σ^* orbital. The suggestion was that the X substituents listed above are able to stabilize the σ^* intermediate (**46**). Arguments using structures similar to **34** and equation 25 for estimating α_A (in this instance α_X) were used. X = F, as noted above, does not have so great an apicophilicity

(higher value of α_F) as Cl and consequently does not stabilize a σ^* radical such as **46** to the extent that Cl would. In fact, F does not speed the M4(ring) exchange, whereas Cl does. With regard to the effect of SH on K_{ex} for M4(ring) isomerization (and for that matter its apicophilicity), it is interesting that by *ab initio* methods[65] SH is predicted to be equatorial, not apical, in $HSPH_3$ (structure **24**) and also in $HSP(OH)_3$.



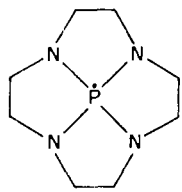
(46)



(47)

Certainly pertinent to the above questions is the *ab initio* calculation which predicts that the energy of $[(HO)_3PCl]^{\cdot}$ is optimized (under the constraint that Cl be on a C_{3v} axis) as a TBP-a species (**47**)[79a]. No stable geometry could be found when one O—P—O angle was held at 100° as it is in ring structure **46** or **35**. A five-membered ring attached to the basal (equatorial) positions of **47** would be very strained, thereby reducing the rate of M4(ring) exchange via such a species. A more tetrahedral geometry would reduce the strain in the five-membered ring. Perhaps the substituents which favor M4(ring) exchange do lower the energy of a more tetrahedral form, even one approaching a σ^* structure (see above)[70].

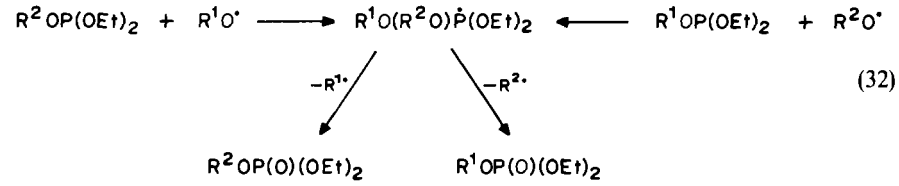
One case, structure **48**, has been presented for which temperature-dependent ESR results in a solid matrix were interpreted to require an M1 exchange, as in pentacovalent phosphorus-containing systems, with the odd electron as pivot (remaining equatorial)[69b]. This result is probably a consequence of the solid matrix or the stereochemical restrictions of the tetracylic ring system, which may favor a permutation of M1 which normally would lie energetically above the usual M4 process.



(48)

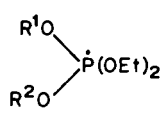
A number of studies designed to look for a memory effect in product distributions formed by two or more β-scissions within a single phosphoranyl radical, generated by more than one route (equation 32), have been carried out. The premise is that the attacking radical will enter the TBP intermediate preferentially in the apical or equatorial position, and all β-scissions will occur preferentially at one of those positions. Then, unless the groups are rapidly exchanged between those two positions prior to β-scission, the product ratio (phosphates of equation 32) will be influenced by, i.e. have a memory of, the pathway of formation of the phosphoranyl radical.

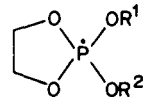
Origin-independent product ratios were found for radicals **49**–**54** by examination of phosphate and/or radical ratios[21,22,42]. A six-membered ring case also was examined[22]. Memory effects were not evident in any instance. Indeed, these results are consistent with the now known rates of apical/equational ligand exchange and measured E_a free energies

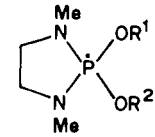


(32)

of activation for β-scission. The one exception reported is for reaction of $PhCH_2O^{\cdot}$ with *p*-$MeC_6H_4CH_2OP(OEt)_2$ and *vice versa*[87]. It now seems questionable that even a benzyloxy ligand can undergo scission more rapidly than exchange.

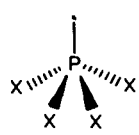


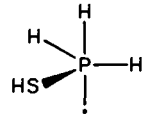




(**49**) $R^1 = s\text{-Bu}; R^2 = Et$ (**51**) $R^1 = t\text{-Bu}; R^2 = t\text{-}C_5H_{11}$ (**53**) $R^1 = i\text{-Pr}; R^2 = s\text{-Bu}$

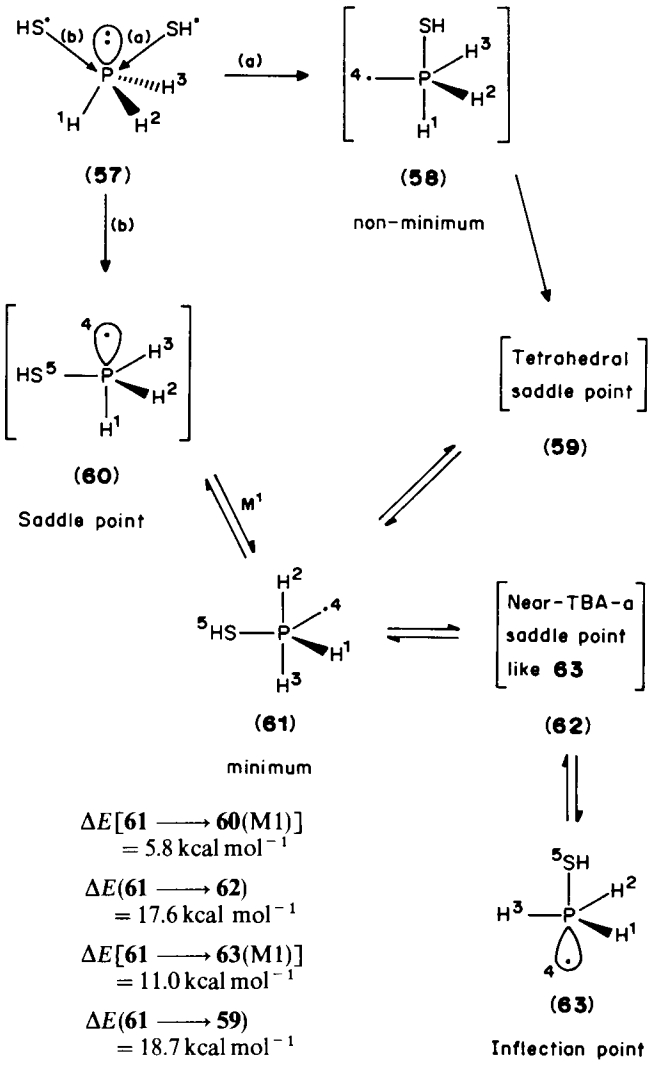
(**50**) $R^1 = Et; R^2 = c\text{-}C_4H_9$ (**52**) $R^1 = t\text{-Bu}; R^2 = i\text{-PrCMe}_2$ (**54**) $R^1 = Et; R^2 = s\text{-Bu}$





(**55**) (**56**)

The mechanism of a permutation of a given mode deals with the pathway. Calculations at several levels[64g,h,i,65,66] have shown that an M1 exchange via a barrier state of square pyramidal configuration with the pivotal odd electron apical (**55**) is a high-energy pathway. Early CNDO calculations suggested that the rearrangement of **15** to a barrier state or intermediate similar to TBP-a **21** (an M2 process) or σ^* **22** would be a relatively low-energy pathway[54h]. Either intermediate could regenerate a TBP-e species with the overall permutation (M2 × M2) exchanging apical and equatorial substituents according to M4. More recently, as stated earlier, *ab initio* calculations[65,66] have indicated that TBP-a structures (**21**) are of lower energy than their more nearly tetrahedral σ^* alternatives (**22**). Even then TBP-a structures are much higher in relative energy than they should be as barrier structures for permutations of substituents, since E_a values (see above) for ligand exchange are relatively low. As mentioned above, structure **25** is calculated to be 11.0 kcal mol^{-1} above the most stable configuration **24**. Similar structures and energies above optimal TBP-e geometries for TBP-a structures include **26** (18.7 kcal mol^{-1}) and $HS\dot{P}(OH)_3$[65] (HS apical, 18.3 kcal mol^{-1}). A structure very close to **56**, however, was calculated to be only 5.8 kcal mol^{-1} higher in energy than **24**[65]. In some cases the TBP-a structures for which energies were calculated did not turn out to be either intermediates or symmetrical barrier states (saddle points). Nonetheless, an estimate of relative energies is provided. Clearly, although somewhat high absolute energies are often calculated for TBP-a species, they still provide relatively low-energy structures as potential intermediates or barrier states for permutation of substituents on phosphoranyl radicals whose lowest energy geometry is TBP-e. Further discussion of the details of mechanism and mode of permutation is given in Sections V.D and V.E in the context of Scheme 1.



SCHEME 1

D. Stereochemistry of Formation

The question was raised above as to the kinetic selectivity for the entrance of the attacking radical, Z˙, into PX_3 to form TBP-e $Z\dot{P}X_3$. Is the Z in the initial adduct apical or equatorial? There is no solid direct experimental evidence on this question such as an ESR measurement showing the initial position (apical or equatorial) of Z to be different than it is after thermal equilibration. A reasonable working assumption has been that Z˙ is introduced intially apical. The microscopic reverse of Z˙ addition is α-scission. The three-center, three-electron apical bonds in a TBP-e phosphoranyl radicals are presumably

longer and weaker than equatorial ones. Kinetic evidence (see below) for preferential, and most reasonably apical, α-cleavage has been presented[26]. Indeed, early calculations by Howell and Olsen[64a] for the reaction of H· with PH_3 favored apical introduction of H.

Later *ab initio* work of Janssen *et al.*[78], however, is in disagreement. Working within a C_{3v} constraint, they concluded that attack of a hydrogen atom along the C_3 axis was more energetically favorable in the direction of the LUMO rather than the HOMO (lone-pair) orbital on phosphorus. This leads to inversion of configuration at phosphorus. On oxidation of a phosphine or trialkyl phosphite, product phosphine oxide or phosphate of inverted configuration would result. This is in contradiction to the known overall stereochemistry of oxidation of such compounds to be discussed below.

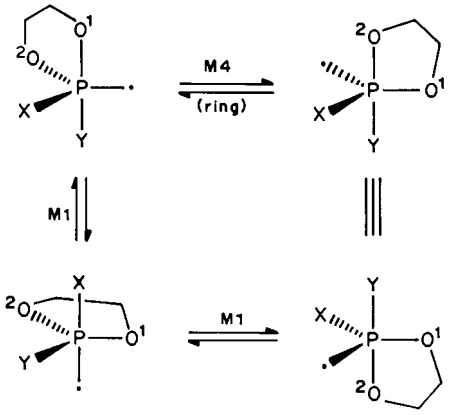
The most recent *ab initio* calculations, those of Gonbeau *et al.*[65], considered for the reaction $HS· + PH_3$ two directions of attack not examined by Janssen *et al.* They too found the HOMO approach along the C_3 axis in the direction of the lone pair (HOMO approach) to be a higher energy pathway than the LUMO approach along the same axis. However, two approaches shown in Scheme 1 have been lower energy barriers than attack on the LUMO and one leads directly to a TBP-e intermediate with SH equatorial (**61**).

Pathway a for apical introduction does not lead to a stable intermediate, **58** (in fact, **58** is a non-minimum on the pathway to **59** and **61**). Path b leads to saddle point structure **60** which is close to a TBP-a species with SH equatorial. Since **58** and **60** are TBP species on the route to the structural minimum, **61**, in Scheme 1, the authors sought to define the permutation pathway which would convert **60** and **58** into **61**. Their treatment led to an M5 process for **58** → **61** with a tetrahedral barrier (saddle point) structure (**59**) 18.7 kcal mol^{-1} above **61**. As noted earlier, **60** (**56**) is just 5.8 kcal mol^{-1} above **61**. It was converted to **61** via an M1 process. Similarly, the exchange to convert **61** to the TBP-a (HS apical) structure (**63**) was examined. The barrier structure for the latter (**62**) was 17.6 kcal mol^{-1} above **61** in energy, the overall isomerization being of M1. The obvious conclusion was that the lowest energy pathway for formation of the only stable TBP structure is **57** → **60** → **61**, i.e. direct equatorial introduction of attacking HS· into TBP-e **61**. This also is the kinetically preferred route for the reverse, α-scission.

This is a most interesting finding. However, it would be dangerous to generalize the kinetic preference for equatorial introduction of HS and α-scission to attacks of all radicals on tricovalent phosphorus. These calculations also should be carried out on systems in which a TBP-e structure related to **58** is a stable minimum and also when it is the more stable minimum. If a structure such as **58** is stable, it may be kinetically preferred regardless of overall thermodynamics. On the other hand, the introduction of the attacking radical may be controlled by the relative thermodynamic stabilities of the structures formed.

Again, no evidence for an M1 pathway through a configuration similar to **55** was found. The difference in permutational properties between phosphoranyl radicals and phosphoranes is again emphasized. If radicals typically are introduced into TBP-e phosphoranyl radicals equatorially, this is another important contrast to pentacovalent phosphorus systems. A third difference concerns the above mentioned apicophilicities. Apparently these calculations also suggest that the mode of permutations may vary with the species being interconverted.

Unfortunately, the low-energy pathway for isomerization **61** → **60** (and return to an isomer of **60**) will not accomplish the M4(ring) or M4(*exo*) processes seen by ESR. It will, however, effect the apical/equatorial exchange of H^1, H^2 and H^3. Both the M4(*exo*) and M4(ring) processes can occur by successive M1 isomerizations of the type **61** → **63**. Equation 33 illustrates the M4(ring) permutation (M1 × M1 = M4). This process differs from that of Roberts which employs σ^* intermediates or barrier structures with Y apical.[42,70,86] It is more difficult to explain the increase in the rate of M4(ring) exchange with increased apicophilicity of Y, since in equation 33 Y moves into the equatorial position.



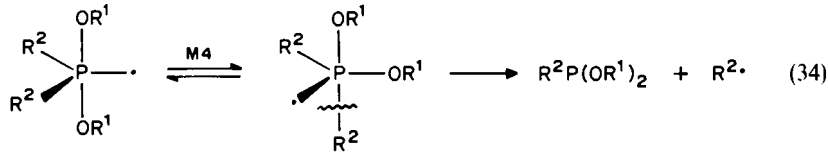
(33)

Sequence 33 again emphasizes the fact that overall M4 processes may proceed by multiple permutations of other modes (M1 × M1, M2 × M2, etc.). The key to specifying pathway is in defining the lowest energy barrier.

Gonbeau *et al.*[65] also made a point about the surprising positioning of the SH equatorial rather than apical as being contrary to what the relative electronegativities of SH and H would predict. In this vein they also calculated an optimized TBP-e geometry with SH equatorial for $HS\dot{P}(OH)_3$. They failed, however, to mention the ideas discussed earlier concerning the influence of a weakened ligand-P bond, such as P—H or P—Me, in favoring apicophilicity as predicted by α_X[70].

E. Stereochemistries of α- and β-Scissions

The microscopic reverse of oxidative addition of a radical to tricovalent phosphorus of course is α-scission. Kinetic work on the decay of phosphoranyl radicals gives strong evidence for the apical site selectivity of the α-scission process[26]. Hence the rate of α-scission for radical **64** depends on both the stability of $R^{1\bullet}$ and the energetic ease of populating presumed **65** in which the alkyl is in the apical position (equation 34). By contrast, R^1OPR_3 radicals undergo α-scission very rapidly, because there is an alkyl group in a position to undergo α-scission without prior permutational rearrangement. Of course, it is possible that the stereospecificity is for the equatorial position. This would require, however, the highly unlikely possibility that the alkyl groups are preferentially apical. Other evidences for site-selective, apical α-scission have been summarized[1b].

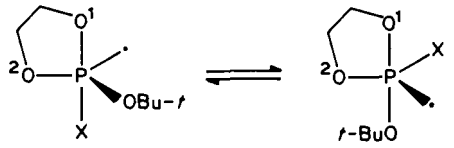


(64) (65) (34)

Many of the arguments for apical α-scission involve a presumed knowledge of the positions of ligands in the TBP-a radicals being studied (see above). The chance that such assignments to apical and equatorial positions, e.g. to RO and R groups, are in fact reversed, which would reverse the inferences regarding apical vs equatorial α-scission, is remote.

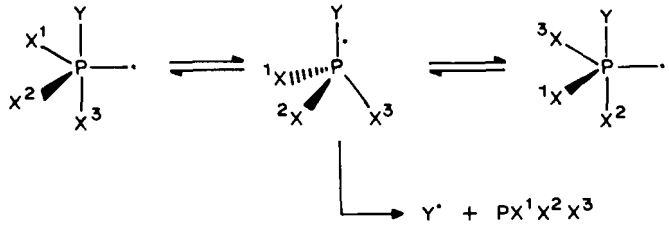
Intuitively, it seems likely that β-scission is also stereoselective for the apical or equatorial position, but convincing experimental evidence is not available. In essence, the argument for preferential equatorial β-scission is derived from the finding that in the equilibrium **66**⇌**67** those substituents, X, which appear to shift the equilibrium in favour of **66** increase the rate of β-scission[88].

The *ab initio* calculations on $HSPH_3$ were also applied to β-scission[65]. Stable **61** underwent S—H bond cleavage from the equatorial position with a transition-state geometry very close to **61** except for stretching of the H—S bond. Only after the transition state does the geometry begin to move towards that of the pyramidal product, $H_3P{=}S$. Although not mentioned by the authors, this transition state explains why the rate of β-scission responds well to changes in the stability of the alkyl radical generated. The negligible amount of rehybridization at phosphorus at the transition state also is consistent with the fact that β-scission for RO substituents is normally slower than α-scission, even though the former is much more favorable energetically overall. The transition state for β-scission simply resembles the reactant phosphoranyl radical, as is often true for strongly exothermic processes.



(66) (67) (35)

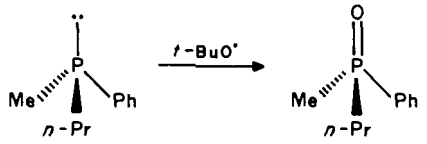
Finally, it should be mentioned that Roberts and coworkers[42,70,86] have attempted to bring together in a reasonable way the M4 permutations and α-scission by suggesting that both proceed by the same sort of σ^* intermediate formed reversibly by elongation of an apical ligand in the TBP-e form to become the apical ligand in the σ^* species (equation 36).



(36)

F. Overall Stereochemistries of Reactions at Phosphorus

The stereochemistries of oxidation, substitution and Arbuzov reactions at tricovalent phosphorus have been determined with a variety of diastereomeric cyclic compounds and optically active phosphines. Such processes are overall stereoselective and stereospecific. Examples of oxidations are reactions 37[46] and 38[46].



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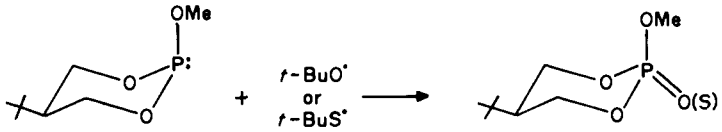
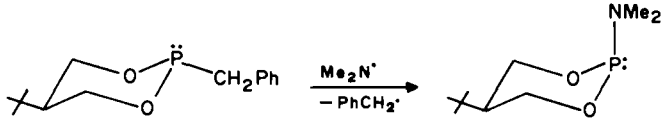
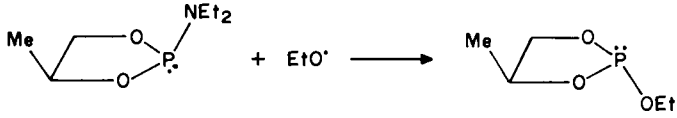


(38)

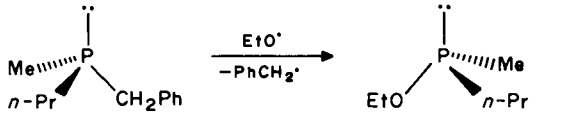
Five-membered ring phosphites behaved analogously.[89] Substitution with inversion at phosphorus was demonstrated in reaction 39 and also with five-membered ring phosphonites[90]. Attack by EtO· at $PNEt_2$ in five-membered rings gave inversion at phosphorus on displacement of Et_2N·[91] (equation 40). Radical displacements involving phosphines proceeded similarly, (equation 41)[92]. Free-radical Arbuzov processes were shown to proceed with the overall stereochemistry shown in equation 42 in both five- and six-membered rings[93].



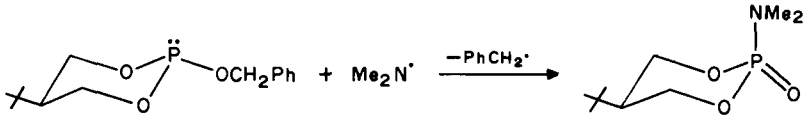
(39)



(40)



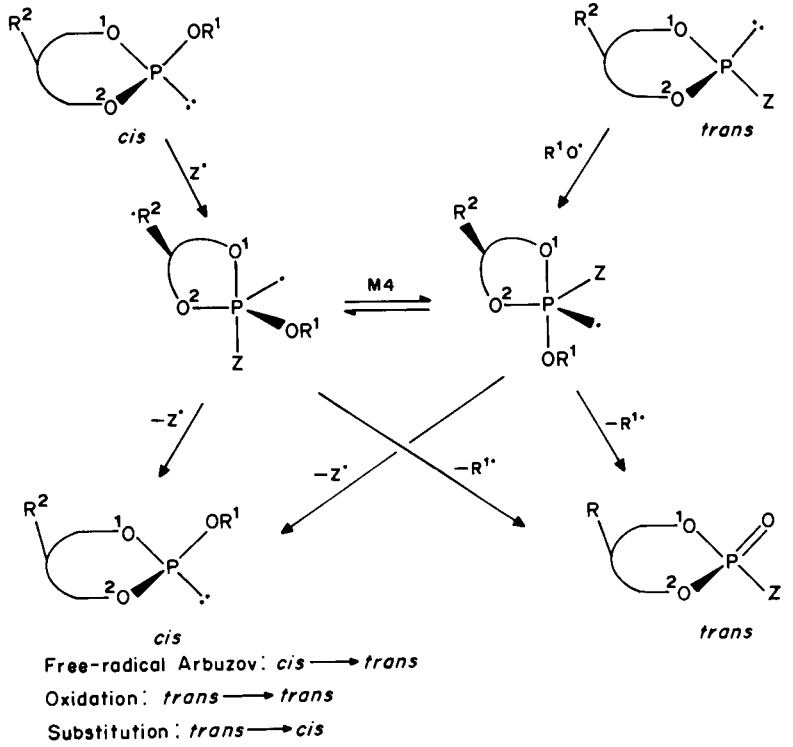
(41)



(42)

All of the observed stereochemistries allow for formation of a TBP-e intermediate by a stereoselective introduction of the attacking radical. Further, the stereochemistries of the overall reactions are unperturbed by subsequent M4 permutations prior to scission which may occur simply because ligand exchange is more rapid than scission, as shown above, or because a permutation is required to move the group undergoing scission into the required apical or equatorial site for that scission.

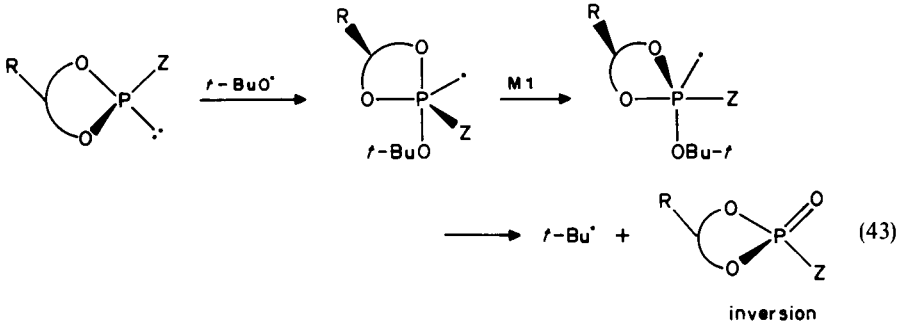
Scheme 2 illustrates this well for the cyclic cases. Starting with the *cis* or *trans* diastereomer, an intermediate which has the ring attached apical–equatorial is formed on apical introduction of attacking radical. The apical/equatorial preference for ring attachment is well demonstrated at least thermodynamically and especially for five-membered rings[1a,b,e]. Immediate α- or β-scission gives the product of stereochemistry required by the experimental observations. Most notably, an M4 permutation prior to scission leaves the overall stereochemistry unperturbed. Although this is a simplified view of the effects of M4 isomerizations on stereochemistry, topological graphs have been given



SCHEME 2 Reprinted with permission from *Acc. Chem. Res.*, **15**, 117 (1982). Copyright (1982) American Chemical Society.

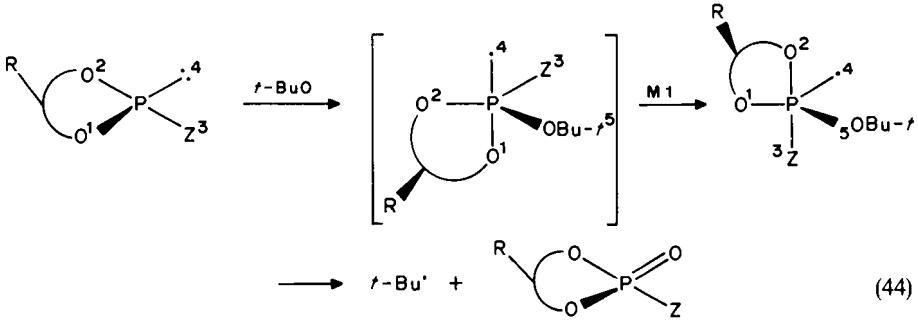
elsewhere[2,46a,93,94] which show that products of stereochemistry opposite to that observed cannot be obtained following M4 exchange except from scission of TBP-a intermediates which are high in energy and not readily populated.

M5 permutation also is permitted by the observed stereochemistry but excluded by the ESR results cited above. M2 and M3 exchanges are excluded by the stereochemical results. The failure of M1 exchange (Berry pseudorotation) to meet the experimentally established stereochemical criterion (retention) is illustrated for oxidation by equation 43.



(43)

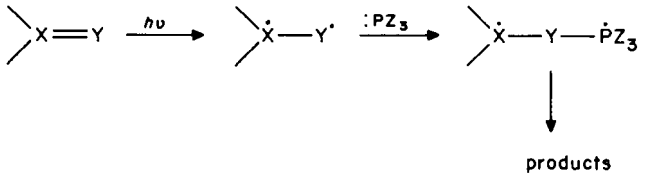
It is interesting to use Scheme 1, including the introduction of the attacking alkoxy radical equatorial, and the concept of equatorial β-scission, to predict the same retentive stereochemistry of oxidation (equation 44). Further, the reverse of **57** → **61**, but with expulsion of $H^{2\bullet}$, for example, would be a substitution process and would proceed with inversion, again as observed experimentally. To bring the $H^{2\bullet}$ back in again equatorially to reform **60**, and then generate $H_3P=S$ by β-scission, models the radical Arbuzov reaction with the stereochemistry observed experimentally.



(44)

VI. PHOTOCHEMICAL ANALOGUES OF RADICAL REACTIONS

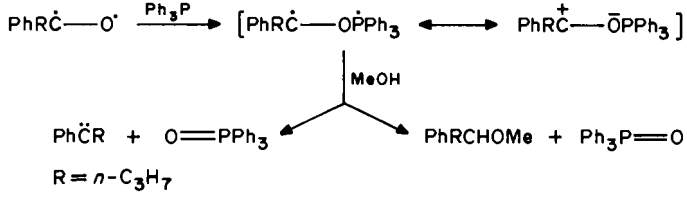
It is well known that excited states of ketones, thioketones and alkenes undergo reactions parallel to those of alkoxy, thiyl and alkyl radicals[95]. With tricovalent phosphorus the premise on which reactivity of electronically excited double bonds would be based is illustrated by equation 45, where a 1,3-biradical intermediate or transition state is depicted. ESR evidence and a limited number of product studies attest to the general correctness of this idea, although the presence of 1,3-biradical intermediates is not necessarily proved. Certain aspects of this research have been reviewed[95].



(45)

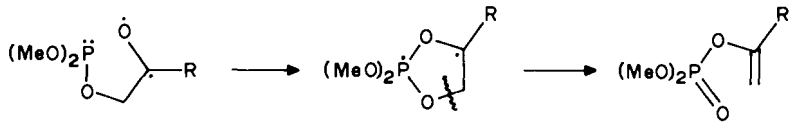
A. Ketones, Quinones and Thioketones

Benzophenone was shown early on[96] to be reactive with Ph_3P and later shown to give $Ph_3P{=}O$ in a reaction that also can be diverted to other products in methanol, as shown for butyrophenone (equation 46)[97].



(46)

Ketophosphites are photorearranged to enol phosphates, perhaps via a cyclic 1,3-biradical (equation 47), which yields stable products in a β-scission step[98]. Since intersystem crossing is so very fast with ketones, presumably these are reactions of triplet excited carbonyls.



(47)

The first photochemical displacement of a group from tricovalent phosphorus by an excited ketone featured benzophenone in an α-scission process, which can be written in terms of an intermediate phosphoranyl radical (equation 48)[99]. Recent ESR evidence has been provided for reaction 48 together with evidence that the phosphoresence of Ph_2CO is indeed quenched by Ph_2PPPh_2[100]. The rate constant for the reaction of triplet benzophenone with tetraphenyldiphosphine was found to be 2×10^8 lmol^{-1} s^{-1} at 300 K. Tetraethyl pyrophosphite reacted with benzophenone triplets ($k = 8.0 \times 10^8$ s^{-1} at 300 K) in a process (reaction 49), also monitored by ESR[100] and intermediate **68** identified. Reactions 48 and 49 have their *tert*-butoxy radical counterparts which give *t*-$BuOPPh_2$ and *t*-$BuOP(OEt)_2$. The latter reaction has a rate constant of 2.9×10^9 lmol^{-1} s^{-1} at 298 K[101]. Anthraquinone and 1,4-di-*tert*-butylbenzophenone gave parallel reactions with tetraethyl pyrophosphite as did di-2-thienyl ketone and thioxanthen-9-one, but only benzophenone was reactive with tetraethyldiphosphine[99]. Fluorenone was unreactive even with the pyrophosphite[102]. A series of quinones similarly reacted only with tetraethyl pyrophosphate.

$$[Ph_2\dot{C}—\dot{O}]_{T1} + Ph_2PPPh_2 \longrightarrow \underset{\underset{Ph_2\dot{C}—O}{|}}{Ph_2\dot{P}—PPh_2} \longrightarrow Ph_2\dot{C}—OPPh_2 + Ph_2P^{\bullet} \quad (48)$$

$$[Ph_2\dot{C}—\dot{O}]_{T1} + (EtO)_2POP(OEt)_2 \longrightarrow \underset{\textbf{(68)}}{Ph_2\dot{C}OP(OEt)_2} + {}^{\bullet}\overset{\overset{O}{\|}}{P}(OEt)_2 \quad (49)$$

The photoreaction of the presumed singlet excited state of 4,4′-dimethoxybenzothioketone with tetraethyl pyrophosphite proceeds analogously[103]. Moreover, with Ph_2PR a variety of R$^{\bullet}$ were displaced (equation 50).

$$\underset{\text{Singlet}}{(p\text{-}MeOC_6H_4)_2\dot{C}—\dot{S}} \xrightarrow{Ph_2PR} \rangle\dot{C}—S\dot{P}Ph_2 + R^{\bullet} \quad (50)$$

$$R = PhCH_2,\ Ph,\ Ph_2P(CH_2)_n,\ (Ph_2P)_2CH$$

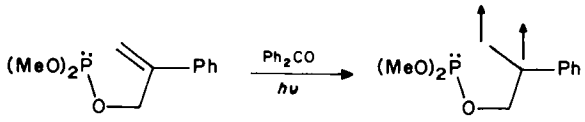
B. Alkenes

Although less extensively explored, photoexcited alkenes also undergo radical-like reactions with tricovalent phosphorus. An intermolecular example is reaction 51, studied from a product standpoint[104]. More recently, intramolecular photorearrangement processes have been investigated[105]. Direct photoirradiation of **69** gave products corresponding formally to both 2,3- and 1,2-sigmatropic shifts. However, sensitization by benzophenone gave a cyclic process (equation 52), characterized by a quantum yield of 0.8 and the required regiospecificity which was demonstrated by deuterium NMR

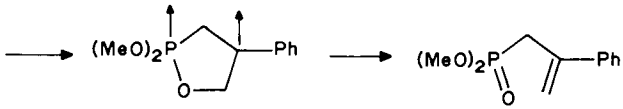
investigations. A triplet, 1,3-phosphoranyl biradical was proposed as a reasonable intermediate, although it has not been detected.

$$Ph_2\dot{C}—\dot{C}H_2 + Ph_2PPPh_2 \longrightarrow Ph_2\dot{C}—CH_2—\underset{\displaystyle PPh_2}{\overset{|}{\dot{P}}}Ph_2 \longrightarrow \tag{51}$$

$$Ph_2\dot{C}CH_2PPh_2 + Ph_2P^{\bullet} \longrightarrow Ph_2C{=}CHPPh_2 + Ph_2PH$$



(69)



(52)

VII. PRACTICAL AND SYNTHETIC APPLICATIONS

As is not unusual in modern organic chemistry, much of the interest in the reactions of free radicals with tricovalent phosphorus compounds has been mechanistic in nature. It has been important to establish the factors which determine the reactivity of a given radical and potential reactant, to understand the influences which will determine the products of the overall reaction, and to characterize fully the chemical and dynamic properties of the phosphoranyl radicals which are intermediates in many of the reactions. Until now there have not been many applications of the chemistry. However, since synthetic chemists have become increasingly aware of the potential of free-radical reactions, one may expect to see more use of the reaction types described here.

Early in the research on the reactions of free radicals with tricovalent phosphorus compounds, it was shown that a radical-chain oxidation could be induced by generating a free radical in the presence of molecular oxygen[106–111]. Moreover, alkanes, PCl_3 and oxygen under free-radical conditions give $RP(O)Cl_2$ in reasonable yields[112]. With *tert*-butoxy radical as initiator, the radical-chain sequence normally written for oxidation of a trialkyl phosphite is given by reactions 53. With n-Bu_3P such an autoxidation sequence can be initiated simply by passing oxygen through a solution of the phosphine[107]. A combination of α- and β-scission steps lead to n-Bu_3PO, n-$Bu_2P(O)OBu$-n, n-$BuP(O)(OBu)_2$ and $(n\text{-}BuO)_3PO$. Indeed, when trialkyl phosphites are irradiated with UV light in the presence of oxygen, a radical of any kind, generated photolytically, can initiate high-yield formation of phosphates[113]. A difficulty arises when t-BuOOBu-t is used to initiate the oxidation of phenyl phosphites. Step 53a is then replaced by a substitution reaction (equation 54). As a result, as was shown about 25 years ago[110], the oxidation is unsuccessful. The relatively stable phenoxy radical is unable to continue the chain because, even if it adds to phosphorus, it cannot undergo β-scission to give Ph$^{\bullet}$, which would carry the chain by formation of PhOO$^{\bullet}$.

$$t\text{-}BuO^{\bullet} + P(OEt)_3 \longrightarrow t\text{-}Bu^{\bullet} + OP(OEt)_3 \tag{53a}$$

$$t\text{-}Bu^{\bullet} + O_2 \longrightarrow t\text{-}BuOO^{\bullet} \tag{53b}$$

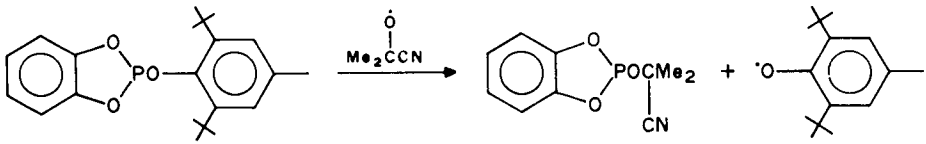
$$t\text{-BuOO}^{\cdot} + \text{P(OEt)}_3 \longrightarrow t\text{-BuO}^{\cdot} + \text{OP(OEt)}_3 \qquad (53c)$$

$$t\text{-BuO}^{\cdot} + (\text{RO})_2\text{POPh} \longrightarrow t\text{-BuOP(OR)}_2 + \text{PhO}^{\cdot} \qquad (54)$$

Aryl phosphites have found value as antioxidant additives to polymers[114-117]. They are not only able to terminate radical chain autoxidation but also react with any hydroperoxides which may result from autoxidation[118]. The displacement of aryloxy radicals from triesters of phosphorous acid has been studied with a wide variety of aryl phosphites by Schwetlick and coworkers[45,114,116], who also have thoroughly investigated the autoxidation phenomenon.

Unlike di-*tert*-butyl peroxide, azobisisobutyronitrile (aibn) can serve to initiate the oxidation of even those tricovalent phosphorus derivatives which contain an aryloxy group attached to phosphorus[110,114-117]. A reasonable rationale, again suggested 25 years ago[110], is that the oxy radical from aibn transfers oxygen to phosphorus in a kinetically favorable reaction (equation 55), to generate [$Me_2\dot{C}CN$], which is more stable than *tert*-butyl. $Me_2\dot{C}CN$ then adds oxygen and carries the chain. This property of aibn has more recently been studied with a wide range of aryl phosphites[114-117]. Sterically hindered aryl phosphites are good inhibitors of oxidation even when aibn is the initiator. Reaction 56 and oxygen transfer occur with approximately equal ease. An unsubstituted phenoxy group is less readily displaced. Thus, the reaction analogous to 56 is totally replaced by the equivalent of equation 55[45,114,116].

$$Me_2\dot{C}CN + (\text{RO})_2\text{POPh} \longrightarrow Me_2\dot{C}\overset{\dot{O}}{\overset{|}{C}}N + (\text{RO})_2\text{P(O)OPh} \qquad (55)$$

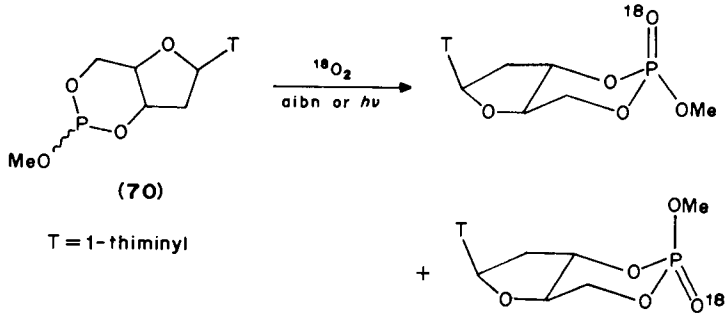


(56)

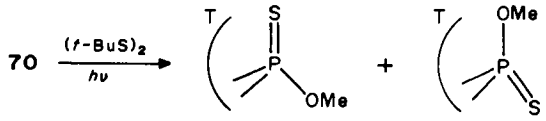
Aibn-initiated radical oxidations of phosphite triesters by oxygen actually provide an efficient, high-yield route to the cyclic methyl 3′,5′-phosphate triesters of thymidine (reaction 57)[113]. In fact, $^{18}O_2$ and $^{17}O_2$ can be introduced both regio- and stereospecifically into the P=O group. Separation of the individual diastereomers, followed by dimethylation, affords the individual, diastereomeric O-labeled diesters in high yields. Refluxing benzene at about 70 °C causes aibn to decompose at a convenient rate. Alternatively, aibn is readily photodisocciated by UV light through Pyrex. The photoinitiated oxidation without aibn is also a high-yield process. These non-aqueous oxidations may prove to be useful in oligonucleotide synthesis.

In a similar manner, *t*-BuSSBu-*t* can be conveniently photolysed to furnish *t*-BuS$^{\cdot}$, which provides a superior route to the methyl thiophosphates (equation 58) in better yields than by their conventional reaction with S_8[119]. Demethylation of the chromatographically separated diastereomeric thiophosphates yields the individual cyclic 3′,5′-phosphorothioate diastereomers of thymidine in high yields. The same starting cyclic 3′,5′-phosphite triester, **70**, affords the phenylphosphonates (equation 59). Phenyl radical was supplied by the thermal decomposition of phenylazotriphenylmethane[120]. Unfortunately, the photolysis of phenyl iodide did not lead to the same reaction. Reaction 59 is not a free-radical chain processes, but nonetheless gives product efficiently.

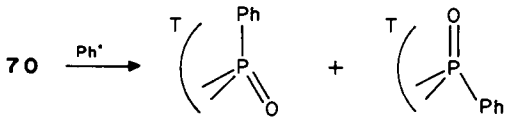
An apparent free-radical Arbuzov reaction (equation 60) yields 5-substituted 2′-


T
MeO
(70)
T = 1-thiminyl
$^{18}O_2$
aibn or hν
^{18}O
OMe
+
OMe
^{18}O

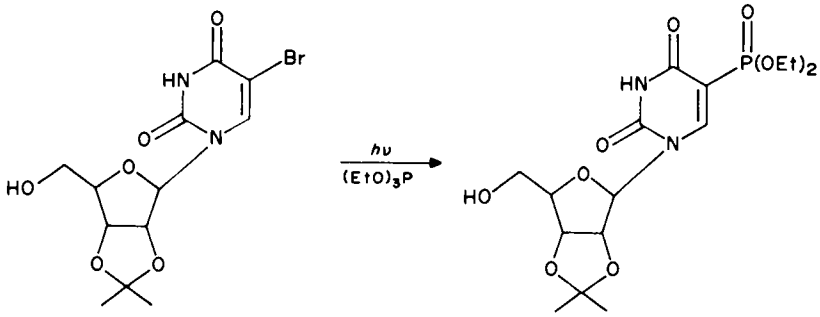
(57)


70
(t-BuS)$_2$
hν
T
S
OMe
+
T
OMe
S

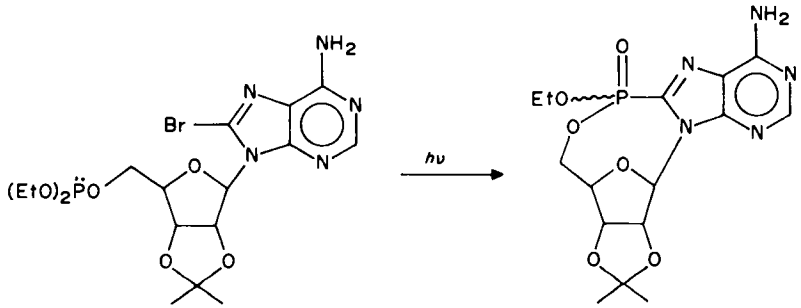
(58)


70
Ph·
T
Ph
O
+
T
O
Ph

(59)


HN
Br
O
N
HO
hν
(EtO)$_3$P
P(OEt)$_2$

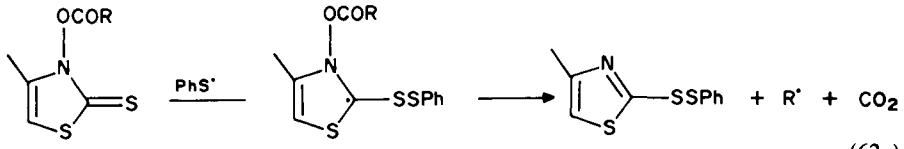
(60)


NH$_2$
N
Br
(EtO)$_2$PO
hν
EtO
P
O

(61)

deoxyuridines, presumably via attack on phosphorus of the allyl radical formed photolytically at the C(5) position of the base[121]. This reaction is analogous to process 59. A similar intramolecular photoreaction proceeded to give two diastereomers of the cyclic phosphonate (equation 61)[122].

Barton *et al.*[123] used a free-radical chain reaction approach to accomplish the decarboxylative phosphonylation of carboxylic acids. The method takes advantage of the ease of displacement of PhS$^{\bullet}$ from $P(SPh)_3$ by R$^{\bullet}$ (reaction 62b). A thiohydroxamic carboxylic mixed anhydride provides a trap for PhS$^{\bullet}$ and a source of R$^{\bullet}$ to continue the chain (reaction 62a). $RP(SPh)_2$ reacts with the dithioproduct to give a pentacovalent intermediate, which is hydrolyzed by water in the reaction medium to $RP(O)(SPh)_2$. With a series of R, the yields were 26–67% [R = n-$C_{15}H_{31}$, Ph_2CHCH_2, cyclohexyl, $PhCH_2$, 1-adamantyl, 1-methylcyclohexyl, $(PhCH_2)_2CH$ and a steroidal moeity].



(62a)

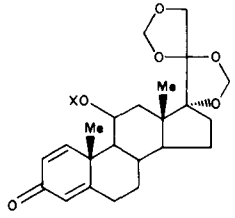
Almost certainly the first synthetic use of free-radical chain reactions involving oxidative addition of a radical to tricovalent phosphorus is given in reaction sequence 63, which produced useful amounts of thioesters[124]. The method is perhaps limited by the fact that mixed thioesters, RCOSR′, cannot be produced.

$$R^{\bullet} + P(SPh)_3 \longrightarrow RP(SPh)_2 + PhS^{\bullet} \tag{62b}$$

$$RS^{\bullet} + P(OEt)_3 \longrightarrow R^{\bullet} + SP(OEt)_3 \tag{63}$$

$$R^{\bullet} + CO \longrightarrow R\dot{C}O \xrightarrow{RSSR} RCOSR + RS^{\bullet}$$

Free-radical methods involving phosphoranyl radicals have been used to accomplish the phosphorylation of alcohols[125]. Thus, in the conversion of **71** to **72**, the precursor alcohol is first converted to the nitrite. The alkoxy radical formed on loss of NO reacts with triisopropyl phosphite to yield **72**. Surprisingly, the presumed intermediate



71 X=H
72 X=P(O)(OPr-i)$_2$

phosphoranyl radical preferentially loses the isopropyl radical, and in cases where $(MeO)_3P$ or $(EtO)_3P$ is used the less stable methyl or ethyl radical is formed on β-scission. This was suggested to be the result of a ponderal effect retarding the formation of very large radicals[125].

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The Chemistry of Organophosphorus Compounds
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CHAPTER **15**

Phosphine complexes of transition metals

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I. INTRODUCTION

A. History and Development

The first tertiary phosphine complexes were made by Hofman[1] in 1857, and further scattered examples appeared over the next 60 years, notably two forms of $[Pt(PEt_3)_2Cl_2]$ in 1870[2], although the correct assignment of *cis* and *trans* geometry to these isomers dates from 1936[3]. However, the development of this area into the vast research field we know today can be traced to independent work in the 1930s, by F. G. Mann in Cambridge and K. A. Jensen in Copenhagen[4], Mann's studies being continued and greatly extended by his student J. Chatt. The early history of tertiary phosphine complexes is intertwined with, and in some cases preceded by, studies of the corresponding arsines. This resulted from the stimulus provided to organoarsenic chemistry in the early years of this century by the therapeutic properties of some arsenicals and the toxicity ('poison gases') of others. Indeed, the synthesis of ditertiary arsines [including the famous $o\text{-}C_6H_4(AsMe_2)_2$ by Chatt and Mann in 1939[5]) and polydentate arsines $[MeAs(CH_2CH_2CH_2AsMe_2)_2$ by Barclay and Nyholm 1953[6]] precede by some years the syntheses of the phosphine analogues. Only in the 1960s did phosphine coordination chemistry overtake and then rapidly outstrip that of arsines prompted both by the superior coordinating ability of phosphines, especially towards 3d metals, and by the advantages conferred by the presence of a spin-$\frac{1}{2}$ nucleus in ^{31}P. The developments in NMR instrumentation and techniques in recent years have greatly reinforced the advantage[a].

Many developments have contributed to the phenomenal growth of tertiary phosphine coordination chemistry and some of the more notable include the following (the list is illustrative not comprehensive and could easily have been much larger): the observation of halide bridges in a molecular complex $[Pd_2(PR_3)_2Cl_4]$, Mann and Purdie (1936)[8]; synthesis of $[Ni(PEt_3)_2Br_3]$ demonstrating that phosphines stabilize unusual oxidation states, Jensen (1936)[9]; catalysis of olefin and acetylene polymerization by $[Ni(CO)_2(PPh_3)_2]$, Reppe and Schweckendiek, (1948)[10]; homoleptic phosphine complexes $[Pt(PPh_3)_4]$, Malatesta (1957)[11]; metal hydride complexes $[PtHCl(PEt_3)_2]$, Chatt *et al.* (1957)[12]; stable alkyl and aryl complexes, Chatt and Shaw (1959)[13]; $[Rh(PPh_3)_3Cl]$ and homogeneous hydrogenation catalysts, Wilkinson (1966)[14]; $[Ir(CO)(PPh_3)_2Cl]$ and reversible O_2 binding, Vaska (1961)[15]; dinitrogen complexes and their protonation to NH_3, Chatt (1975)[16]; the first diphosphine complexes $(Et_2PCH_2CH_2PEt_2)$, Wymore and Bailar (1960)[17]; the tetraphosphine $P(o\text{-}C_6H_4PPh_2)_3$ promoting TBP geometry (one of many examples of unusual geometries produced by phosphines), Venanzi (1963)[18]; metallation of a coordinated phosphine $[Ru(Me_2PCH_2CH_2PMe_2)_2]$, Chatt and Davidson (1965)[19]; bulky substituents in phosphines leading to facile metallation, unusual coordination numbers and large rings with $Bu^t_2P(CH_2)_nPBu^t_2$, Shaw (1970's)[20]; polydentate phosphine ligands by P—H bond addition to vinylphosphines, King (1971)[21]; chiral phosphines, e.g. diop and enantioselec-

[a] Among Group VB and VIB donor atoms, only ^{15}N [0.37%, D_p (respectivity relative to the proton[7]) $= 3.8 \times 10^{-6}$], ^{77}Se (7.6%, $D_p = 5.3 \times 10^{-4}$), ^{125}Te (7.0%, $D_p = 2.2 \times 10^{-3}$), ^{123}Te (0.87%, $D_p = 1.6 \times 10^{-4}$) have $I = \frac{1}{2}$. All can be 'routinely' studied with modern multinuclear FT-NMR instruments, but the ease of observation is much less than that of ^{31}P (100%, $D_p = 0.066$).

tive catalysis by their metal complexes, Kagan (1971)[22]; and phosphinomacrocycles[23]. To these chemical examples one could justly add the M—PR_3 bonding model σ donor–π acceptor, Chatt (1950–52)[24]; steric effects in phosphines (cone angle concept), Tolman (1970)[25]; application of ^{31}P NMR to phosphine complexes[26,27]; and 'virtual coupling in *trans*-R_2MeP—M—$PMeR_2$ units—the use of ^1H NMR spectra as a structural probe, Jenkins and Shaw (1963)[28].

Many of these developments are of major importance to other areas of inorganic or organometallic chemistry, e.g. the alkyl, hydrido and dinitrogen complexes, and although subsequent work showed that the presence of the phosphines was not essential to the stabilization of such bonds, the phosphine complexes were crucial to the initial development of the chemistries, and remain among the easiest examples to prepare and manipulate.

Key features of transition metal phosphine complexes are that they provide transition metal centres in discrete molecular forms, soluble in a wide range of organic media[29]. Both properties significantly extend the scope of transition metal chemistry, and are essential to their roles in homogeneous catalysis and much organometallic chemistry. The use of tertiary phosphines with long alkyl chains, PR_3 ($R = n\text{-}C_{10}H_{21}\text{–}C_{19}H_{39}$ or $p\text{-}C_6H_4R^1$, $R^1 = C_2H_5\text{–}C_9H_{19}$), leads to platinum metal complexes which are soluble even in saturated hydrocarbons[30,31], whilst incorporation of a hydrophilic group such as quaternary ammonium (e.g. $Ph_2PCH_2CH_2NMe_3^+$) can give water-soluble complexes[32,33]. The majority of phosphine complexes are insoluble in water, and many are decomposed by it.

B. Scope and Previous Reviews

Transition metal phosphine complexes have been the subject of two books (the later one covering the literature through 1977), and several review articles, with a larger number of articles dealing with specific aspects of the field. The more important of these previous treatments are listed in Table 1. Full coverage of the post-1977 literature would produce a

TABLE 1. Previous reviews on metal-phosphine chemistry

Topic	Authors	Reference
Transition metal complexes of phosphorus, arsenic and antimony ligands	C. A. McAuliffe (Ed.)	29
Phosphine, arsine and stibine complexes of the transition elements	C. A. McAuliffe and W. Levason	34
Phosphine, arsine and stibine complexes	G. Booth	35
Phosphine complexes	G. Booth	36
Transition metal complexes of phosphines	O. Stelzer	37
Diphosphine complexes	W. Levason and C. A. McAuliffe	38
Fluoroalicyclic phosphines and arsines	W. R. Cullen	39
Tripodal phosphine complexes	L. Sacconi and F. Mani	40
Olefin–phosphines	D. I. Hall, J. H. Ling and R. S. Nyholm	41
Phosphite, phosphonite and phosphinite complexes	J. G. Verkade and K. J. Koskran	42
Phosphorus, arsenic, antimony and bismuth ligands	C. A. McAuliffe	23
Tripod tetradentate ligand complexes	L. M. Venanzi	18
Phosphole complexes	F. Mathey, J. Fischer J. H. Nelson	43
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work of book length, prohibitively long and inappropriate in the context of the present volume. The more modest goal attempted here is to illustrate the characteristic chemistry of transition metal phosphine complexes, with examples taken mostly from the post-1977 literature (literature coverage extends to the end of 1987), and concentrating on halide and carbonyl systems. Complexes with other co-ligands, organometallics, nitrosyls, dinitrogen, etc., are included only where of particular interest from the point of view of the phosphine. Work in recent reviews or in other chapters in this present volume (e.g. phosphole and phospha-alkene or -alkyne complexes) are excluded. Recently obtained complexes of the f-block elements are included, but Main Group (p-block) complexes are not. Although some phosphine complexes are known for all the heavier p-block elements[45], their study has been neglected, and appears to be an area ripe for development. The synthesis of the ligands also falls outside the scope of this chapter, but is discussed elsewhere in this volume.

C. Group VB Ligands—Overview

Review articles detailing the coordination chemistry of arsines, stibines[29-34,35] and PF_3[46] are available. As already indicated, there is a large chemistry of mono-, bi- and polydentate arsenic donor ligands. Towards metal ions in low oxidation states, and 4d and 5d metals in normal (medium) oxidation states, the differences in behaviour between *analogous* phosphine and arsine ligands are often small, but for normal oxidation states of the 3d elements, and in higher oxidation states generally, phosphine complexes are markedly more stable, and many have no arsine analogues. The emphasis on *analogous* ligands is intentional. For many years, *o*-phenylenebis(dimethylarsine) was famed for its 'unique' ability to stabilize unusual oxidation states and coordination numbers[29], properties not shared by available diphosphines such as $Ph_2PCH_2CH_2PPh_2$. More recent studies[47] of the diphosphine analogue *o*-$C_6H_4(PMe_2)_2$ have shown it to be very similar in behaviour to *o*-$C_6H_4(AsMe_2)_2$ towards many transition metals, and in demanding cases, e.g. manganese(II)[47], iron(IV)[48] or nickel(IV)[49], the diphosphine complexes are markedly more stable. Antimony donor ligands (stibines) have much weaker coordinating ability, and this has restricted both the range of complexes known and the amount of effort devoted to them. In general they do not afford stable complexes with normal oxidation states of the 3d metals, although nickel(II) complexes of the bidentates *o*-$C_6H_4(SbMe_2)_2$[50] and $Me_2Sb(CH_2)_3SbMe_2$[51] and cobalt(III) complexes of *o*-$C_6H_4(SbMe_2)_2$[52] are known. Bismuthines are very poor donors and this, coupled with the ease with which C—Bi bond fission occurs, severely restricts the examples obtainable[53]; few have been thoroughly characterized.

II. BONDING IN TRANSITION METAL PHOSPHINE COMPLEXES

A. Electronic Effects

The standard textbook description of the transition metal—phosphine bond is based on the proposal by Chatt[24] that the lone pair on the phosphine is donated into an empty metal d orbital (σ bond), and the empty phosphorus 3d orbitals accept electron density from filled metal d orbitals of suitable symmetry ('π backbonding'), the bonding being mutually reinforcing (synergic). The model was widely accepted and used to rationalize many of the properties of such complexes. However, by the mid-1960s the accumulation of spectroscopic and structural data allowed detailed reconsideration of the model, and differing views were taken by different workers. Some argued that many properties, e.g. variations in $^1J(^{31}P-^{195}Pt)$ coupling constants, the *trans*-influence of phosphines or the

effects of PR_3 substituents on ν(CO) and force constants in carbonyls, could be explained by anisotropic σ bonding effects, with the π-component unimportant or absent. It was argued that the 3d orbitals on phosphorus were of too high energy and too diffuse to contribute significantly to the bonding. However, it remained difficult to explain, for example, the stability of zerovalent metal phosphine complexes and the high spectrochemical position of phosphines by σ bonding alone. The difficult, often subtle (and not infrequently subjective) detailed arguments by different workers are best followed in the original papers. This work has been reviewed[11,24], is further considered in Chapter 2, Section IV.E, and will not be repeated here.

A summary of the generally accepted view would be that the σ bonding was dominant, especially in $P(alkyl)_3$ complexes with metals in positive oxidation states, and that this was supplemented by a significant π component when the phosphine carried electronegative substituents and with metals in low oxidation states, although quantification of the π component remains elusive. When one remembers that phosphines bond to d-block metals in oxidation states ranging from (formally) $-$II to $+$VI, and to p- and f-block metals, it is clear that the nature of the phosphine bonding will vary considerably to accommodate the very different properties of the metal centres. It is also now clear that many of the trends in spectroscopic parameters reflect the bonding in the complex *as a whole*, and separation of the effects due to the M—P bond and further subdivision of this into σ and π components is extremely difficult. Steric effects (below) are a further complication.

In the last 10 years, some interesting new insights into the M—P bond have emerged and these will be briefly discussed. The σ-donor power of phosphines has usually been estimated from their proton basicity [$pK_a(H_2O)$], either determined experimentally or estimated from Hammett σ_p or Kabachnik σ^{ϕ} constants[54]. The pK_a values range from 11.4 for PBu^t_3 to ca 2.0 for $4\text{-}XC_6H_4PPh_2$[55,56]. More recently, gas-phase photoelectron spectroscopy (PES) has been used to provide a direct measure of the binding energy of the phosphorus lone pair. The initial results indicated that the order of the σ-donor power was $PPh_3 > PPh_2Me > PPhMe_2 > PMe_3$[57], the opposite of the pK_a-derived order and of that intuitively expected, and these results provoked considerable controversy[58]. The PES data were subsequently supported by gas-phase proton affinity measurements[59]. The PES measurements have since been extended to several series of complexes, including $[AuMe_3(PR_3)]$[60], $[W(CO)_5(PR_3)]$[61], $[W(CO)_4(R_2P(CH_2)_2PR_2)]$[61] and $[Mo(CO)_{6-n}(PR_3)_n]$ $(n = 1\text{–}3)$[62], which again suggested that aryl substituents increase the phosphine donor power in comparison with the alkyl groups. Gas-phase PES data differ from solution pK_a data since the latter will also involve a substantial contribution from solvation energies, and this may be a better reflection of solution chemical reactivities. Nonetheless, the PES data are most interesting in the context of a deeper understanding of the M—P bond, and similar data on a large number of examples, varying the metal and oxidation state, are desirable.

In addition to these new results on the σ-donor power, our understanding of the π component in the M—P bond has also changed. Earlier workers had assumed that the π bond was M(dπ)—P(3dπ), but recent molecular-orbital calculations (self-consistent multipolar Xα type) have suggested that[63] the LUMO in PH_3 has 36% 3p and only 23% 3d character, whereas in PMe_3 the proportions are 14 and 10%, respectively. Marynick[64] showed that for $[Cr(NH_3)_5(PH_3)]$ or $[Ni(NH_3)_3(PH_3)]$, *ab initio* MO calculation could acceptably describe the π-acceptor bond without including *any* 3d orbitals in the phosphines basis set. Experimental support for these calculations has been provided by electron transmission spectroscopy[65]. The proposal that the π-acceptor orbital on P is actually a P—X (X = H or C)σ^* [or contains substantial P—X σ^* admixed with P(3d)[66], Figure 1] is attractive, removing the difficulty of utilizing the high-energy diffuse 3d orbitals alone. Orpen and Connelly[66] examined X-ray data on several pairs of complexes

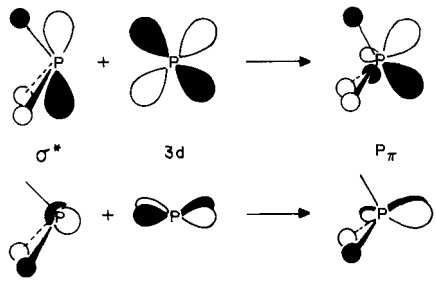


FIGURE 1. Doubly degenerate PX_3 LUMO (C_{3v} local symmetry assumed). Reproduced by permission of the Royal Society of Chemistry from Reference 66.

which differ only in the metal oxidation state, e.g. $[Mn(CO)(Ph_2PCH_2CH_2PPh_2)(\eta^5\text{-}C_6H_6Ph)]^{0/+}$ or $[Fe(CO)\{P(OMe)_3\}_2[\eta^4\text{-}C_4Ph_4]]^{0/+}$ and showed that the changes in M—P and P—X bond lengths are consistent with expectations of the π bond having a P—X σ^* component. Essentially, as the oxidation state of the metal increases d(M—P) increases but d(P—X) decreases.

In addition to these studies of the M—PR_3 linkage, several comparable studies of Group VB donor complexes have been carried out. X-ray structural data on $[Cr(CO)_5(EPh_3)]$ (E = P, As, Sb, Bi) indicated that the s component of the Cr—E bond increased down Group VB[67]. PES data[68], gas-phase proton affinities[69], enthalpy data for BX_3 adducts[70] and ^{13}C NMR[71] of $[Ni(CO)_3(ER_3)]$ suggested that ER_3 basicity falls in the order $PR_3 > AsR_3 > SbR_3$ whilst the donor/acceptor ratio is $SbR_3 > AsR_3 > PR_3$, with the heavier donors being less influenced by changes in the R group.

B. Steric Effects

Although the steric properties of phosphines had occasionally been suggested to influence the nature of their complexes, e.g. the planar $\rightleftharpoons$ tetrahedral equilibrium in $[Ni(PR_3)_2X_2]$, until 1970 the observed effects were usually attributed to electronic effects. The seminal work of Tolman[25,72] and his proposal of the cone angle model for treating steric effects in a semiquantitative manner revolutionized thinking in this area. The familiar 'definition' of cone angles for symmetric and unsymmetric ligands is shown in Figure 2a and b. For the unsymmetric ligand,

$$\Theta = \tfrac{2}{3}\sum_{i=1}^{3}\Theta_{i/2} \qquad (1)$$

The cone angle is not appreciably affected by small changes in the M—P (or the P—C) bond length[72], but where rotation about the P—C bonds is possible, the conformation chosen will have a marked effect on Θ. Tolman[72] chose to use the CPK models with the substituents folded back to give a minimum cone. Other choices are possible and, as discussed by DeSanto *et al.*[73], lead to significant variations in the values of Θ. A different definition of cone angle appropriate to cluster compounds has been proposed by Mingos[74] which relates to the cluster—PR_3 distance rather than the P—M distance to the bonded metal centre (Figure 3). Mingos's value is clearly less than Tolman's for any particular ligand. Using d(M—P) = 2.28 Å (Tolman's value), DeSanto *et al.*[73] used MINDO/3 semiempirical molecular orbital calculations to examine the effect of

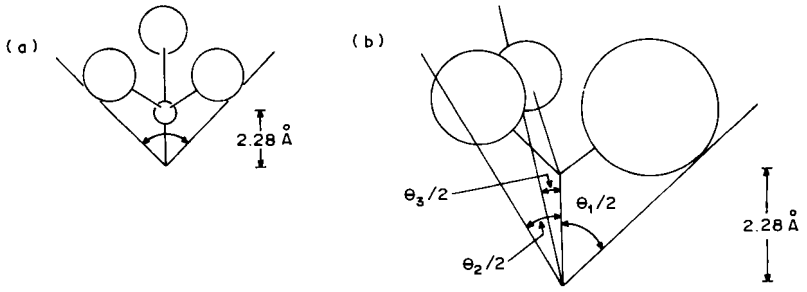


FIGURE 2. 'Definition' of cone angles for (a) symmetric and (b) unsymmetric legands. Reproduced by permission of the American Chemical Society from Reference 25. Copyright (1977) American Chemical Society.

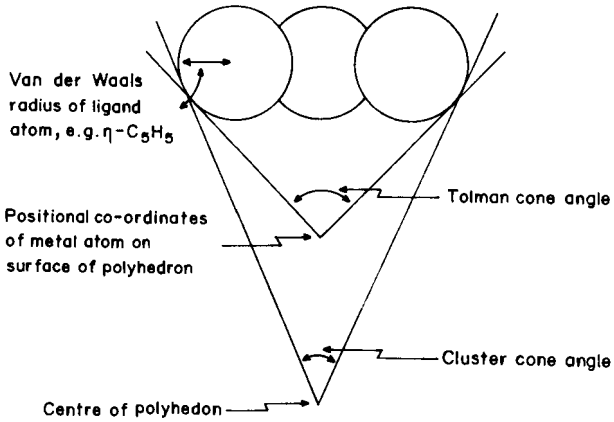


FIGURE 3. Definition of cluster cone angle and comparison with the Tolman cone angle. Reproduced by permission of the American Chemical Society from Reference 74. Copyright (1982) American Chemical Society.

substituent conformation on the cone angle. Listings of cone angles for many tertiary phosphines have been published[23,72,73,75], typical values ranging from MeH_2P (103°), Me_3P(118°), PPh_3 (145°) to P(*o*-$MeC_6H_4)_3$ (194°) and P(mesityl)$_3$ (212°). As pointed out by Tolman[25], treating ligands as solid cones does not allow for the intermeshing of substituents on neighbouring ligands, or for the ability of ligands to accommodate crowding by compressing the C—P—C angles, and thus cone angles tend to overestimate steric effects. The value of Tolman's approach lies more in providing a framework for discussing steric properties in a semiquantitative way, and in classifying phosphine ligands in terms of their *relative* steric properties. Too much emphasis should not be placed on the numerical Θ values for similar-sized ligands.

The obvious limitations of the simple cone angle method led to a number of more sophisticated models, which address the problem of the irregular shapes of real ligands, but lose the simplicity and ease of use of the original. Ferguson and coworkers[76,77] introduced the ligand profile approach based on X-ray data for bulky ligands such as P(*c*-

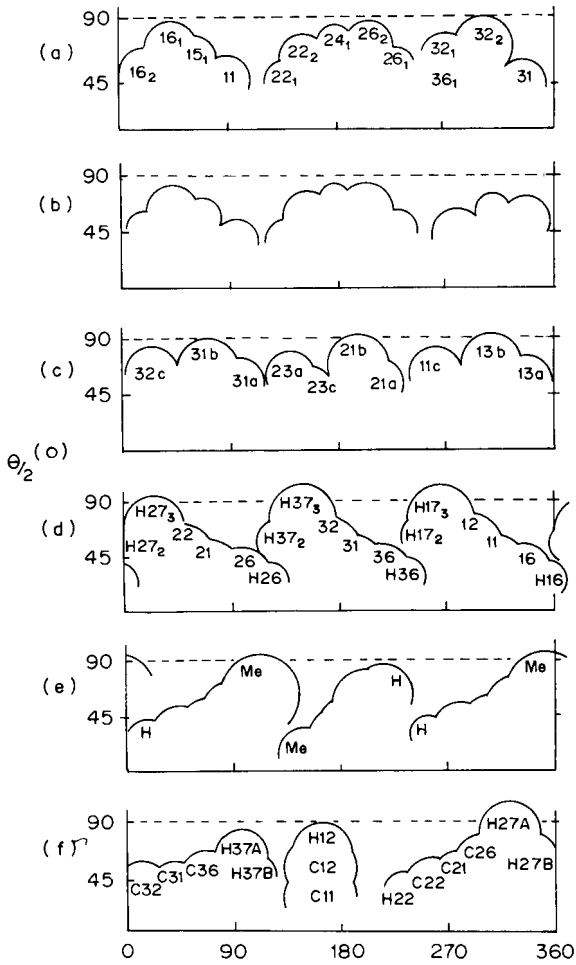


FIGURE 4. Ligand profiles for (a) *c*-Hex_3P in *c*-$Hex_3PHgSCN)_2$; (b) *c*-Hex_3P in (*c*-$Hex_3P)_3Pt$; (c) *t*-Bu_3P *in t*-$Bu_3PHg(OAc)_2$; (d) (*o*-Tol)$_3$P in [(*o*-Tol)$_3$PHgCl·$ClO_4]_2$; (e) (*o*-Tol)$_3$P in [(*o*-Tol)$_3$PHg(OAc)$_2]_2$; (f) (*o*-Tol)$_3$P in [(*o*-Tol)$_3$P]$_2PtI_2$. The ordinate is the maximum semicone angle $\theta/2$. The abscissa is the angle ϕ through which the vector M → X has been rotated about the M—P bond; the origin of ϕ was arbitrarily chosen. Reproduced by permission of the American Chemical Society from Reference 76. Copyright (1978) American Chemical Society.

Hex)$_3$, P(*o*-$MeC_6H_4)_3$ and PBu^t_3. The ligand profile is generated by rotating the phosphine about the M—P axis (ϕ = rotation angle) and measuring $\Theta/2$, the angle formed by the tangent to the 'proudest' hydrogen. A typical ligand profile is shown in Figure 4, which displays the 'cog-like' structure, and shows how intermeshing can occur between the

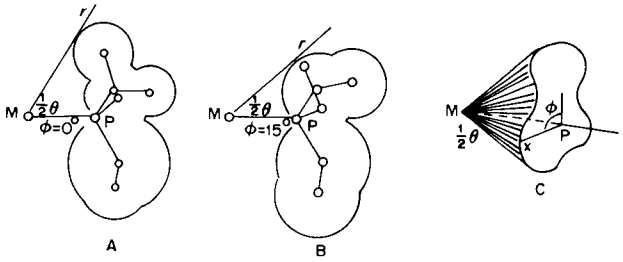


FIGURE 5. Dependence of the angular encumbrance of a coordinated phosphorus ligand (PEt_3 as a working example) on the ligand orientation. Hydrogen atoms are omitted for clarity. In A and B the curved line indicates the section in the plane of the drawing of the space filling molecular model (carbon radius 1.8 Å). For each orientation ϕ the $\frac{1}{2}\theta$ angle is defined by the straight line r tangent to the model in the plane of the figure. C represents the generalized non-circular cone described by r on changing ϕ and $\frac{1}{2}\theta$ angles. X, a point of r at an arbitrary fixed distance from M, describes a closed non-circular belonging to a sphere centered on M. Reproduced by permission of Elsevier Sequoia from Reference 78.

cogs. It should be noted that this approach results in different values of Θ for the same ligand in different complexes, reflecting the different degrees of crowding and the accommodation to them.

A different approach was taken by Immirzi and Musco[78], who introduced the idea of angular encumbrance ($\frac{1}{2}\Theta$). Again, tangents are drawn to the periphery of the ligands as a function of its rotation (ϕ) about the M—P bond. Changes in $\Theta/2$ with ϕ are termed the ligand angular encumbrance. The result is a solid figure, 'cone-like' but with an irregular non-circular section (Figure 5). The solid angle Ω of this irregular cone is given by

$$\Omega = \int_{\phi=0}^{2\pi} (1 - \cos^{1/2}\Theta)\,d\phi \tag{2}$$

Also introduced was the idea of angle $\bar{\Theta}$, the aperture of a circular cone having the equivalent solid angle:

$$\bar{\Theta} = 2\arccos(1 - \Omega/2\pi) \tag{3}$$

which should correlate with Tolman's cone angle Θ.

A further way of displaying the steric properties of a ligand has been proposed by Oliver and Smith[79] (Figure 6).

The accumulation of a large body of X-ray crystallographic data has allowed detailed comparisons of the steric effects in related series of compounds. Several examples of this will be discussed in later sections, but here we note two. Clark and Hampden-Smith[80] correlated data on about thirty platinum(II) complexes of P (*c*-Hex)$_3$. The conclusions were that steric overcrowding in such molecules was accommodated in various ways, in order of decreasing importance, lengthening of the Pt—P bond > deviation from 90° angles in the square-plane > distortion of Pt—P—C angle and of the phosphine > deviation from planarity.

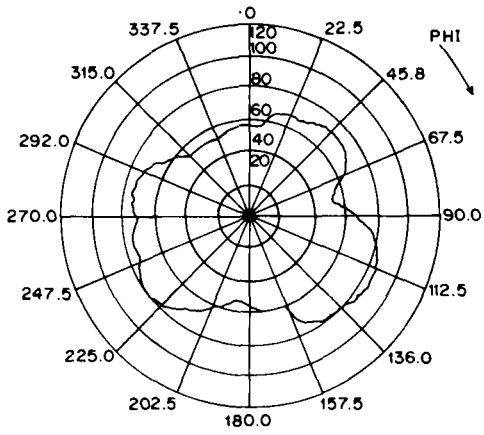


FIGURE 6. A method of displaying the steric properties of a ligand. Reproduced by permission of the American Chemical Society from Reference 79. Copyright (1978) American Chemical Society.

By supplementing the X-ray studies by solid-state ^{31}P and solution ^{1}H NMR spectroscopy, it is possible to correlate these observations with solution properties. An alternative approach is to compare X-ray data for the same substrate with varying phosphines, and an example of this is the vitamin B_{12} models $[Co(Hdmg)_2L(PR_3)]$ [Hdmg = dimethylglyoximato(−)]. The d(Co—P) increases with the bulk of the phosphine, although electronic effects from the *trans* ligand L are also involved[81-83].

Although it was Tolman's work on steric effects that is best known; he also[84] introduced an electronic parameter v, based on the A_1 carbonyl frequency in $[Ni(CO)_3(PR_3)]$, and showed that the substituent contributions χ^i for $PR^1R^2R^3$ could be estimated via

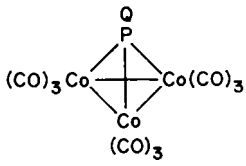
$$v = 2056.1 + \sum_{i=1}^{3} \chi^i \tag{4}$$

It is appropriate to close this section by recalling the fact that steric and electronic effects are intimately related, and correspondingly difficult to separate in many systems. For sterically crowded systems, ligand size may dominate, whereas for complexes of low coordination number with small ligands, electronic effects are paramount. Many protagonists have stressed one effect over the other and much ink has been spilled in resulting disputes. In many systems both steric and electronic models predict similar trends; to take a simple example, σ donor power (pK_a model) increases in the order $PPh_3 < PMePh_2 < PMe_2Ph < PMe_3$ whereas the cone angle decreases in the same order (145° > 136° > 122° > 118°); if a particular trend in properties of $ML_x(PR_3)$ varies in this order, it is not always clear how one should apportion the underlying effects (see ref. 25—steric and electronic map). Finally, attempts to separate σ, π and steric effects by combination of electrochemical (CV) data, pK_a values and cone angles have recently been described for a number of systems[85]. The generality and success of this interesting approach awaits data on a larger number of systems.

III. COMPLEXES OF PH_3, PH_2R AND PHR_2

A. Complexes of PH_3

The coordination chemistry of phosphine has not been investigated in great detail, but complexes with most metal carbonyls are known[86], and there is the homoleptic $[Ni(PH_3)_4]$[87]. Recently studies examples include $[V(CO)_5PH_3]^-$ [88] and $[QPH_3]$ $[Q = Cr(CO)_5, Mo(CO)_5, W(CO)_5]$[89]. The latter react with $[Co_2(CO)_8]$ to give $[QPCo_3(CO)_9]$ (**1**)[89]. From $[Os_3(CO)_{11}(MeCN)]$ and PH_3, $[Os_3(CO)_{11}PH_3]$ is formed and this is readily converted into $[Os_3(CO)_{10}(\mu\text{-}PH_2)]$ and $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PH_2)]$[90]. When the latter is heated with $[Os_3(CO)_{12-n}(MeCN)_n]$ the hexanuclear clusters $[Os_6H_2(CO)_{20}(\mu^3\text{-}PH)L](L = MeCN \text{ or } CO)$ (**2**)[91] are formed. Other X-ray characterized examples with μ-PH_2 groups include $[\{(CO)_4Mn(PH_2)\}_2]$ and $[\{(CO)_4Mn(PH_2)\}_3]$[92] (**3** and **4**). Phosphine also adds oxidatively to the Vaska-type complex $[Ir(CO)Br(PEt_3)_2]$ to give $[Ir(CO)BrH(PEt_3)_2(PH_2)]$[93]. The terminal PH_2 group adds selenium to give a PH_2Se complex and is protonated by HCl to a coordinated PH_3 group $[Ir(CO)BrH(PEt_3)_2(PH_3)]^+$. Singly-bridged platinum(II) dimers $[\{PtX(PEt_3)_2\}_2(\mu\text{-}PH_2)]Y$ (X = H, Cl, Br; Y = Cl, Br) have also been prepared[94].



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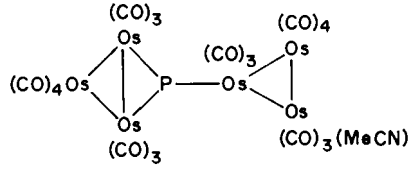

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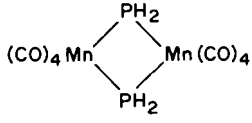

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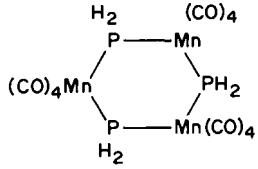


(4)

B. Complexes of PH_2R and PHR_2

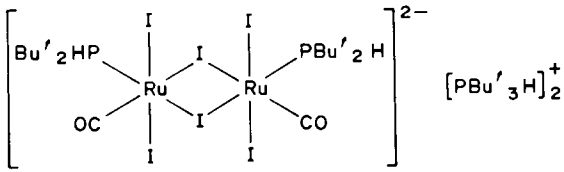
The coordination chemistry of primary (PH_2R) and secondary (PHR_2) phosphines has been much less thoroughly investigated than that of tertiary phosphines, although there has been considerable recent interest in using PHR_2 ligands in particular as precursors to bi- and poly-nuclear phosphido-linked species (see below). Stepwise replacement of the R group in PR_3 by H decreases the basicity (pK_a scale) and the cone angle. The smaller steric requirements of primary and secondary phosphines [e.g. $\Theta = 87°$ (PH_3), 103° (PH_2Me), 108° ($PHMe_2$), 118° (PMe_3)] potentially means that a larger number of such ligands could be accommodated around the metal centre compared with the tertiary phosphine analogue, and there is some evidence from the stoichiometries of several series of complexes that this is so in practice. The main difference, however, between these ligands and tertiary phosphines is the ease with which the weak P—H bonds in the former break

on reaction with metal centres, producing phosphido (PR_2^- or PHR^-) or phosphinidine (PR^{2-}) ligands.

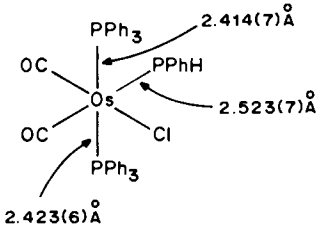
Typical examples of these ligands behaving as formally two-electron donors towards metal carbonyl centers, which have been studied recently, include $[LM(CO)_5]$ (L = PH_2Me, PH_2Ph, M = Cr, Mo, W)[89], $[(PBu_2^tH)Cr(CO)_5]$[95], $[LV(CO)_5]^-$ (L = $PH_2\{c\text{-Hex}\}$, $PH\{c\text{-Hex}\}_2$)[88] and $[Co_2(CO)_6(PBu_2^tH)_2]$[96]. Diphenylphosphine complexes of manganese carbonyl $[Mn(CO)_{6-n}(PHPh_2)_n]^+$ ($n = 1$–4) have been obtained from reaction of $PHPh_2$ with $[Mn(CO)_5OClO_3]$ under various conditions[97]. Thermal isomerization, *fac* → *mer* ($n = 3$) and *cis* → *trans* ($n = 2$), is also observed.

The zerovalent $[Ni(PHPh_2)_4]$, which was erroneously identified as a phosphidonickel(II) complex, $[Ni(PPh_2)_2(PHPh_2)_2]$, in the older literature, has been re-examined[98]. It is only slightly air-sensitive in the solid state, reacts with HgX_2 (X = Cl, Br, I, SCN) to give $[Ni(PHPh_2)_3X_2]$ and the $PHPh_2$ is readily displaced by phosphites. Some years ago the diphosphane $(c\text{-Hex})_2PP(c\text{-Hex})_2$ was reported to give three-membered chelate ring complexes with nickel(II) halides, but a re-examination[99] has shown that these are $PH(c\text{-Hex})_2$ complexes which can also be formed directly from the latter. The complexes have a *cis*-$[NiX_2\{PH(c\text{-Hex})_2\}_2]$ structure in both solid and solution and this was confirmed by an X-ray study of the chloride. Detailed studies on the reaction of $Co(BF_4)_2 \cdot 6H_2O$ with $PHEt_2$, PHMeEt and PHEtPh showed that red low-spin five-coordinate $[Co(PHR_2)_5]^{2+}$ are readily produced. A closely related green form, which may contain either water or a coordinated BF_4^- ion in the sixth coordination site, were observed, and the red↔green interconversion is facile[100]. Cobalt(III) hydrides $[CoH(PHR_2)_5](BF_4)_2$ were also characterized. An unusual generation of a secondary phosphine complex (**5**) occurs when PBu_3^t is heated with $RuCl_3 \cdot nH_2O$ in 2-methoxyethanol containing NaI and in the presence of CO[101].

Bohle and Roper[102] showed that PPh_3 is readily displaced by PH_2Ph or $PHPh_2$ from $[MHCl(PPh_3)_3]$ or $[M(CO)_2(PPh_3)_3]$ and that the products may be deprotonated at phosphorus to give rare examples of terminal phosphido complexes, e.g. $[M(CO)_2(PPh_3)_2(PPhR)]$ (R = Ph or H). An X-ray study showed (**6**) that the M—PPhH bond was unusually long compared with the M—PPh_3 bond[103].



(**5**)



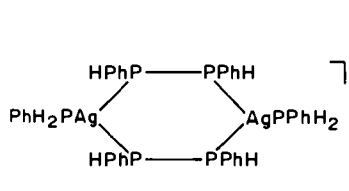
(**6**)

Cadmium and mercury complexes $[Cd(PH(c\text{-}Hex)_2)_nX_2]$ ($n = 1,2$ X = halogen) and $[Hg(PHR_2)_nX_2]$ ($n = 1,2$, R = *c*-Hex, Bu^t, X = halogen)[104,105] have been prepared. The mercury complexes are deprotonated by triethylamine to $HgXPR_2$, also prepared directly from HgX_2 and $LiPR_2$, and add a third molecule of PHR_2. $[AuCl(Bu_2^tPH)]$ has also been described[106].

Some of the complex chemistry which results from the ready P—H bond fission in secondary phosphines is illustrated in rhodium chemistry. Thus, in some cases simple substitution occurs, for example in the reaction[107] of $PHPh_2$ with $[\{Rh(CO)_2Cl\}_2]$ in a 1:4 molar ratio, when $[Rh(CO)Cl(PHPh_2)_2]$ is formed. However, with a smaller proportion of phosphine the products include phosphido-bridged species such as $[Rh_3(\mu^2\text{-}PPh_2)_3Cl_2(CO)_4]$. Related complexes obtained by varying the reaction conditions include $[Rh_3(\mu^2\text{-}PPh_2)_3(CO)_5]$, $[Rh_3(\mu^2\text{-}PPh_2)_3(CO)_7]$ and $[Rh_3(\mu^2\text{-}PPh_2)_3(CO)_6(PPh_2H)]$[107,108]. The reactions with cluster carbonyls in some cases result in substitution, e.g. $[Ru_5C(PPh_2H)(CO)_{14}]$, which decomposes on heating to $[Ru_5C(H)(PPh_2)(CO)_{13}]$[109], whereas in other cases the deprotonated form is obtained directly, e.g. $[Fe_3(CO)_{12}]$ and $PPhH_2$ give the $[Fe_3(CO)_9(\mu^3\text{-}PPh)]$[110] and $[Rh_4(CO)_{12}]$ and Bu_2^t HP produce $[\{Rh(CO)(Bu_2^tPH)\}_2(\mu\text{-}Bu_2^tP)(H)]$[111].

One example where a diphosphane R_2PPR_2 is cleaved and adds hydrogen presumably from the solvent has been referred to above; the opposite reaction in which secondary or primary phosphines couple in the presence of a metal to yield diphosphane complexes is also known. Thus $AgClO_4$ reacts with PPh_2H in pyridine solution to form $[(py)_3Ag(Ph_2PPPh_2)Ag(py)_3](ClO_4)_2$[112], whereas $PPhH_2$ reacts with $AgPF_6$ to give **7**, containing PhHPPPhH[113]. The Cu(I) analogue of the latter is formed using $Cu(PF_6)_2$.

Diphosphanes can also function as bidentate (usually bridging) or monodentate ligands without cleavage of the P—P bond, e.g. **8** and **9**[114,115]. Subsequent reaction of these monodentate derivatives with more metal substrate may lead to homo- or hetero-nuclear



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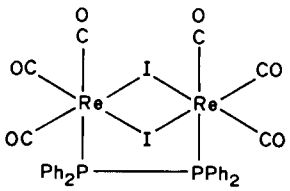

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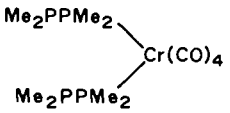

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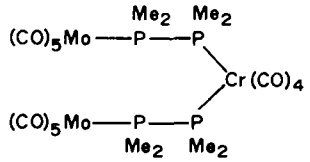

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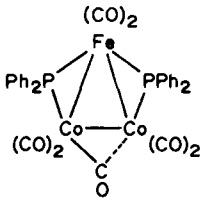
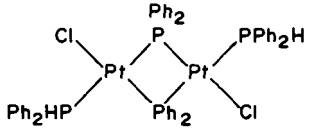


(11)

dimers such as **10**, which may then be pyrolysed to phosphido-bridged materials such as **11**[115,116].

Strictly, phosphido-bridged species fall outside the scope of this chapter, but are related since one route to them is from primary or secondary phosphines, which are deprotonated either spontaneously on reaction with the metal centre, with base (NEt_3), photochemically or by the pyrolysis of preformed metal primary or secondary phosphine complexes. Other preparations include direct reaction of an alkali metal phosphide with a metal complex. Much recent interest has centred on the use of phosphido groups to assemble bi- and polynuclear complexes or to stabilize metal clusters. Several recent reviews have covered aspects of this area[117–120], and the few examples quoted below are meant merely to illustrate some of the known types. Homonuclear dimers without an M—M bond e.g. (**12**)[121], and with single M—M (**13**)[122] or formally double M—M bonds (**14**)[123], are known, and there are a large number of heteronuclear dimers (**15** or **16**)[95,124]. Larger clusters are also easily obtained, such as **17** and **18**[125,126].



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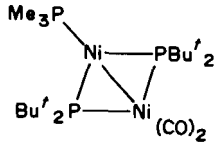

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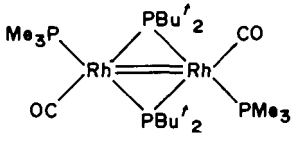

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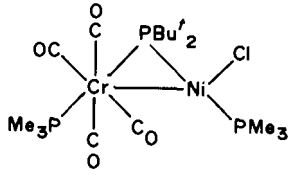

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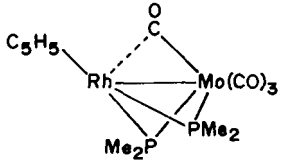

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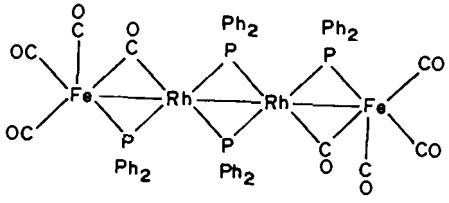

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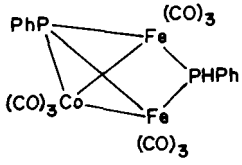

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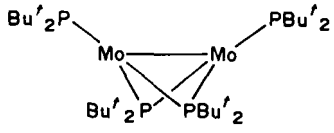
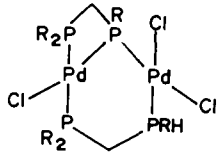


(19)

Homoleptic phosphido complexes were prepared some years ago, notably by Isslieb and coworkers, but detailed characterization has been achieved only recently, e.g. $[Mo_2(Bu_2^tP)_4]$ (**19**)[127] or $[M(P\{c\text{-Hex})_2\}_n]^-$ (M = Zr, Hf $n = 5$; M = Ti, V, Re, Nb, $n = 4$)[128]. Actinide phosphido complexes have also been obtained, e.g. $[(C_5Me_5)_2Th(PPh_2)_2]$[129]. Finally, it should be noted that it is sometimes possible to reduce phosphido species to secondary phosphines which remain coordinated to the metal[130].

The chemistry of bi- or multi-dentate ligands containing one or more PH or PH_2 functions has been investigated only recently. In general, it appears that these ligands often behave as 'normal' neutral donors towards metal halides in positive oxidation states, although the P—H bond can be broken by treatment with base to give the phosphido derivative. The chemistry is complicated by the presence of chiral phosphorus centres and hence diastereoisomers are observed. With metal carbonyls and probably with low oxidation state metal centres, very complex chemistry occurs; depending on the conditions, simple coordination, deprotonation at phosphorus (to give phosphido complexes), P—C bond cleavage and cluster formation can all take place and complex mixtures of products are often present. Nucleophilic attack at coordinated phosphido groups by strong nucleophiles such as RLi has also been observed.

The reaction of $Pr_2^iPCH_2PHPr^i$ with $[PdCl_2(PhCN)_2]$ gives the novel dinuclear complex **20**[131]. Brauer *et al.*[132] prepared complexes of this ligand with copper(I) and silver(I) halides; the 1:1 materials are dinuclear with bridging ligands affording eight-membered rings, whilst the 2:1 complexes have structure **21**. The disecondary phosphine $HPhP(CH_2)_3PPhH$ produces simple substitution products with nickel and molybdenum carbonyls, $[Ni(CO)_2L\text{–}L]$ and $[Mo(CO)_4L\text{–}L]$, and an X-ray structure of the nickel complex reveals the expected tetrahedral geometry (*meso* isomer)[133]. Several papers[134–137] have discussed the reaction chemistry of similar ligands bound to metal carbonyl fragments. The bidentate tertiary–secondary phosphines $PhHP(CH_2)_3PR_2$. (R = Ph or *c*-Hex) form $[MCl_2(L\text{–}L)]$ complexes with palladium or platinum, which can be



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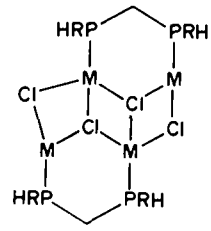

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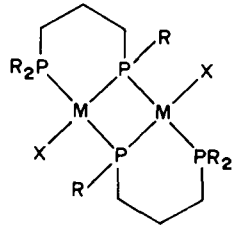

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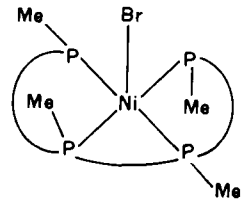


(23)

deprotonated with base to give the phosphido-phosphines **22**. X-ray studies of the both *meso*- and DL-diastereoisomers of the platinum chloro complex (R = *c*-Hex) have been reported[138]. Stelzer's group[139,140] have reported nickel(II), palladium(II) and platinum(II) complexes of the tridentates $H_{2-n}R_nP(CH_2)_3PR'(CH_2)_3PR_nH_{2-n}$ ($n = 0$–2, R, R′ = Me, Ph) and the tetradentates $H_{2-n}R_nP(CH_2)_3R'P(CH_2)_3\ R'P(CH_2)_3\ PR_nH_{2-n}$ and $RR''P(CH_2)_3PMe(CH_2)_3PMe(CH_2)_3PRR''$ (R, R′ = Ph, Me, R″ = H, Me). Again, diastereoisomerism results in complex mixtures; generally the nickel complexes exhibit equilibria between 5- and 4-coordinate metal centres, and an X-ray structure of one of the five-coordinate complexes (**23**) reveals square-pyramidal geometry.

IV. COMPLEXES OF TERTIARY PHOSPHINES PR_3

Thousands of tertiary phosphine complexes are known, although in many of the organometallic derivatives the interest centres elsewhere in the molecule. The most popular ligands remain triphenylphosphine and phenylalkylphosphines, but recently much interest has been shown in trimethylphosphine and in bulky ligands such as tricyclohexylphosphine and tri-*tert*-butylphosphine. For many years trimethylphosphine was not widely used, reflecting both its difficult synthesis and the much greater difficulties compared with other trialkylphosphines of manipulation of a very volatile and air-sensitive material. However, its combination of strong donor power and modest steric requirements means that it differs in significant ways from other trialkylphosphines, and this accounts for the recent interest. Bulky phosphines have produced very different chemistry from that of ligands with smaller cone angles; thus bulky ligands promote low coordination numbers, coordinatively unsaturated metal centres and sometimes facile metallation; examples of all these effects will be illustrated in the following sections.

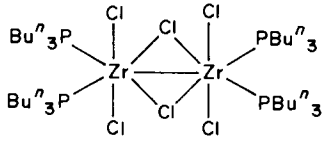
The majority of complexes contain the later transition metals, and examples with the f-block metals, Group IV and Group V are few. The organization in this section is by Periodic Group, and the coverage especially of the later elements is highly selective. An attempt has been made to illustrate the breadth of the field, rather than the depth of certain areas, and coverage has been concentrated on those areas which are new or have developed rapidly since previous reviews were written. The references have been chosen both for the work described in them and for their citation of other related work to provide the reader with ready access into a particular area.

A. Complexes of the f-Block metals

There are few reports of attempts to prepare phosphine complexes with either the lanthanide or actinide elements, and it is apparent that several of the actinide complexes reported in the early literature are in fact phosphine oxides or phosphonium salts. Nontheless, the recent succesful synthesis of complexes with bidentate phosphines indicates that similar examples with monodentates should be obtainable under appropriate conditions. One X-ray study of a cerium(III) complex, the yellow, air-sensitive $[(MeC_5H_4)_3Ce(PMe_3)]$ (Ce—P = 3.072 Å), has appeared[141]. The complex is made from $CeCl_3$, $NaMeC_5H_4$ and PMe_3 in diethyl ether. An isostructural red uranium(III) complex, $[(MeC_5H_4)_3U(PMe_3)]$, is made similarly from UCl_3[142].

B. Complexes of the Titanium Group (IV)

Few recent studies have been reported, and the low oxidation states of these elements remain almost unexplored. The best known are the adducts of the tetrahalides $[MX_4(PR_3)_2]$, which are very moisture sensitive, and often undergo rapid phosphine exchange in solution[143].



(24)

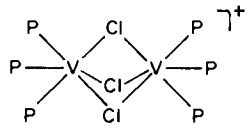
Dinuclear zirconium(III) complexes $[\{ZrCl_3(PR_3)_2\}_2]$ (R = Me, Et, Pr^n, Bu^n) are formed[144] by sodium amalgam reduction of a mixture of $ZrCl_4$ and the phosphine in toluene. An X-ray study of the PBu_3^ncomplex revealed structure **24** with a single Zr—Zr bond. This complex appears to be the only structurally characterized zirconium(III) complex. Tertiary phosphine complexes of titanium(II) and zirconium(II) $[(C_5H_5)_2M(PR_3)_2]$ are readily prepared and appear to be useful starting materials for the synthesis of other complexes, since the phosphines are readily displaced[145,146].

C. Complexes of the Vanadium Group (V)

Vanadium phosphine chemistry in positive oxidation states is largely unexplored, and the only extensive series of complexes are the substituted carbonylvanadates and related nitrosyls and organometallic derivatives.

Substitution of L in $[V(CO)_5L]^-$ (L = dimethyl sulphoxide or ammonia) by PR_3 is the prefered route to $[V(CO)_5(PR_3)]^-$ anions[88,147]. Direct substitution into $[V(CO)_5(NO)]$ produces $[V(CO)_4(NO)(PR_3)]$[148]. Both vanadium(III) and vanadium(II) cyclopentadienyl derivatives are known. $[(C_5H_5)VX_2(PR_3)_2]$ can be reduced with zinc or aluminium to dimeric $[\{(C_5H_5)VX(PR_3)\}_2]$, which add phosphine to form $[(C_5H_5)VX(PR_3)_2]$[149]. Alkyl derivatives $[(C_5H_5)VR_2(PR_3)_2]$ are also known[150].

Two independent X-ray studies of the distorted trigonal bipyramid $[VCl_3(PMePh_2)_2]$ have been reported, as has a study of the six-coordinate $[VCl_3(PMePh_2)_2(MeCN)]$[151,152]. The dinuclear $[V_2Cl_3(PMe_3)_6]^+$ has been characterized[153]; it has structure **25** and is paramagnetic with $\mu = 3.73$ BM.



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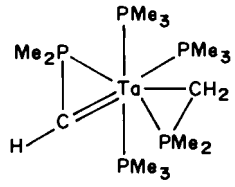
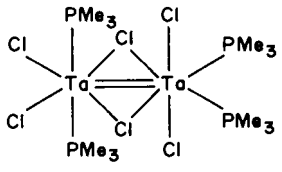
In contrast to vanadium, the recent interesting developments in niobium and tantalum chemistry concern the phosphine adducts of the halides, which exhibit considerable structural diversity. Carbonyl complexes of niobium and tantalum are known, but are less common that for vanadium, but two recent X-ray studies of seven-coordinate tantalum complexes are notable; in $[Ta(CO)_3Cl(PMe_3)_3]$ the structure is a capped trigonal prism[154], whereas in the cation of $[Ta(CO)_3(PMe_3)_4][Ta(CO)_5(PMe_3)]$ the geometry is capped octahedral[155].

Sodium sand reduction of $TaCl_5$ in liquid PMe_3 gives the dark-green metallated phosphine derivative, $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$ (**26**)[156]. Phosphine adducts of niobium and tantalum alkylidenes and related organic derivatives are also known[157,158].



(26)

The pentahalides MCl_5 form 1:1 and 1:2 adducts with phosphines[159], whereas their reduction in the presence of a phosphine, usually with Na/Hg, can lead to complexes of M(II), M(III) or M(IV), depending on the conditions. The brown $[MCl_2(PMe_3)_4]$ (M = Nb or Ta) have *trans* octahedral structures, and the tantalum complex adds hydrogen to form red $[TaH_2Cl_2(PMe_3)_4]$, which is a distorted dodecahedron[160]. The latter can be reduced by Na/Hg under argon to green $[TaH_2Cl(PMe_3)_4]$, which is pentagonal bipyramidal with two axial phosphines[161]. Typical examples of the M(III) halides are *mer* $[NbBr_3(PMe_2Ph)_3]$[162], $[TaCl_3(PMe_3)_3]$[163], $[M_2Cl_6\{P(c\text{-}Hex)_3\}_3]$[164] and $[M_2Cl_6(PBu^t_3)_2]$[164]. The dimeric $[Ta_2Cl_6(PMe_3)_4]$ has structure **27** with a Ta—Ta double bond of length 2.721 Å [165]. It adds molecular hydrogen to form **28** with Ta—Ta = 2.62 Å[166].



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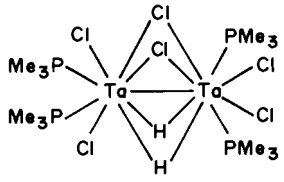

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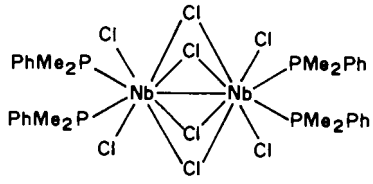
The M(IV) halides have an unexpectedly rich structural chemistry, which has only become clear very recently. Examples of the various types of monomeric complexes are $[TaCl_4(PMe_2Ph)_2]$ (*cis* octahedral)[167]; $[TaCl_4(PEt_3)_2]$, $[NbCl_4(PR_3)_2]$ ($PR_3 = PEt_3$ or $PEtPh_2$) (*trans* octahedral)[167,168]; and $[MCl_4(PMe_3)_3]$ and $[NbBr_4(PMe_2Ph)_3]$ (capped octahedral)[162,167,169]. Dimers with unusual $(\mu\text{-}Cl)_4$ bridges are known for both elements (**29**)[168–171]; the M—M separations of ca 2.83 Å are interpreted as being due to single M—M bonds. Cluster complexes have been little studied, but the characterization of $[Nb_3Cl_7(PMe_2Ph)_6]$, an Nb_3 triangle with one

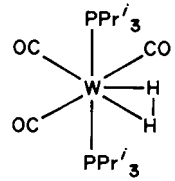


(29)

capping and three edge bridging chlorines[172], and $[M_6Cl_{14}(PR_3)_4]^{0/+}$ [173], suggests a rich area awaiting development.

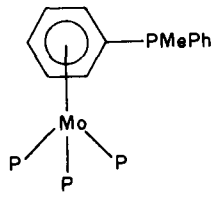
D. Complexes of the Chromium Group (VI)

A short review on tungsten phosphines has been published[174]. A large number of substituted carbonyl complexes $[M(CO)_{6-n}(PR_3)_n]$ ($n = 1$–3, rarely 4) are known for all three elements, and for Mo and W seven-coordinate carbonyl halides are well established. Dinitrogen complexes of molybdenum and tungsten have also been intensively investigated, and have led to the study of much related phosphine chemistry. The dinitrogen area has been reviewed several times, most recently by Henderson *et al.*[175], and will not be discussed here. The most interesting recent work on the carbonyl complexes are the electrochemical studies of Bond and coworkers[176–179]. They examined in detail the properties of the systems *trans*-$[Cr(CO)_4(PPh_3)_2]^{0/1+}$, *fac*- and *mer*-$[Cr(CO)_3(PR_3)_3]^{0/1+}$, *cis*- and *trans*-$[Mo(CO)_4(PR_3)_2]^{0/1+}$ and *fac*- and *mer*-$[Mo(CO)_3(PR_3)_3]^{0/1+}$, which show surprisingly complicated relationships between isomer stability and redox chemistry. Also notable are several X-ray studies which have attempted to probe whether steric or electronic factors dominate the observed reactivities of *fac*-$[Cr(CO)_3(PEt_3)_3]$[180], $[W(CO)_5(PMe_3)]$[181] and *cis*-$[Mo(CO)_4(PR_3)_2]$ ($PR_3 = PMe_2Ph$, $PMePh_2$, PPh_3)[182]. Sterically bulky phosphines produce purple $[M(CO)_3(PR_3)_2]$ (R = *c*-Hex, Pr^i), the X-ray structures of which reveal essentially octahedral structures with the 'sixth' site occupied by an agostic C–H interaction[183]. Most interestingly, these materials add hydrogen reversibly to give $[M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$, the first structurally characterized examples of dihydrogen complexes (**30**)[184], and it now clear that some of the reported phosphine polyhydride complexes of other metals may need to be reformulated as dihydrogen complexes.



(30)

Homoleptic phosphine complexes of both Mo and W are known. The condensation of molybdenum atoms with PMe_3 affords $[Mo(PMe_3)_6]$[185,186], which in solution in benzene is in equilibrium with the metallated derivative $[Mo(PMe_3)_4(Me_2PCH_2)H]$, and readily loses some phosphine on reaction with other ligands such as N_2, CO, C_5H_6 and C_2H_4. Similar co-condensation with tungsten atoms does not give the homoleptic complex, but rather the metallated $[W(PMe_3)_4(Me_2PCH_2)H]$ is produced in low yield, and the latter is best obtained by reduction of WCl_6 with sodium sand in the presence of the phosphine[156]. Molybdenum differs in that reduction of $MoCl_5$ with Na sand and PMe_3 produces a hydride, $[Mo(PMe_3)_5H_2]$[156]. The metallated tungsten complex is extremely reactive; for example, reaction with aqueous acids gives a variety of hydrido, aquo, hydroxo and fluoro species[174,186]. Phenylphosphines produce a different type of complex where one of the phenyl rings bonds in an η^6 manner to the metal. Thus, $MoCl_5$ reduced with magnesium under argon in the presence of $PMePh_2$ generates $[Mo(PPh_2Me)_4]$ (**31**)[187]. Related complexes are known including dimers (**32**), $[W(\eta^6\text{-}PhPPr^n_2)(N_2)(PPhPr^n_2)_2]$ and $[Mo(\eta^6\text{-}PhPEt_2)(PR_3)(Ph_2PCH_2CH_2PPh_2]$[188,189].



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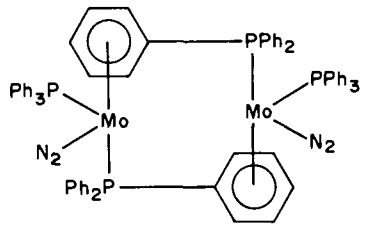

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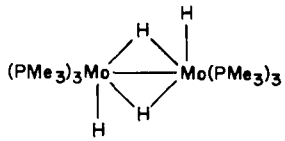
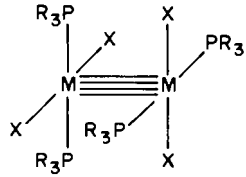


(33)

Both molybdenum and tungsten form a variety of polyhydrides, of types $[M(PR_3)_3H_6]$[190,191], $[M(PR_3)_4H_4]$[186,190], $[M(PMe_3)_5H_2]$[156,192], $[Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6]$ (33) and $[W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5]$[193]. An X-ray and neutron diffraction study of $[WH_6(PPhPr^i_2)_3]$ revealed a tricapped trigonal prismatic structure[194], whilst the tetrahydrides are thought to be distorted dodecahedra and $[Mo(PMe_3)_5H_2]$ is pentagonal bipyramidal[192]. Barron *et al.*[195] have shown that when $LiAlH_4$ is the reductant used to produce tungsten polyhydrides, intermediate aluminohydride complexes are formed, and these have been fully characterized. The reaction of $[WH_6(PMe_3)_3]$ with NaH or KH in the presence of crown ethers produces complexes such as $[W(PMe_3)_3H_5M(crown)]$ (M = Na, K)[196].

Tertiary phosphine complexes of chromium halides are limited to a few intractable materials, but a wide variety of molybdenum and tungsten complexes exist. Mononuclear complexes such as octahedral *trans*-$[MX_4(PR_3)_2]$ and capped octahedral seven-coordinate $[MCl_4(PR_3)_3]$ are well known[197,198]. Cautious reduction of the M(IV) complexes in the presence of PR_3 yields M(III) materials such as *mer*-$[WCl_3(PMe_3)_3]$ and *mer*-$[MoCl_3(PMe_3)_3]$[199,200], which can be further reduced to *trans*-$[MCl_2(PR_3)_4]$[201-203]. Hydrido-halides including yellow $[WCl_2H_2(PMe_3)_4]$, red $[WCl_2H_2(PMe_3)_4]^+$ and blue $[WClH_2(PMe_3)_4]^+$ can also be made[203,204].

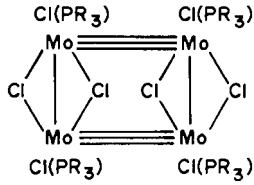
Most effort has been devoted to the M—M-bonded dimers and the field has been reviewed[205]. $[Mo_2X_4(PR_3)_4]$ are obtainable by a number of routes including substitution into an M—M-bonded species such as $[Mo_2Cl_9]^{5-}$ or $[Mo_2Cl_4(py)_4]$, or by reduction under carefully controlled conditions of a molybdenum halide monomer, $[MoCl_4(PR_3)_2]$[205]. The initially more elusive tungsten complexes are usually made by Na/Hg reduction of WCl_4 in the presence of the phosphine, but can also result from the decomposition of $[WCl_2(PR_3)_4]$ or $[WCl_3(PR_3)_3]$ on heating[206]. All have structure **34** with an eclipsed geometry indicating a quadruple bond[207]. Methyl analogues $[Mo_2Me_4(PMe_3)_4]$[208] and heteronuclear dimers $[(PR_3)_2Cl_2MoWCl_2(PR_3)_2]$[209] are known, the latter being made from $[Mo(PR_3)_4]$ (PR_3 = phenylalkylphosphine) and $[WCl_4(PR_3)_2]$. It has recently been shown that substitution of the phosphine into the



(34)

carbonyl halides $[Mo_2(CO)_8X_4]$ is a convenient route to these dimers[210]. Detailed X-ray studies on $[Mo_2(PMe_3)_4X_4]$ (X = Cl, Br, I) reveal that the Mo—Mo bond length (ca 2.13 Å) is insensitive to the halide present[211]. Detailed spectroscopic data are also available on these complexes[205,211]. $[W_2Cl_4(PMe_3)_4]$ undergoes a le oxidation to $[W_2Cl_4(PMe_3)_4]^{+}$ [206], and iodine converts $[Mo_2I_4(PMe_3)_4]$ into $[PR_3H]$-$[Mo_2I_7(PMe_3)_2]$, a confacial bioctahedron[212].

McCarley and coworkers[213–215] have described some tetranuclear species $[Mo_4Cl_8(PR_3)_4]$ (R = alkyl) which have structure **35**, in which the short unbridged Mo—



(35)

Mo distances (2.21 Å) are believed to correspond to a triple bond and the bridged edges (2.90 Å) have single bonds. Tungsten analogues have been prepared[206]. Heating these tetramers with $[Mo(CO)_6]$ produces species $[\{Mo_4Cl_8(PR_3)_2\}_n]$ and, although structural data are not yet available, it is thought that these are 'dimers of tetramers', i.e. $n = 2$. Phosphine-substituted hexanuclear clusters have recently been described; they are of type $[\{W_6Cl_8\}Cl_4(PR_3)_2]$, which have the basic hexanuclear unit with a *trans* disposition of the phosphines[216].

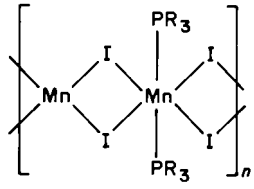
A variety of oxide halide adducts are known for both molybdenum and tungsten. Generally these are made by direct reaction of the phosphine with the oxide halide in a suitable solvent, with an oxide halide complex such as $[WOCl_3(thf)_2]$ or by cautious hydrolysis of the halide complexes. Typical examples are $[WOCl_4(PR_3)_2]$[217], $[WOCl_3(PR_3)_2]$[218,219] $[MoOCl_2(PR_3)_3]$[200] and $[WOCl_2(PR_3)_3]$[198,204]. Some years ago, Chatt and coworkers recognized two forms (blue and green) of *mer-cis*-$[MoOCl_2(PR_3)_3]$ which differed in the bond lengths and angles about the metal centre, and named this new form of isomerism 'distortional isomerism'. Further examples of this effect have been observed[200,220], although it remains a poorly understood phenomenon. Finally, the reaction of $WYCl_4$ (Y = O, S, Se) with PPh_3 has been shown to generate the tungsten(IV) complex $[WCl_4(PPh_3)_2]$ and Ph_3PY[221].

E. Complexes of the Manganese Group (VII)

There is an extensive chemistry of phosphine-substituted manganese carbonyls: neutral dimers $[Mn_2(CO)_{10-n}(PR_3)_n]$, cationic species $[Mn(CO)_{6-n}(PR_3)_n]^{m+}$, anions

$[Mn(CO)_{5-n}(PR_3)_n]^{1-}$, carbonyl hydrides and nitrosyls, which have been described in previous reviews. However, the most interesting new developments are in the preparation of phosphine adducts of manganese(II) alkyls and halides.

Reaction of manganese(II) dialkyls with PR_3 in toluene or direct combination of manganese(II) chloride, a dialkylmagnesium and the phosphine in diethyl ether produces $[Mn_2R_4'(PMe_3)_2]$ ($R' = CH_2SiMe_3$, CH_2CMe_3, CH_2Ph) and $[Mn_2(CH_2SiMe_3)_4(PR_3)_2]$ ($PR_3 = PEt_3$, PMe_2Ph, $PMePh_2$, $P(c\text{-}Hex)_3$)[222]. The structures are $[(PR_3)R'Mn(\mu\text{-}R')_2MnR'(PR_3)]$. Mononuclear $[MnR_2'(PR_3)_2]$ are formed in solution with excess PR_3, and the distorted tetrahedral $[Mn(CH_2CMe_2Ph)_2(PMe_3)_2]$ has been structurally characterized[223]. Under rigorously anhydrous conditions, manganese(II) halides react with phosphines in tetrahydrofuran or diethyl ether to give 1:1 and 1:2 complexes[224-227]. The latter are tetrahedral, e.g. $[Mn(PEt_3)_2I_2]$[226], whereas the structure of $[\{Mn(PMe_2Ph)I_2\}_n]$ reveals a polymeric chain, with alternating 4- and 6-coordinate manganese[225] (**36**). Depending on the particular phosphine and the halide involved, some



(**36**)

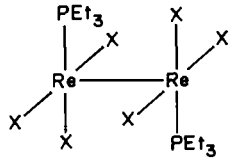
of the 1:1 complexes bind a variety of small molecules including O_2, CO, C_2H_4 and NO, in some cases reversibly[224,228,229]. In contrast, the $[Mn(PMe_3)X_2]$ are irreversibly oxidized by oxygen, and manganese(III) complexes $[Mn(PMe_3)_2X_3]$ (X = Cl, Br, I) can be sublimed from the products *in vacuo*. The structure of the iodo complex is trigonal bipyramidal with axial phosphines[230].

The phosphine chemistries of technetium and rhenium are generally similar, although that of the former is much less developed. In fact, little new work on technetium complexes of tertiary phosphines has been reported; examples are some substitution reactions of the carbonyl halides $[Tc(PMe_2Ph)_3(CO)_2Cl]$ and $[Tc(PMe_2Ph)_2(CO)_3Cl]$[231] and the reaction of $[TcO_4]^-$ with PPh_3 and HCl[232], which leads to $[Tc(PPh_3)_2Cl_4]$ and $[Tc(PPh_3)Cl_5]^-$.

Rhenium has a very complicated coordination chemistry and a wide variety of phosphine complexes are known, with the most interesting recent work involving the polyhydrides and the derivatives of the dinuclear Re_2^{n+} units. The unique $[ReH_7(PR_3)_2]$ type ($PR_3 = PMe_3$[190], PMe_2Ph[233], $PPhPr_2$ and PPh_3[234]) are non-rigid in solution, and several X-ray diffraction studies have revealed wide P—Re—P angles, although not all the hydrogen atom positions have been definitely located. On heating, the compounds decompose to $[Re_2H_8(PR_3)_4]$, which can also be made by BH_4^- reduction of the $[Re_2Cl_8]^{2-}$ in the presence of the phosphine. The dimers have four hydrido bridges and formally a triple M—M bond[235]. Notably, the corresponding complex of the bulky tricyclohexylphosphine, $[ReH_7\{P(c\text{-}Hex)_3\}_2]$, does not decompose to the dimer on heating[236]. Pentahydrides $[ReH_5(PR_3)_3]$ are dodecahedral[233,237]. The latter can be protonated to $[ReH_6(PR_3)_3]^+$ whereas in the presence of ligands such as RCN or RNC, $[ReH_4(PR_3)_3L]^+$ are formed[238]. The reaction chemistry of $[Re_2H_8(PR_3)_4]$, including electrochemical or chemical oxidation to the blue paramagnetic monocation and substitution reactions with isonitriles, has also been examined[238].

Rhenium halide derivatives include mononuclear species such as *mer*-$[ReX_3(PR_3)_3]$, *trans*-$[ReX_4(PR_3)_2]$, $[ReCl_5(PEt_3)]^-$ [239] and $[ReCl(PMe_3)_5]$[240]. The last species is produced together with $[ReH(PMe_3)_5]$ by Na/Hg reduction of $[ReCl_4(thf)_2]$ in the presence of PMe_3, and can be converted into a range of related complexes including $[ReMe(PMe_3)_5]$, $[ReHCl(PMe_3)_5]^+$ and $[Re(CO)_2(PMe_3)_3Cl]$[240]. Extensive studies of the multiply bonded Re_2^{n+} species have been carried out, much of it by the groups of Cotton and Walton who have reviewed the field[205]. The synthetic conditions necessary for the production of a particular complex, and the reactions and interconversions of the various complexes, vary considerably with the phosphine involved, and the reviews or the original papers should be consulted for details; only a general overview is given here.

Under mild conditions, $[Re_2X_8]^{2-}$ (X = Cl or Br) and PR_3 give $[Re_2X_6(PR_3)_2]$ and under more forcing conditions, for example in boiling alcohol, reduction occurs with $PR(alkyl)_2$ or $P(alkyl)_3$ to $[Re_2X_4(PR_3)_4]$. The former type have the eclipsed structure **37** whereas the latter are of type **34**. With less basic phosphines, $[Re_2X_5(PR_3)_3]$ are formed



(37)

which can be reduced to $[Re_2X_4(PR_3)_4]$ by BH_4^- [241]. Chemical or electrochemical oxidation of $[Re_2Cl_4(PR_3)_4]$ gives mono- and di-cations[242,243]. The electrochemically generated $[Re_2X_4(PR_3)_4]^{2+}$ chemically convert into $[Re_2X_5(PR_3)_3]^+$ and $[Re_2X_6(PR_3)_2]$[243]. X-ray studies on $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ ($n = 0, 1, 2$), all with structure **34**, reveal that whereas the Re—Cl distance shortens and Re—P lengthens on oxidation, Re—Re is little changed, demonstrating that a simplistic interpretation of bond length in terms of bond order in these systems is not possible[244]. The Re_2^{n+} units are disrupted by strong π-acceptors such as CO or RNC in very complex reactions which produce mixtures of mononuclear species[245,246]. More surprising is the reaction of $[Re_2Cl_4(PEt_3)_4]$ with molecular hydrogen under pressure (120 atm, 60 °C), which gives *trans*-$[ReCl_4(PEt_3)_2]$, $[Re_2Cl_6(PEt_3)_2H]^-$ and $[ReCl_5(PEt_3)]^-$[239].

Phosphine-substituted trinuclear species $[Re_3Cl_9(PR_3)_3]$ are well known[205], and the corresponding alkyls $[Re_3Cl_3R_6]$, $[Re_3Cl_3(c\text{-}Hex)_6(PMe_2Ph)_3]$ and $[Re_3Me_9(PR_3)_n]$ ($PR_3 = PEt_2Ph$, $n = 2$, 3; PMe_2Ph, $n = 3$) have been obtained by Edwards *et al.*[247]. Under certain conditions these can be cleaved to dimers, $[Re_2Me_6(PMe_2Ph)_3]$ or $[Re_2Cl_2(CH_2SiMe_3)_2(PMe_3)_4]$. Triethylphosphine reduces Re_2O_7 in the presence of pyridine-type bases to $[ReO_2(py)_4][ReO_4]$[248], but excess of PMe_3 affords *trans*-$[ReO_2(PMe_3)_4][ReO_4]$[249]. Whereas phosphine complexes of high-valent oxide halides are well known, those of oxo species alone are rare at present.

F. Complexes of the Iron Sub-group

The site preference of ligands in trigonal bipyramidal $[M(CO)_4L]$ (M = Fe, Ru, Os; $L = PR_3$, AsR_3, SbR_3) has been examined[250]. For iron the axially substituted isomer is usually found, e.g. in $[Fe(CO)_4PPh_3]$[251], but X-ray studies of $[Os(CO)_4SbPh_3]$ and $[Ru(CO)_4SbPh_3]$ (equatorial) and of $[Ru(CO)_4AsPh_3]$ or $[Ru(CO)_4SbMe_3]$ (axial) show

that the pattern is less clear for the heavier elements, and in solution several complexes exhibit axial↔equatorial isomerism. The tendency to form the equatorial isomer was observed to be Ru > Os ≫ Fe, Sb > As > P and Ph > Me, and it was suggested that the weaker σ donor occupies the equatorial site, whilst differences in π-bonding ability may account for the order with metal[250]. A further interesting comparison between metals is found in the $[MH_4(PR_3)_3]$ compounds, where a recent re-examination has shown that for M = Os the complex is a genuine M(IV) hydride, but for M = Fe or Ru the materials should be formulated as $[MH_2(H_2)(PR_3)_3]$ containing one dihydrogen ligand[252].

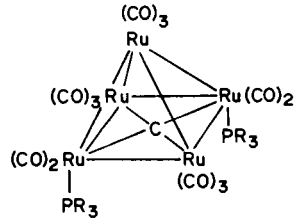
The formally iron(0) homoleptic complex $[Fe(PMe_3)_4]$ has attracted considerable study[253-255]. It is produced by $LiAlH_4$ reduction of $FeCl_2$–PMe_3 in thf, and in solution is in equilibrium with the metallated form $[(PMe_3)_3Fe(CH_2PMe_2)H]$, the equilibrium lying in favour of the latter. It is a highly reactive system, substituting some phosphine by CO or phosphites (L') to give $[Fe(L')_3(PMe_3)_2]$, adds MeX to give $[FeMeX(PMe_3)_4]$, and with HX produces tetrahedral $[Fe(PMe_3)_2X_2]$ (X = Cl, Br, I) and octahedral $[Fe(PMe_3)_4I_2]$. The $[Fe(PMe_3)_4Me_2]$ is also known. With CO_2 it produces an unusual cleavage reaction affording $[Fe(CO)(CO_3)(PMe_3)_3]$.

Finally notable is the demonstration that at low temperatures $[Fe(C_5H_5)\{1,2\text{-}C_6H_4(PMePh))_2\}(PHRPh)]$ can be deprotonated with base to the phosphido complex, and alkylated stereoselectively to yield chiral phosphines[256].

The reactions of the cluster carbonyls of this group have been intensively investigated. Attempted direct substitution into $[Fe_3(CO)_{12}]$ often results in cluster breakdown, whereas with $[Ru_3(CO)_{12}]$ the product is usually the trisubstituted $[Ru_3(CO)_9(PR_3)_3]$. Forcing conditions are necessary with $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{12-n}(PR_3)_n]$ (n = 1, 2 or 3) and clusters containing fragmented phosphines resulting from C—H or P—C cleavage are also present. Recent developments have included the use of labile starting materials such as $[Os_3(CO)_{12-n}(MeCN)_n]$, and of Me_3NO or sodium diphenylketyl which allow facile CO replacement, leading to a wider range of products. Reviews describing the chemistry of $[Os_3(CO)_{12}]$[257] and ruthenium cluster carbonyls[258] have recently appeared, and phosphine fragmentation in these systems has also been reviewed[259,260]. Substitution usually produces $[M_3(CO)_{12-n}(PR_3)_n]$ (n = 1–3) although $n > 4$ is known with phosphites and $PPh(OMe)_2$[258,261,262]. X-ray studies show that the phosphines usually occupy equatorial positions on different metal atoms[257,263]. However, using $[Os_3(CO)_{10}(L)_2]$ (L = MeCN or 1/2 butadiene) with PMe_2Ph leads to new isomers of the di- and tri-substituted types (**38**)[264]. Phosphine complexes of other cluster carbonyls and hy-

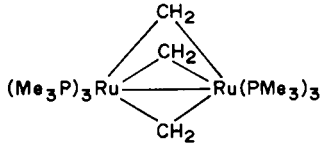
(38)

dridocarbonyls are known, e.g. $[Ru_5C(CO)_{15}]$ affords $[Ru_5C(CO)_{15-n}(PPh_3)_n]$ (n = 1, 2) and $[Ru_5C(CO)_{12}(PMe_2Ph)_3]$ with the phosphines occupying axial positions on different ruthenium atoms in the basal plane of the square-pyramidal unit[265] (**39**). Reaction of $RuCl_3 \cdot nH_2O$ with CO and PR_3 affords a variety of six-coordinate carbonyl halides $[Ru(CO)_x(PR_3)_yCl_2]$ ($x + y = 4$), but Bu_3^tP generates dinuclear $[(Bu_3^tP)(CO)_2Ru(\mu\text{-}Cl)_2Ru(CO)_2(Bu_3^tP)]$, which chlorine oxidizes to $[Ru_2(CO)_4(Bu_3^tP)_2Cl_2(\mu\text{-}Cl)_2]$[266,267]. The less bulky Bu_2^tRP (R = Me, Et) yield five-coordinate monomers $[Ru(Bu_2^tRP)_2(CO)HCl]$, which can, however, add CO to give the dicarbonyl[268].



(39)

Sodium sand reduction of $RuCl_3$ in liquid PMe_3 produces the metallated $[(PMe_3)_3HRu(\eta^2\text{-}CH_2PMe_2)]$ and $[(PMe_3)_3HRu(\mu\text{-}CH_2PMe_2)_2RuH(PMe_3)_3]$[156]. Similar metallated $[Ru(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3Cl]$ and $[Ru(\eta^2\text{-}CH_2PMe_2)_2(PMe_3)_2]$ are known[269], the Ru—C bonds being cleaved by molecular hydrogen to give $[RuHCl(PMe_3)_4]$ and $[RuH_2(PMe_3)_4]$, respectively. *o*-Metallated triphenylphosphine complexes $[RuH(o\text{-}C_6H_4PPh_2)(PPh_3)_2(solvent)]$ result from reaction of $[RuHCl(PPh_3)_3]$ with RLi, via intermediate alkyl hydrides which eliminate alkane on warming[270]. Anionic ruthenium complexes with metallated ligands are known, e.g. $K[Ru(H)_2(PPh_3)_2(o\text{-}C_6H_4PPh_2)]$[271]. Metallated phosphine derivatives of osmium are readily obtained, e.g. $[OsHMe(o\text{-}C_6H_4PPh_2)(PPh_3)_2]$[272], $[OsX(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ (X = H, Cl)[273,274]. Interaction of the dinuclear acetates of ruthenium or osmium with alkylating agents is a convenient route to mononuclear alkyls[273,275], whilst $[Ru_3O(OAc)_6(H_2O)_3]^+$ and $Me_2Mg\text{–}PMe_3$ produce the unusual compound **40**, which can be protonated by HBF_4 to $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}Me)(PMe_3)_6]^+$ and $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$[276]. Further studies[277] isolated $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6]^+$ and $[Ru_3(\mu\text{-}CH_2)_4(PMe_3)_8](BF_4)_2$ (**41**).



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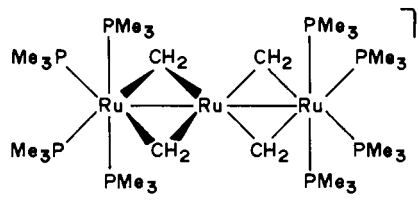
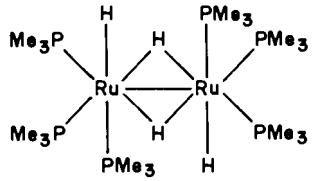


(41)

Osmium polyhydrides have been well characterized, recent neutron diffraction studies supporting a classical hydride constitution for $[OsH_4(PMe_2Ph)_3]$ (pentagonal bipyramidal with axial phosphines)[278] and $[OsH_6(PPr^i_2Ph)_2]$ (dodecahedral)[279]. An X-ray study of $K[OsH_3(PMe_2Ph)_3]$[280] revealed a *fac* anion geometry with significant anion–cation interactions. Ruthenium hydrides are generally less stable. The $[RuH_6\{P(c\text{-}Hex)_3\}_2]$ has recently been obtained[281]; on heating it gives $[Ru_2H_6\{P(c\text{-}Hex)_3\}_4]$, and with hydrogen and P(*c*-Hex)$_3$ produces $[RuH_4\{P(c\text{-}Hex)_3\}_3]$. The PPh_3 analogues are also known[282]. Although the osmium complexes are classical hydrides, it seems likely that all the ruthenium species may be Ru(II)$(H)_2$ moieties with the remaining hydrogen present as $\eta^2\text{-}H_2$[184]. The structure of the monohydride $[RuH(PMe_2Ph)_5]PF_6$ reveals a crowded molecule with significant interligand repulsions, which may account for its high reactivity[283]. Hydrogenolysis of the $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ and $[Ru_2(\mu$-



(42)

$CH_2)_2(PMe_3)_6](BF_4)_2$ produces dinuclear $[Ru_2H_4(PMe_3)_6]$ (**42**) and $[Ru_2(\mu\text{-}H)_3(PMe_3)_6](BF_4)$, both of which have been structurally characterized[284].

The chemistry of phosphine complexes of ruthenium halides encompasses a wide range of 5- and 6-coordinate monomers, and doubly and triply halide-bridged dimers described in previous reviews. All known examples contain ruthernium(II) or (III), although higher oxidation states are known in the nitrido complexes[285], and in the recently described ruthenium(IV) oxo–bipyridyl complexes[286]. A detailed review of the chemistry and catalytic reactions of $[Ru(PPh_3)_3Cl_2]$ is available[287], and this also includes data on a variety of related species. The PMe_3 complexes differ from the others; recently characterized examples[288] include $[Ru(PMe_3)_5Cl]^+$, $[Ru_2Cl_4(PMe_3)_4]$, *trans*-$[RuCl_2(PMe_3)_4]$ and *cis*-$[RuCl_2(PMe_3)_4]$.

Osmium halide phosphine chemistry covers oxidation states VI and IV–II. Salmon and Walton[289] showed that the reported $[OsOX_3(PPh_3)_2]$ (X = Cl or Br) obtained from OsO_4, HX and PPh_3 were mixtures of the osmium(VI) $[OsO_2X_2(PPh_3)_2]$ and osmium(IV) $[OsX_4(PPh_3)_2]$, and prepared examples of the former type with PMe_2Ph, $PEtPh_2$ and PEt_2Ph[284]. Reduction of $[OsO_2X_2(PR_3)_2]$ with HX–ROH or directly from OsO_4–PR_3–HX or $[OsX_6]^{2-}$–PR_3 gives *trans*-$[OsX_4(PR_3)_2]$ and *mer*-$[OsX_3(PR_3)_3]$[272,290]. An X-ray study of $[Os(PPh_3)_3Cl_2]$ confirmed that it is square pyramidal with apical PR_3, like its ruthenium analogue[291], but with smaller phosphines 6-coordinate osmium(II) complexes, e.g. $[OsCl_2(PMe_3)_4]$, result[272]. A wide variety of mixed-ligand complexes can be prepared by reduction of $[OsO_2X_2(PR_3)_2]$ or $[OsX_4(PR_3)_2]$ in the presence of suitable ligands. Electrochemical studies have generally found that the $[OsX_4(PR_3)_2]^{0/-}$ and *mer*-$[OsX_3(PR_3)_3]^{0/+}$ couples are reversible, but reduction to osmium(II) is usually irreversible[289,290,292,293]. A detailed investigation[292] into the electrochemical reduction of *mer*-$[OsCl_3(PMe_2Ph)_3]$ showed that the $[OsCl_3(PMe_2Ph)_3]^-$ is initially formed, but that this loses chloride to give $[OsCl_2(PMe_2Ph)_3(solvent)]$, and under different conditions $[Os_2Cl_4(PMe_2Ph)_6]$ and $[Os_2Cl_3(PMe_2Ph)_6]^+$ are formed.

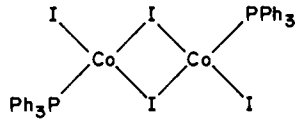
In contrast to the $[X_4MMX_4]^{n-}$ of rhenium or tungsten, which substitute phosphine with retention of the multiple bonds, $[Os_2X_8]^{2-}$ are cleaved to the mononuclear species *trans*-$[OsX_4(PR_3)_2]^-$, *mer*-$[OsX_3(PR_3)_3]$, *trans*-$[OsX_2(PR_3)_4]$ and *trans*-$[OsX_2(PR_3)_4]^+$ on reaction with PMe_3 or PMe_2Ph in alcohols[293]. With PEt_3 or $PMePh_2$ the products are binuclear halide-bridged $[Os_2X_3(PR_3)_6]^+$, and an X-ray study of $[Os_2Cl_3(PEt_3)_6]PF_6$ revealed the expected confacial octahedron.

Notable examples of metallated triphenylphosphine are $[Os_2(OAc)_2Cl_2(o\text{-}C_6H_4PPh_2)_2]$ and $[Os_2Cl_4(o\text{-}C_6H_4PPh_2)_2]$, where there are short Os—Os triple bonds present[294,295].

G. Complexes of the Cobalt Sub-group

The phosphine chemistry of this group has been extensively studied for many years, and much of the recent work is an extension or confirmation of previous results rather than an inherently new departure. Rhodium hydrido and halo complexes in particular continue to be intensively examined as catalysts.

Dicobalt octacarbonyl and phosphines generally produce $[Co_2(CO)_6(PR_3)_2]$ with organo-Group IV phosphines, $(Me_3E)_3P$ (E = C, Si, Ge, Sn), and in some cases $[Co(CO)_4(PR_3)]$ also form[96]. Trimethylphosphine complexes of cobalt have been reported in oxidation states from -1 to $+3$, and the low-valent complexes have an extensive organometallic chemistry. The 'parent' homoleptic species $[Co(PMe_3)_4]$ can be reduced to the very nucleophilic $[Co(PMe_3)_4]^-$ by alkali metals[296], and this reacts with MeI to give $[Co(PMe_3)_4Me]$ and $[Co(PMe_3)_3Me_2I]$, and substitutes with CO to form $[Co(PMe_3)(CO)_3]^-$. X-ray structures have been reported for $[\{Co(PMe_3)(CO)_3\}_2]$[297], $[Co(PMe_3)_3I]$[298] and $[Co(CO)_2(PMe_3)_2Cl]$[297]. The cobalt(I) complex $[Co(PMe_3)_3Br]$ is converted by $NaBPh_4$ into blue–green $[Co(PMe_3)_4]BPh_4$ and brown $[Co(PMe_3)_2BPh_4]$, the latter containing a CoP_2 unit η^6-coordinated to one phenyl ring of the BPh_4[299]. $[Co(PMe_3)_3Br]$ adds ethylene and acetylenes[300,301]. Cobalt(II) halides typically form 2:1 complexes and more rarely 3:1 complexes with tertiary phosphines, but with PMe_3 the products are $[Co(PMe_3)_2X_2]$, $[Co(PMe_3)_3X_2]$ and $[Co(PMe_3)_4X]^+$, depending on the reaction conditions; the five-coordinate complexes are trigonal bipyramidal with axial phosphines[302]. The familiar $[Co(PPh_3)_2X_2]$ (X = Cl, Br) have been structurally characterized and their magnetic properties studied at low temperatures[303]. An unusual 1:1 complex '$Co(PPh_3)I_2$' has been prepared using excess CoI_2 and has been shown to be a halide-bridged dimer (**43**) by an X-ray study[304]. Relatively few cobalt(III) complexes of



(43)

monodentate phosphines are known, but X-ray data have been published on $[Co(PEt_3)_2Cl_3]$ (trigonal bipyramidal axial phosphines)[305], *mer-cis*-$[Co(PMe_3)_3Me_2(N_3)]$[306] and *mer*-$[Co(PMe_3)_3(NCS)_3]$[307].

The structures of two $[Ir_4(CO)_8(PR_3)_4]$ complexes ($PR_3 = PMe_2Ph$[308] and PMe_3[309]) have been determined; there is one phosphine on each iridium atom of the tetrahedral core and, in contrast to $[Ir_4(CO)_{12}]$, edge-bridging carbonyls are present in the phosphine complexes.

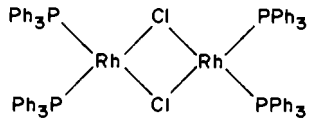
trans-$[Rh(CO)Cl(PR_3)_2]$ are among the most familiar rhodium carbonyl complexes; new examples reported include $PR_3 = PMe_3$[288], $PMe\{CH(SiMe_3)_2\}_2$[310] and Bu^t_3P[311,312]. For $PR_3 = Bu^t_3P$, $[(Bu^t_3P)(CO)Rh(\mu\text{-}Cl)_2Rh(CO)(Bu^t_3P)]$ and $[(Bu^t_3P)(CO)Rh(\mu\text{-}CO)_2Rh(CO)(Bu^t_3P)]$ were also obtained. $[Rh(CO)I(PR_3)_2]$ are considerably harder to isolate in the pure state owing to a tendency to dissociate phosphine in solution[313]. Tri-*tert*-butylphosphine reacts with $[Ir(CO)_3Cl]$ to give $[Ir(CO)_2Cl(Bu^t_3P)]$ and $[Ir(CO)Cl(Bu^t_3P)_2]$[314], but under reflux in *N,N*-dimethylformamide both rhodium and iridium trichloride cleave a *tert*-butyl group to give $[M(CO)Cl(Bu^t_2PH)_2]$[315].

The rhodium complex of metallated PMe_3, $[Rh_2(CH_2PMe_2)_2(PMe_3)_4]$, is formed from $[Rh(PMe_3)_4](OAc)$ and $LiN(SiMe_3)_2$; it is cleaved by molecular hydrogen to *fac*-$[RhH_3(PMe_3)_3]$[269]. Bulky alkyl phosphines including $Bu^t_2Pr^nP$, $Bu^t_2Bu^nP$, Bu^t_3P and Pr^i_3P are readily metallated on reaction with $[\{Ir(cyclooctene)_2Cl\}_2]$ to give a variety of four- and five-membered chelate ring (P,C) complexes[316].

The most important rhodium hydride is probably $[RhH(CO)PPh_3)_3]$, which is the active hydroformylation catalyst in the Rh–PPh_3 systems. Its synthesis, reactions and catalytic abilities have been reviewed[317]. Other hydridocomplexes include the distorted planar $[RhH(PPh_3)_3]$[318] and $[RhH(Pr^i_3P)_3]$[319], the *trans* trigonal bipyramidal $[RhH_2Cl(Bu^t_3P)_2]$[320] and $[RhH_2(PMe_3)_4]Cl$[288]. Iridium hydrides are generally more

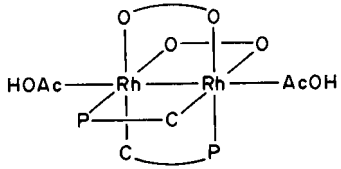
stable, and two with no rhodium analogues are $[IrH_5(Pr_3^iP)_2]$, which on the basis of a neutron diffraction study has a pentagonal bipyramidal structure with axial phosphines[321], and the purple $[IrH_2Cl_2(Pr_3^iP)_2]$, which has an 'all-*trans*' octahedral geometry and is a rare example of a paramagnetic hydride[322].

The most used single complex of rhodium is undoubtedly 'Wilkinson's complex', $[Rh(PPh_3)_3Cl]$, the first homogeneous hydrogenation catalyst. A recent review by Jardine[323] describes the properties and catalytic reactions of this material, and should be consulted for further details. We mention here only the X-ray data on the two forms (red and orange), which differ slightly in the orientation of the phosphines and have inexplicably different Rh—Cl bond lengths[324]. The reaction of $[Rh(PPh_3)_3Cl]$ with PMe_3 in light petroleum affords $[Rh(PMe_3)_4]Cl$, which loses a phosphine on heating in toluene to give $[Rh(PMe_3)_3Cl]$[288]. Both complexes are square-planar with a tetrahedral distortion, and on treatment of their aqueous solutions with PF_6^- precipitate $[Rh(PMe_3)_3]PF_6$. $[Rh(PPh_3)_3]ClO_4$, made from $[Rh(PPh_3)_3Cl]$ and $TlClO_4$, has a planar structure with a T-shaped RhP_3 core and with the fourth position in the plane occupied by an *o*-H(phenyl) contact[325]. The dinuclear $[\{Rh(PPh_3)_2Cl\}_2]$ has a planar Rh_2Cl_2 core (**44**)[326]. The formally three-coordinate $[Rh\{P(c\text{-}Hex)_3\}_2X]$ (X = F, Cl, Br, I)



(44)

halogen oxidize to rare paramagnetic rhodium(II) complexes[327,328]. Dinuclear rhodium(II) complexes are represented by the *ortho*-metallated triphenylphosphine complexes $[Rh_2(OAc)_2(o\text{-}C_6H_4PPh_2)_2]\cdot 2HOAc$ (**45**) and $[Rh_2(OAc)_3(o\text{-}C_6H_4PPhC_6F_4Br)(PPh_2C_6F_4Br)]$[329,330].



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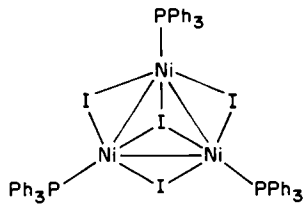
Dinuclear rhodium(III) complexes have not been greatly studied, but there is evidence that a variety of triply halide-bridged materials can be obtained, either from reaction of rhodium trichloride with the phosphine under carefully controlled conditions or specifically removing chloride with silver salts from mononuclear complexes[331]. Robertson and Tucker[332,333] compared X-ray data on *mer*- and *fac*-$[IrCl_3(PMe_2Ph)_3]$ and some related hydrido-chlorides in an attempt to clarify the effects of ligand set and packing factors on the bond lengths and angles in iridium(III) phosphines. Extensive studies by Shaw and coworkers in the 1970s showed that bulky phosphines metallated readily on iridium(III), and more recently they have shown that small phosphines in $[Ir(PMe_2R)_3Cl_3]$ (R = Me or Ph (metallate on treatment with $LiNPr_2^i$ to give three-membered ring metallacycles $[IrCl_2(PMeRCH_2)(PMe_2R)_2]$, the reaction being reversed by HX, whilst halogens give $[IrCl_2X(PMeRCH_2X)(PMe_2R)_2]$[334].

No rhodium(IV) phosphine complexes are known, but purple *trans*-$[Ir(PR_3)_2Cl_4]$ and dark-green $[Ir(PR_3)_2Br_4]$ are easily made by halogen oxidation of the corresponding $[Ir(PR_3)_2X_4]^-$ anions[335]. The iridium(III)–iridium(IV) couples are electrochemically reversible. $[Ir(PMe_2Ph)_2Cl_4]$ is a convenient 1e oxidant in organometallic chemistry, and reacts with $[Pd(AsMe_3)_2Cl_2]$ to give the novel bimetallic $[Cl_2(PMe_2Ph)_2Ir(\mu\text{-}Cl)_2Pd(AsMe_3)Cl]$[336].

H. Complexes of the Nickel Sub-group

Tertiary phosphine complexes of nickel, palladium and platinum were among the first to receive detailed study and, although still very popular, new work is largely an extension or reinvestigation of previous studies. The chemistry of nickel with tertiary phosphines is essentially much simpler than that of earlier Group VIII metals, and mostly concerns carbonyl or homoleptic materials in low oxidation states, and nickel(II) or rarely nickel(III) halide complexes.

Very nucleophilic homoleptic complexes $[Ni(PR_3)_n]$ are obtained by reduction of nickel(II) salts in the presence of the phosphine and in other ways[11], the value of n depending on the phosphine concerned and the reaction conditions. The coordinatively unsaturated $[Ni\{P(c\text{-}Hex)_3\}_2]$ is more reactive than either $[Ni(PEt_3)_3]$ or $[Ni(PMe_3)_4]$ and rapidly cleaves various RX (R = alkyl and sometimes aryl, X = Cl, Br, I, CN) to form $[NiX\{P(c\text{-}Hex)_3\}_2]$ or $[NiHX\{P(c\text{-}Hex)_3\}_2]$ and coupled organic products[337]. Unexpectedly sodium reduction of $[Ni\{P(c\text{-}Hex)_2Ph\}_2Cl_2]$ under nitrogen results in cleavage of a phenyl group to give $[Ni_2\{\mu\text{-}P(c\text{-}Hex)_2\}_2\{P(c\text{-}Hex)_2Ph\}_2]$[338]. An unusual trimeric species (**46**) has been obtained by decomposition of $[Ni(cod)I(PPh_3)]$ in solution[339].



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Careful reduction of nickel(II) phosphine complexes leads to nickel(I) complexes $[Ni(PR_3)_3X]$ (X = halide), and the structure of the distorted tetrahedral $[Ni(PMe_3)_4]BPh_4$ (μ = 2.4 BM), obtained serendipitously, has been determined[340].

The phosphine chemistry of nickel carbonyls is remarkably simpler than that of earlier metals; typically the complexes are $[Ni(CO)_{4-n}(PR_3)_n]$ (usually $n = 1$ or 2), whereas carbonyl halides have been relatively little studied. It has now been shown that carbonylation of $[Ni(PR_3)_2X_2]$ affords $[Ni(CO)(PR_3)_2X_2]$ (PR_3 = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3)[341], and the structures of $[Ni(CO)(PMe_3)_2X_2]$ (X = Cl and I) are trigonal bipyramidal with axial phosphines[342].

Nickel(II) phosphines are familiar complexes, usually of the type $[Ni(PR_3)_2X_2]$ and more rarely $[Ni(PR_3)_3X_2]$. For the 2:1 complexes those of P(aryl)$_3$ are usually tetrahedral, those of P(alkyl)$_3$ or P(alkyl)$_2$(aryl) are square-planar and P(alkyl)(aryl)$_2$ complexes often exhibit planar↔tetrahedral isomerism. Recently, in addition to the common green tetrahedral isomer of $[Ni(PPh_3)_2Cl_2]$, a red planar form $[Ni(PPh_3)_2Cl_2]\cdot 2C_2H_4Cl_2$ has been isolated, and the X-ray structures of both forms were determined and compared[343].

The planar form has shorter Ni—P and Ni—Cl bonds, but otherwise the structures show no unusual features. The complexes of PMe_3 are more varied than those of other alkyl phosphines, with complexes of types $[Ni(PMe_3)_2X_2]$, $[Ni(PMe_3)_3X_2]$, $[Ni(PMe_3)_4X]^+$ and $[Ni(PMe_3)_5]^{2+}$ (X = Cl, Br, I, CN, etc.) all being observed[344–348]. The four-coordinate nickel complexes are *trans* square-planar and the five-coordinate complexes are trigonal bipyramidal with axial halides, but the cyano complexes have equatorial cyanide ligands. In $[Ni(PMe_3)_4Me]^+$ the Me group is axially disposed[346]. The equilibria between the various types in solution, as a function of temperature, anion and solvent and with added PMe_3 have been studied in some depth, and provide a unusually detailed insight into the relationships of a series of complexes.

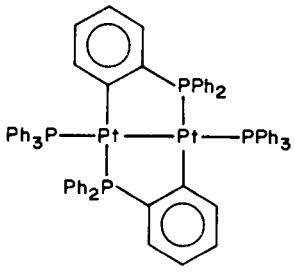
The unstable nickel(III) complexes $[Ni(PR_3)_2X_3]$ (PR_3 = PMe_3, PEt_3, PBu_3^n, PMe_2Ph, PEt_2Ph, $PMePh_2$; X = Cl, Br) have been reinvestigated[349]. They are best obtained by oxidation of $[Ni(PR_3)_2X_2]$ with NOX at low temperatures, and all have *trans* trigonal-bipyramidal structures (axial phosphines). The only example of a nickel(III) iodo complex is $[Ni(PMe_3)_2I_3]$, obtained from the reaction of $[\{Ni(\mu\text{-}Bu_2^tAs)(PMe_3)_2\}_2]$ with I_2, and the structure is a distorted trigonal bipyramid which has been rationalized as being due to the expected Jahn–Teller effects in a d^7 ion[350].

The carbonyl chemistry of palladium and platinum is considerably simpler than that of the other platinum group metals. Mononuclear and dinuclear species include phosphine-substituted carbonyls and carbonyl halides, e.g. *cis*-$[Pt(CO)Cl_2(PEt_3)]$[351] and $[Pd_2(CO)Cl(PEt_2Ph)_3]$[352], and there are cluster carbonyls of both metals. The structures and reactions of platinum clusters of types $[Pt_3(CO)_3(PR_3)_3]$, $[Pt_3(CO)_3(PR_3)_4]$ and $[Pt_4(CO)_5(PR_3)_4]$ have been reviewed[353]. The less stable palladium clusters include $[Pd_4(CO)_5(PR_3)_4]$ (PR_3 = PPh_3, PMe_2Ph, $PMePh_2$, PEt_3), which have distorted tetrahedral Pd_4 cores and with five of the six edges bridged by CO groups[352], and $[Pd_7(CO)_7(PMe_3)_7]$, a Pd_6 octahedron with one face capping Pd and with each metal atom carrying a phosphine[354].

The homoleptic phosphine complexes of these two metals $[M(PR_3)_n]$ have been known for over 30 years, and have been reviewed several times[11,355,356]. Their reactions, which have been studied in great detail, include addition of small molecules (SO_2, C_2H_4, CO) and oxidative addition (RX, HX, O_2, etc.), reactions which may also involve loss of one or two phosphines. With small phosphines $[M(PR_3)_n]$ (n = 3, 4) may be obtained[11,357], but with bulky ligands the two-coordinate 'coordinatively unsaturated' $[M(PR_3)_2]$ [PR_3 = Bu_3^tP, $PhBu_2^tP$, $P(c\text{-}Hex)_3$, $PMeBu_2^t$] are formed[358–362]. These have approximately linear P—M—P skeletons and undergo a wide range of oxidative additions, including reactions with aryl halides, nitriles and water, and extract chlorine from chlorinated solvents. Detailed ^{31}P NMR studies of $[M(PR_3)_n]$ in solution[362] have shown that the corresponding palladium and platinum complexes are generally similar, but that ligand exchange is slower in the platinum systems. The value of n correlates well with the trend in ligand cone angles. The isolation of $[M(PPh_3)_2]$ reported some years ago is now discounted, and the products are believed to be polymeric and/or to contain fragmented ligands[260], but '$Pt(PPh_3)_2$' can be generated and used in solution either by photolysis of $[Pt(PPh_3)_2C_2O_4]$[363] or by electrochemical reduction of $[Pt(PPh_3)_2Cl_2]$[364].

Bennett *et al.*[365] have shown that comproportionation of $[Pt(o\text{-}C_6H_4PPh_2)_2]$ {from $[Li(o\text{-}C_6H_4PPh_2)]$ and $[Pt(SEt_2)_2Cl_2]$} and $[Pt(PPh_3)_3]$ gives **47**, a dinuclear platinum(I) complex. Typical of the 'clusters' obtained during attempts to isolate $[Pt(PPh_3)_2]$ or by prolonged heating of $[M(PPh_3)_4]$ in solution are $[Pt_3(\mu\text{-}PPh_2)_2(PPh_3)_3(\mu\text{-}H)]BF_4$[366] (**48**) and $[Pd_3Cl(\mu\text{-}PPh_2)_2(PPh_3)_3]^+$ (**49**)[367], for which more rational syntheses have subsequently been developed[368].

Platinum hydrides $[PtH_2(PR_3)_2]$, $[PtHX(PR_3)_2]$ and $[PtH(PR_3)_3]^+$ are well known, but the palladium analogues are unstable and have been little studied. Treatment of $[Pt(C_2H_4)(PR_3)_2]$ (PR_3 = PMe_3 or PEt_3) with dihydrogen or sodium naphthalenide



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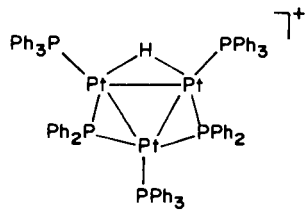

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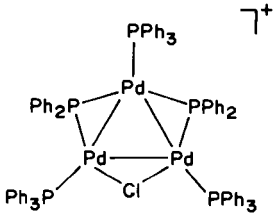
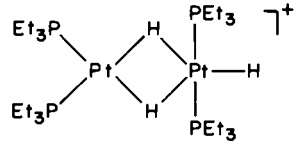


(49)

reduction of *cis*-$[Pt(PR_3)_2Cl_2]$ forms $[PtH_2(PR_3)_2]$, which exist as *cis–trans* mixtures in solution depending on the polarity of the solvent[369,370]. X-ray structures have been reported for *trans*-$[PtH_2(PR_3)_2]$ ($PR_3 = PEt_3$, a rare isolated example with a small phosphine[370], PPr^i_3[371], PBu^t_3[372]), whilst three-coordinate T-shaped $[PtH(PBu^t_3)_2]PF_6$ is formed by removing chlorine from *trans*-$[PtHCl(PBu^t_3)_2]$ with silver ions[373]. Unusual dinuclear hydrides which contain both 4- and 5-coordinate platinum (**50**) are also known[374,375].

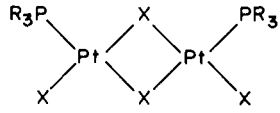


(50)

Planar $[M(PR_3)_2X_2]$ are known for many phosphines, and *cis* and *trans* isomers are well established with both metals, in contrast to early work which suggested that *cis* isomers were not formed by palladium. Small- or medium-sized phosphines also form $[M(PR_3)_3X_2]$, which ionize in solution to $[M(PR_3)_3X]X$ but are five-coordinate in the solid state. A few square pyramidal $[M(PR_3)_4X]^+$ are known[376–378]. Bulky phosphines usually only produce four-coordinate *trans*-$[M(PR_3)_2X_2]$ although an X-ray study of *cis*-$[Pt(PBu^t_2Ph)_2Cl_2]$ showed that even large ligands may produce *cis* isomers if the interligand repulsions can be accommodated[379]. The *cis*↔*trans* isomerization of $[M(PR_3)_2X_2]$ and ligand addition and displacement have been much studied, although considerable disagreement about the details remain[376–378,380,381]. $[M(PR_3)_2X_2]$ have been studied by most spectroscopic techniques and compilations of the data were given in previous reviews. Many have been X-rayed, the bond lengths generally reflecting the *trans*-influence series, and d(M—P) is usually greater with bulky ligands reflecting accommodation to the interligand repulsions[80]. Representative recent structural studies are *cis*-$[Pt(PMe_3)_2I_2]$[382], *cis*-$[Pd(PMePh_2)_2Cl_2]$[383], *trans*-$[Pt\{P(c\text{-}Hex)_3\}_2X_2]$ (X = Cl[384] or I[385]), *trans*-$[Pt(PPr^i_3)_2Cl_2]$[371], *cis*-$[Pt(PMe_2Ph)_2Cl_2]$[386], *trans*-$[Pd(PR_3)_2Cl_2]$ [PR_3 = PMe_2(neomenthyl), PMe_2(menthyl)][387], *trans*-$[Pd\{P(o\text{-tolyl})_3\}_2I_2]$[388] and *cis*-$[Pd(PPr^n_3)_2Cl_2]$[381]. Structural data have been obtained for the tris-phosphines $[Pt(PMe_3)_3Cl]Cl$[377] and $[Pt(PEt_3)_3X]PF_6$ (X = F, Cl, H)[389]. Many alkyl and aryl analogues of the halo complexes are known, and an interesting structural comparison is of $[Pd(PPh_2Me)_2Me_2]$ and $[Pt(PPh_2Me)_2Me_2]$ where the bond lengths are Pd < Pt for

M—C but Pd > Pt for M—P, reflecting the different interactions of the ligands with the two metal centres[390].

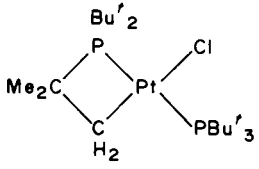
Treatment of $[M(PR_3)_2X_2]$ with PR_3 and Ag^+ can lead to $[M(PR_3)_3X]^+$ and $[M(PR_3)_4]^{2+}$, and an X-ray study of $[Pd(PEt_3)_4](ClO_4)_2$ showed a tetrahedrally distorted planar geometry[391,392]. Halide-bridged dimers $[(PR_3)XM(\mu\text{-}X)_2MX(PR_3)]$ usually have *trans* PR_3 groups, but a ^{195}PtNMR study of the reaction of $[Pt(cod)X_2]$ with bulky phosphines $[P(CH_2Ph)_3$, $P(c\text{-}Hex)_3$, $P(c\text{-}Hex)_2Ph$, $P(c\text{-}Hex)Ph_2]$ gave evidence for both *trans* and *cis* **51** isomers[393]. Neutral ligands (L) cleave the halide bridges to generate



(51)

$[M(PR_3)LX_2]$ in most cases, but a detailed study of the reaction of PMe_2Ph with $[Pt_2(PMe_2Ph)_2Cl_4]$ at low temperatures showed that asymmetric cleavage to give $[Pt(PMe_2Ph)_3Cl]^+$ and $[Pt(PMe_2Ph)Cl_3]^-$ may also occur[394]. The reaction appears to be sensitive to the phosphine concerned.

Cyclometallation of bulky phosphines is well established for both metals, and has been reviewed[20,259,395,396]. Generally platinum complexes metallate more easily than the palladium analogues, and the site of metallation is influenced by the ring size formed, five-membered being preferred over four-or six-membered. The metallation of Bu^t_3P has received recent attention and illustrates the typical chemistry[315,397–400]. Platinum(II) chloride reacts with Bu^t_3P to give $[Pt(CH_2CMe_2Bu^t_2P)Cl(Bu^t_3P)]$ (**52**) and $[\{Pt(CH_2CMe_2Bu^t_2P)_2Cl\}_2]$ (**53**), addition of PR_3 to the latter cleaving the bridges to



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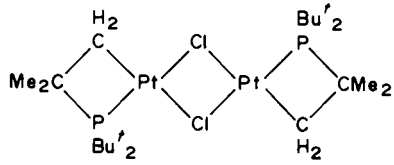


(53)

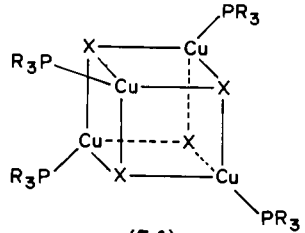
form $[Pt(CH_2CMe_2Bu^t_2P)Cl(PR_3)]$. Palladium affords $[Pd_2Cl_2(\mu\text{-}Cl)_2(Bu^t_3P)_2]$, which can be converted into the analogue of **53**. Studies on $PBu^t_2Bu^i$ show that the Bu^i group is preferentially metallated[401].

Palladium(IV) complexes *trans*-$[Pd(PPr^n_3)_2Cl_4]$ and $[Pd(PPr^n_3)X_5]^-$ (X = Cl, Br) have been characterized only recently[402]; they are unstable orange–brown solids made by oxidation of the palladium(II) analogues with halogen, and decompose in a few days at room temperature. The platinum(IV) complexes $[Pt(PR_3)_2X_4]$ are thermally stable, and both *cis* and *trans* isomers are known[403]. Oxidative addition of Br_2 to *trans*-$[Pt(PEt_3)_2Cl_2]$ in the dark gives 'all-*trans*'-$[Pt(PEt_3)_2Cl_2Br_2]$, but in the light halogen scrambling occurs to produce mixtures $[Pt(PEt_3)_2Cl_{4-n}Br_n]$[404].

I. Complexes of the Copper Sub-group (IB)

Tertiary phosphine complexes are known only for the d^{10} copper(I), silver(I) and gold(I) and the d^8 gold(III). The presence of only a single oxidation state might have been expected to lead to a simple chemistry for copper and silver, but the lack of a strong stereochemical control by the d^{10} ions results in wide structural diversity, and a large amount of work has been carried out.

Copper(I) halides form phosphine complexes in ratios 1:1, 1:2, 1:3, 1:4 and 2:3 with small phosphines, and 1:1 and 1:2 complexes have been reported with bulky phosphines. In solution complex equilibria between the various types are present[405]. For the 1:1 complexes two basic structural types have been identified, the cubane **54** and the step **55**, and it was thought that the steric properties of the phosphines and the halides were



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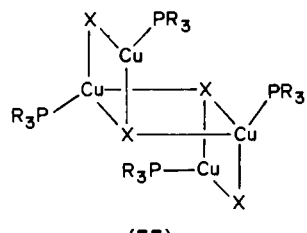


(55)

responsible for the structure adopted, larger ligands favouring the more open step form. However, $[\{Cu(PPh_3)X\}_4]$ (X = Br, I) are known with both cubane and step structures[406–408], and it seems that at least in borderline cases both the solvent and the crystallization conditions may have some control over the geometry. $[Cu(PPh_3)_3X]$ (X = F[409], Cl, Br, I[410]) have distorted tetrahedral structures and the $[Cu(PPh_3)_2X]$ (X = Cl, Br) are trigonal planar[411]. The effects of bulky ligands are less clear; thus 1:1 complexes of P(*c*-Hex)$_3$ are halide-bridged dimers $[(P(c\text{-Hex})_3)Cu(\mu\text{-Cl})_2Cu(P(c\text{-Hex})_3)]$[412], but those of Bu^t_3P, although extensively dissociated in solution, are unexpectedly cubanes in the solid state[413]. $[Cu\{P(o\text{-tolyl})Ph_2\}_2X]$ are also known[414].

Oxo-anion complexes include tetrahedral $[Cu(PPh_3)_4]ClO_4$[415] and trigonal pyramidal $[Cu(PPh_3)_3Y]$ (Y = ClO_4, NO_3). In the latter the nitrate is strongly η^1-bonded but the perchlorate is much more weakly coordinated. Recent studies have also included the use of solid-state ^{31}P CP-MAS NMR spectroscopy to study $[Cu(PR_3)_nX]$ structures[406,407,410,416].

Silver(I) phosphine chemistry closely resembles that of copper(I), and again there are cubane and step 1:1 adducts[407] ($[\{Ag(PPh_3)I\}_4]$ is known in both forms[417]), and distorted tetrahedral $[Ag(PPh_3)_3X]$[418,419]. The very bulky P(mesityl)$_3$ produces a two-coordinate complex $[Ag\{P(mesityl)_3\}_2]PF_6$ with a linear skeleton[420], and $[Ag(Bu_3^tP)_2]Y$ (Y = ClO_4, BF_4, PF_6, etc.) are similar, but the structures of $[Ag(Bu^t_3P)X]$ are unclear[421]. Silver nitrate forms $[Ag(PPh_3)_nNO_3]$ (n = 1–4), all of which have been structurally characterized. The 1:1 complex is polymeric with the silver coordinated to one bidentate and one monodentate nitrate; the 1:2 and 1:3 complexes are monomeric with distorted tetrahedral structures completed by bi- and mono-dentate nitrate groups, respectively[422,423]. The 1:4 and the corresponding perchlorate complexes have ionic anions-[415,423]. Studies by ^{31}P CP-MAS NMR revealed that $^1J(^{109}Ag–^{31}P)$ decreases with an increase in the number of phosphines attached to the metal.

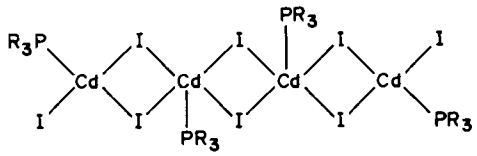
Gold(I) complexes with 1:1, 1:2, 1:3 and 1:4 Au:PR_3 ratios are well established[424–426]. X-ray studies reveal that $[Au(PPh_3)X]$[426,427] and $[Au\{P(c\text{-Hex})_3\}Cl]$[428] are linear, but

$[Au(PMe_3)I]$ is weakly associated via an Au—Au interaction[427]. $[Au\{P(c\text{-}Hex)_3\}_2]Cl$ is linear two-coordinate[428], but $[Au(PPh_3)_2X]$ (X = Cl, Br, I) are trigonal planar although with long Au—X bonds[411]. Three-coordinate gold is present in $[Au(PPh_3)_3]^+$ [429] and gold is four-coordinated in $[Au(PPh_2Me)_4]^+$ and $[Au(PPh_3)_3Cl]$[430,431]. In contrast to the lighter elements, gold has an accessible +3 oxidation state, and $[Au(PR_3)X_3]$ are easily made from $[Au(PR_3)X]$ and halogen.

Gold also forms a unique series of phosphine clusters with Au_n cores ($n = 4, 5, 6, 7, 9, 11, 13$). There is a recent detailed review of these clusters by Hall and Mingos[432], and they will not be discussed here. The Au–PR_3 unit (isolobal with H) has been incorporated into many other clusters[432].

J. Complexes of the Zinc Sub-group (IIB)

Little recent interest has been shown in zinc phosphines, although 1:1 complexes have been described for PBu^t_3 and $P(c\text{-}Hex)_3$, which are probably halide-bridged dimers[433,434]. Cadmium complexes have been more thoroughly studied, in solution by ^{31}P and ^{113}Cd NMR[435] and by X-ray crystallography. $[\{Cd(PEt_3)I_2\}_2]$ is a dimer with tetrahedrally coordinated cadmium[436], whilst $[Cd\{P(c\text{-}Hex)_3\}I_2]$ has structure **56** with both four- and



(56)

five-coordinate metal centres[436]. In $[\{Cd(PMe_2Ph)Cl_2\}_n]$ there is an elongated trigonal bipyramidal geometry composed of four bridging halides and one phosphine[437].

Mercury phosphines have attracted a surprisingly large amount of work. The nature of the solution species and of the various equilibria present have been elucidated by combined ^{31}P–^{199}Hg NMR studies[438–440]. The structural chemistry is complex: for the 1:1 stoichiometry symmetric and asymmetric dimers, tetramers and chain polymers are known, depending on the X and PR_3 present, and some complexes are known in more than one form[441–444]. $[Hg(PR_3)_2X_2]$ are distorted tetrahedral[445]. Complexes with pseudohalides and oxo-anions include tetrahedral $[Hg(PPh_3)_2Y_2]$ (Y = CN,NO_3)[446], the distorted trigonal bipyramidal $(O_4P)[Hg(Bu^t_3P)(OAc)_2]$[447], the trigonal pyramidal $[Hg\{P(c\text{-}Hex)_3\}(NCS)_2]$[448] and the square pyramidal $[(Hg\{P(c\text{-}Hex)_3\}(NO_3)_2)_2]$[449,450].

V. COMPLEXES OF DIPHOSPHINE LIGANDS

Many diphosphine complexes have been characterized and there is a large chemistry of mixed donor bidentates containing one phosphorus and a second donor which may be As, Sb, N, S, Se, etc. The chemistry of these mixed donors can be particularly complicated, and owing to space limitations it has generally not been covered, although a few examples are referred to for comparison purposes. The most widely used diphosphine is probably still 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$ (dppe), although much recent interest has been shown in bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (dppm), which has a very characteristic chemistry owing to the short interdonor linkage, and 1,2-

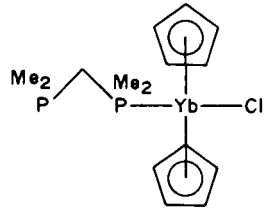
bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$ (dmpe), which combines strong binding ability with small steric requirements (cf. PMe_3)[a]. The length and nature of the backbone connecting the two phosphorus donors is a major factor determining their chemistry, and it is convenient to divide the discussion into four main types: (a) one-carbon backbones, $R_2PCH_2PR_2$; (b) two- and three-carbon backbones, $R_2PCH_2CH_2PR_2$, *cis*-$R_2PCH{=}CHPR_2$, *o*-$C_6H_4(PR_2)_2$ and $R_2PCH_2CH_2CH_2PR_2$; (c) longer backbones, $R_2P(CH_2)_nPR_2$, $n \geqslant 4$; and (d) ligands with backbones which sterically prevent chelation, $R_2PC{\equiv}CPR_2$, 1,3- or 1,4-$(R_2P)_2C_6H_4$, and *trans*-$R_2PCH{=}CHPR_2$. The last group have been little studied, but the others have all received considerable attention. The introductory remarks to Section IV are relevant to the coverage in this present section, and emphasis has been placed on cases where the chemistry of the diphosphines differs from that of two *cis*-monodentates in the same system.

A. Diphosphines with a Single Methylene Bridge Group Backbone, $R_2PCH_2PR_2$

Bis(diphenylphosphino)methane can chelate to metal centres, but this results in a strained four-membered ring. The strain disfavours chelation sufficiently for other bonding modes (η^1-monodentate or bridging bidentate) to be important competitors. Much recent effort has been devoted to complexes where dppm bridges two metal centres, which may be otherwise unconnected, bridged by other ligands or M—M bonded. This behaviour extends to other ligands with similar steric properties, e.g. $Me_2PCH_2PMe_2$, $Ph_2PCH_2AsPh_2$, 2-$C_5H_4NPPh_2$. The use of such ligands to connect two different metals and hence assemble bimetallic species has been much studied, especially by the groups of Shaw and Balch. The chemistry of these ligands was comprehensively reviewed by Puddephatt[44] in 1983, and a recent account by Chaudret *et al.*[451] described recent developments with emphasis on the dinuclear complexes. These two reviews (containing > 450 references) provide a comprehensive coverage, and no treatment of this chemistry will be attempted here. Some comparisons do appear in the next section.

B. Diphosphines with Two- or Three-carbon Backbones. Early Transition Metals, Groups III–VII

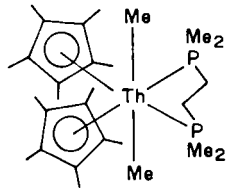
Structurally characterized lanthanide and actinide diphosphines have been reported only in the last few years, and lanthanide examples are still very scarce. The green $[Yb(Me_5C_5)_2(dmpe)]$ and red $[Eu(Me_5C_5)_2(dmpe)]$ are insoluble and probably polymeric with diphosphine bridges. The corresponding complexes of $Me_2PCH_2PMe_2$ are more soluble[452]. Reaction of the former with $YbCl_3$ produces $[Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)]$, which has been structurally characterized (**57**). A



(**57**)

[a]Abbreviations are a potential source of confusion owing to the variety of representations used for the same ligand by different authors. Only the commonest ligands will be given abbreviations have (dppe, dppm, dmpe).

ytterbium silylamide complex of dmpe is also known[453]. Eight-coordinate complexes of thorium (colourless) and uranium (green) of type $[MCl_4(dmpe)_2]$ were the first unequivocally established actinide phosphines[454]. Analogues $[MX_4(dmpe)_2]$ (X = Br, I, OPh, Me) are known. Benzyllithium converts the tetrachlorides into 6-coordinate $[M(CH_2Ph)_4(dmpe)]$[455]. Other types structurally characterized in this rapidly developing field are $[ThMe_2(Me_5C_5)_2(dmpe)]$ and $[ThCl_2(Me_5C_5)_2(dmpe)]$ (**58**)[456], $[\{(C_5H_5)_3U\}_2(\mu\text{-dmpe})]$[457] and several borohydrides of uranium[458–460].



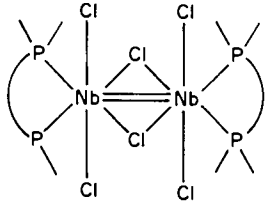
(**58**)

The diphosphine chemistry of Group IV is fragmentary, but recent results suggest that an important (and experimentally challenging) area is beginning to be explored. A rare example of a stable titanium carbonyl is the seven-coordinate $[Ti(CO)_3(dmpe)_2]$[461]. X-ray and neutron diffraction data have shown that in $[TiCl_3(dmpe)]$ (R = Me, Et) there are agostic hydrogen interactions between the R group and the metal[462]. The first titanium(II) diphosphines are red–black $[TiCl_2(dmpe)_2]$[463], red $[TiMe_2(dmpe)_2]$ and $[Ti(BH_4)_2(dmpe)_2]$[464], all of which have been X-rayed. Interestingly, whereas the dichloride is paramagnetic ($\mu = 2.9$ BM), the dimethyl complex is diamagnetic. Eight-coordinate $[MCl_4(dmpe)_2]$ (M = Zr, Hf) can be obtained directly from the tetrachlorides[465], and these react with alkylating agents to give dodecahedral $[MMe_4(dmpe)_2]$ and octahedral $[Zr(CH_2Ph)_4(dmpe)]$[466]. Various diene derivatives are also well characterized[465,467]. Zirconium(II) is represented by $[(C_5H_5)ZrCl(dmpe)_2]$, prepared by sodium reduction of $[(C_5H_5)ZrCl_3]$ in the presence of dmpe[468], and a rare hafnium(II) complex is $[(C_5H_5)Hf(CO)_2(dmpe)Cl]$[469].

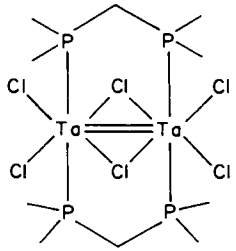
Diphosphine derivatives of vanadium carbonyl include $[V(CO)_4L\text{–}L]^-$ [L–L = *o*-$C_6H_4(PPh_2)_2$, *cis*-$Ph_2PCH{=}CHPPh_2$[470,471]], which contain chelated ligands, and $[V(CO)_5L\text{–}L]^-$ (L–L = dppe, $Ph_2PCH_2CH_2PEt_2$[88,147]) where the ligand is η^1-bonded to the metal. Related complexes are $[(C_5H_5)V(CO)_2L\text{–}L]$ and $[(C_5H_5)V(CO)_3L\text{–}L]$[470]. Contact of the tetracarbonyls with silica gel converts them into the hydrides $[HV(CO)_4L\text{–}L]$[472] which have pentagonal bipyramidal structures with axial COs[473]. Tantalum and niobium carbonyl derivatives are uncommon, but include $[M(CO)_4(dppe)]^-$ and $[HM(CO)_4(dppe)]$[474,475]. Monocapped trigonal prismatic $[TaX(CO)_2(L\text{–}L)_2]$ (X = Cl, I) have been made with the ligands $Me_2PCH_2CH_2PR_2$ (R = Et, Pr^i) and the exchange between cis–trans arrangements of the unsymmetrical ligands has been observed[476].

Condensation of the metal vapours with dmpe produced octahedral homoleptic $[M(dmpe)_3]$ (M = V, Nb, Ta)[477]. The orange–red *trans*-$[VCl_2(dmpe)_2]$ is produced from '$VCl_2(thf)_n$' and the ligand[463]. It is converted to the yellow *trans*-$[VMe_2(dmpe)_2]$ by MeLi, and Na/Hg reduction under CO affords *trans*-$[V(CO)_2(dmpe)_2]$, which in turn adds HX (X = Cl, OAc, propionate) to form the seven-coordinate $[V(CO)_2(dmpe)_2X]$[478]. The halide chemistry of niobium and tantalum is more extensive. Sodium reduces MCl_5–dmpe mixtures to $[MCl_4(dmpe)_2]$, which can be further reduced to red–brown $[MCl_2(dmpe)_2]$[160,479]. The structure of $[TaCl_4(dmpe)_2]$ is square antiprismatic rather than the expected dodecahedron[480], but the monocation $[TaCl_4(dmpe)_2]^+$ is dodeca-

hedral. The $[MCl_2(dmpe)_2]$ add hydrogen to give orange–red $[MCl_2H_2(dmpe)_2]$, also square antiprisms[160]. Other interesting derivatives are $[TaH(PPh_2)_2(dmpe)_2]$, which is pentagonal bipyramidal with axial terminal phosphido groups[481], and $[TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2]$[482]. The dinuclear $[M_2Cl_6(diphosphine)_2]$ are of two basic types: with $R_2PCH_2CH_2PR_2$ (R = Me, Et, Ph) (**59**) in which the ligands chelate to each metal centre[483–485], and for $[Ta_2Cl_6(Et_2PCH_2CH_2PEt_2)_2]$ two diastereoisomers were observed which differ in the orientation of the chelate backbones[486]. Shorter backbones exemplified by $Me_2PCH_2PMe_2$ bridge the M=M bonds as in **60**[487].

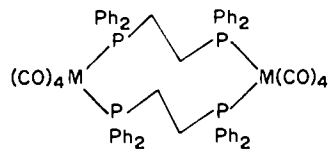


(**59**)



(**60**)

Many examples of $[M(CO)_4L\text{–}L]$ and $[M(CO)_2(L\text{–}L)_2]$ (M = Cr, Mo, W) are known, and have the expected octahedral geometries[488,489]. An unusual square pyramidal $[Mo(CO)(dppe)_2]$ has, however, been isolated and structurally characterized[490]; the sixth site is 'occupied' by an *o*-H(phenyl) atom at 2.98 Å from the molybdenum. Electrochemical oxidation of $[M(CO)_4L\text{–}L]$ (L–L = dppm, dppe, dmpe) generates unstable 17e cations which, unlike the tertiary phosphine analogues, cannot rearrange to the more stable *trans* isomers[491]. Although direct substitution into the $[M(CO)_6]$ is not a viable route to monodentate dppe complexes, these have been prepared by base-catalysed addition of PPh_2H to $[M(CO)_5(PPh_2CH{=}CH_2)]$, and use of *trans*-$[M(CO)_4(PPh_2CH{=}CH_2)_2]$ yields the *trans*-disubstituted complexes[492]. Extension of this method using $[(PPh_2H)M'(CO)_5]$ and $[M(CO)_5(PPh_2CH{=}CH_2)]$ (M and M′ can be the same or different metals, Cr, Mo or W) leads to bridged $[(CO)_5M'(\mu\text{-dppe})M(CO)_5]$[493], whereas *cis*-$[(PPh_2H)_2M'(CO)_4]$ and *cis*-$[(PPh_2CH{=}CH_2)_2M(CO)_4]$ produce ten-membered ring complexes (**61**)[494] (examples with all combinations of the three metals have been isolated).

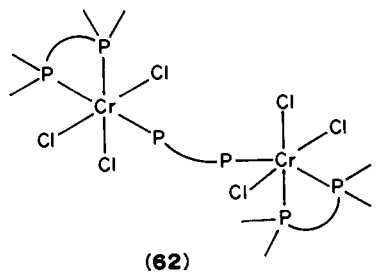


(**61**)

Seven-coordinate carbonyl halides are well known for molybdenum and tungsten and for the type $[M(CO)_3(L\text{–}L)X_2]$ the structures depend on the length of the chelate backbone, with dppm producing a pentagonal bipyramid, but for dppe and $Ph_2P(CH_2)_3PPh_2$ the structures are best described as capped trigonal prisms with the

bidentate spanning one edge of the prism *cis* to the cap[495]. The hydrides $[MoH(CO)_2(R'_2P(CH_2)_2PR''_2)_2]$ ($R' \neq R''$) have monocapped octahedral structures but are fluxional in solution[496]. Other hydrides include $[MoH_4(dmpe)_2]$[497] and $[(CO)_4Mo(\mu\text{-}H)(\mu\text{-}PPh_2(CH_2)_nPPh_2)Mo(CO)_4]^-$ ($n = 1$–4), where the different backbone lengths are accommodated by varying torsional angles within the dimer[498].

Homoleptic $[M(dmpe)_3]$ of all three metals are formed by co-condensation of dmpe and the metal vapours[477]. Chromium(II) complexes are represented by yellow–green *trans*-$[Cr(dmpe)_2Cl_2]$[463], green $[Cr(dmpe)_2I_2]$[477] and orange $[Cr(dmpe)_2Me_2]$[463], all of which are low-spin complexes. Bright-green moisture-sensitive $[Cr(L\text{–}L)_3](BF_4)_3$ (L–L = dppe, dmpe, *cis*-$Ph_2PCH{=}CHPPh_2$, *o*-$C_6H_4(PMe_2)_2$] are formed from $[Cr(thf)_6]^{3+}$ and the ligands in thf solution; the electronic spectra are consistent with the expected octahedral geometry[499]. Chromium(III) halides produce a variety of structural types with diphosphines. From a 1:1 ratio of L–L: $[Cr(thf)_3X_3]$ in the presence of NR_4X, the products are $[NR_4][Cr(L\text{–}L)X_4]$ [X = Cl, Br, I; L–L = dppe, *cis*-$Ph_2PCH{=}CHPPh_2$, *o*-$C_6H_4(PMe_2)_2$] with octahedral anions as established by an X-ray study of $[NPr_4][Cr(Ph_2PCH{=}CHPPh_2)Cl_4]$[500]. A 2:1 ratio of *o*-$C_6H_4(PMe_2)_2$: Cr yields *trans*-$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2X_2]X$, but most other alkyl arsines and phosphines give $Cr(L\text{–}L)_{1.5}X_3$, which are probably $[Cr(L\text{–}L)_2X_2][Cr(L\text{–}L)X_4]$. Weaker donor phenyl diphosphines produce green $[Cr(L\text{–}L)_2X_3]$ (L–L = dppe, *cis*-$Ph_2PCH{=}CHPPh_2$), which probably contain one chelating and one monodentate L–L, and in the presence of moisture blue $[Cr(L\text{–}L)(H_2O)X_3]$ form[500]. From $[Cr(thf)_3Cl_3]$ and dmpe at low temperature, a red $[Cr(dmpe)_{1.5}Cl_3]$ forms which is binuclear (**62**)[501]. The dinitrogen



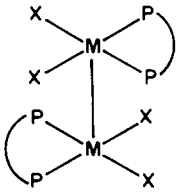
(62)

complex *trans*-$[Cr(N_2)_2(dmpe)_2]$ formed by reduction of $[Cr(dmpe)_2Cl_2]$ under nitrogen {under CO the product is *cis*-$[Cr(CO)_2(dmpe)_2]$} proves to be a good starting material for the synthesis of unusual chromium complexes, most notably the dodecadedral chromium(IV) hydride $[CrH_4(dmpe)_2]$ obtained on photolysis under H_2[502]. $[CrH_2Cl_2(dmpe)_2]$ is formed on reaction of the dinitrogen complex with HCl[503]. X-ray structures for *trans*-$[Cr(CO)_2(dmpe)_2]BPh_4$, $[CrH(CO)_2(dmpe)_2]BPh_4$ and *trans*-$[Cr(dmpe)_2Cl_2]BPh_4$ were also reported in the course of this study[503].

For molybdenum and tungsten halides, most interest concerns the M—M bonded dimers. However, new work on mononuclear species has appeared and includes the synthesis of *trans*-$[Mo(dmpe)_2Cl_2]$ from $MoCl_2$, and its oxidation with $AgPF_6$ to *trans*-$[Mo(dmpe)_2Cl_2]PF_6$[504]. A minor byproduct of the reaction of $[Mo_2Br_6]^{2-}$ with dppe is the anion $[MoBr_4(dppe)]^-$, which has been X-rayed[505]. Diphosphine complexes of oxotungsten(V) are $[WOCl_3(L\text{–}L)]$ [L–L = dppe, $Ph_2PCH{=}CHPPh_2$, *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_3PMe_2$], which have a *fac* structure on the basis of ESR studies[218].

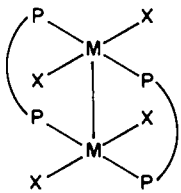
A large body of synthetic, spectroscopic and particularly structural data is available on $[M_2X_4(L\text{–}L)_2]$ (M = Mo, W; X = Cl, Br, somtimes I), and this has been reviewed[205,506];

only a summary is given here. Best *et al.*[507] noted that reaction of $[Mo_2Cl_4(PEt_3)_4]$ with dppe gave green (α) and grey (β) forms of $[Mo_2Cl_4(dppe)_2]$ and suggested that these were isomers with bridging and chelating dppe. Subsequently green (α) and brown (β) forms of $[W_2Cl_4(dppe)_2]$ were isolated and X-ray structures showed them to be **63** and **64**[508]. Analogues with dmpe, $Ph_2PCH_2CH_2AsPh_2$, $Ph_2P(CH_2)_3PPh_2$, etc., were obtained, as were examples with other halides, and structural studies showed them to be of the same two structural types[207,509–512]. For the $R_2PCH_2PR_2$ ligands the structures were different (**65**), reflecting the short interdonor linkage[205], but for two- or three-carbon backbones α



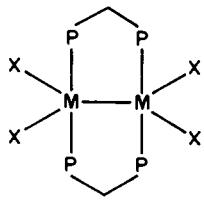
α-form

(**63**)



β-form

(**64**)



(**65**)

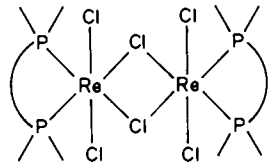
and β types are generally obtainable, and for the β type the torsional angle depends on the ligand and the halide[510,511,513]. Interconversion of the isomers has been observed[514,515]. Use of unsymmetrical ligands adds the possibility of further isomers, e.g. *syn* or *anti* α forms of $Ph_2PCH_2CH_2P(p\text{-tolyl})_2$[516], although in some cases, e.g. the β form with $Ph_2PCH_2CH_2AsPh_2$, disorder is found. Chiral diphosphine complexes, e.g. with 2,3-$(PPh_2)_2C_4H_8$, have been prepared[517]. Halogen oxidation of the α forms retains the chelating diphosphines and generates $[M_2(\mu-Cl)_2(L\text{–}L)_2Cl_4]$[518], but again $[Mo_2Cl_4(Me_2PCH_2PMe_2)_2]$ is different, being of type **60**[487].

Manganese dialkyls react with dmpe in light petroleum to give colourless or yellow high-spin tetrahedral $[MnR_2(dmpe)]$ ($R = CH_2CMe_2Ph$, CH_2CMe_3, CH_2SiMe_3), but $MnCl_2$, dmpe and $o\text{-}C_6H_4(CH_2MgCl)_2$ afford red low-spin octahedral $[Mn(dmpe)_2(o\text{-}C_6H_4(CH_2)_2)]$[223]. Reaction of $[Mn(acac)_3]$ with LiMe results in disproportionation into $[MnMe_2(dmpe)_2]$ and yellow $[MnMe_4(dmpe)]$[519]. Although the manganese (III) alkyls have not been obtained, a yellow hydride, $[MnH_3(dmpe)_2]$, is formed by hydrolysis of the manganese(I) complex $[\{Mn(AlH_4)(dmpe)_2\}_2]$, itself formed from $[Mn(dmpe)_2Br_2]$ and $LiAlH_4$[520]. The manganese(II) halide complexes are usually high-spin *trans*-$[Mn(L\text{–}L)_2X_2]$ (e.g. L–L = dmpe; X = Br, I) but curiously $MnCl_2$ forms only a 1:1 adduct with dmpe. $[MnMe_2(dmpe)_2]$ is low-spin, in contrast to the halides[463].

Diphosphines react with $[NR_4]_2[TcX_6]$ to form *trans*-$[Tc(L\text{–}L)_2X_2]$ [X = Cl, Br; L–L = dmpe, dppe, $o\text{-}C_6H_4(PPh_2)_2$, $Et_2PCH_2CH_2PEt_2$, *cis*-$Ph_2PCH{=}CHPPh_2$][521]. Electrochemical studies reveal that the $Tc^{3+/2+}$ couples are reversible, but further reduction to technetium(I) is irreversible. Pertechnetate and dmpe react, depending on the conditions, to give technetium(V), technetium(III) or technetium(I) complexes, $[TcO_2(dmpe)_2]^+$, $[Tc(dmpe)_2X_2]^+$ or $[Rc(dmpe)_3]^+$[522], and X-ray structures have been determined for $[TcO(OH)(dmpe)_2]^{2+}$, *trans*-$[Tc(dmpe)_2Cl_2]^+$, *trans*-$[Tc(dppe)_2Cl_2]^+$ and *trans*-$[Tc(dppe)_2(NCS)_2]$[522–524].

Rhenium carbonyl diphosphines, $[Re_2(CO)_8L\text{–}L]$ (L–L = dppm, dppe, dmpe), have the diphosphine bridging the Re—Re bond, and can be photolysed in water or alcohols to hydroxo or alcoxo complexes[525]. Mononuclear rhenium(III) halides, *trans*-

$[Re(L\text{–}L)_2X_2]^+$, (L–L = dppe, dmpe, $Et_2PCH_2CH_2PEt_2$, *cis*-$Ph_2PCH{=}CHPPh_2$; X = Cl, Br), have been obtained[526,527]. Reduction to *trans*-$[Re(L\text{–}L)_2X_2]$ is reversible, and comparison with the technetium analogues shows that, as expected, rhenium is more difficult to reduce[526]. X-ray structures for *trans*-$[Re(dmpe)_2Cl_2]^+$ and *trans*-$[Re(Ph_2PCH{=}CHPPh_2)_2Cl_2]$ have been reported[527,528]. Dinuclear rhenium halide derivatives were first obtained nearly 25 years ago, although the nature of some of the complexes was not correctly established until more recently[205]. Under some conditions $[Re_2X_8]^{2-}$ are cleaved by diphosphines to mononuclear rhenium(III) complexes, but under other conditions $[Re_2X_6(L\text{–}L)_2]$ (L–L = dppe, etc.) which are centrosymmetric dimers (**66**) without an M—M bond are formed, although dppm results in a structure



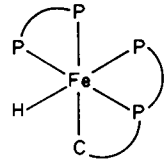
(66)

similar to **60**. Under reflux in alcohols for several days, reduction of these to $[Re_2X_4(L\text{–}L)_2]$ occurs, usually better obtained from $[Re_2X_4(PR_3)_4]$ and L–L[205,506]. Like the molybdenum and tungsten analogues, these can be obtained in both chelated α and bridged β forms **63** and **64**. For example, $[Re_2Cl_8]^{2-}$ and *cis*-$Ph_2PCH{=}CHPPh_2$ in ethanol yields α-$[Re_2Cl_4(Ph_2PCH{=}CHPPh_2)_2]$, whereas the β isomer is best made from $[Re_2Cl_4(PEt_3)_4]$ in benzene[506]. Structures of typical α and β isomers have been reported[529–531]. Electrochemical oxidation of $[Re_2X_4(L\text{–}L)_2]$ (L–L = dppe, $Ph_2PCH_2CH_2AsPh_2$; X = Cl, Br, I) forms stable monocations, also obtainable chemically using $AgPF_6$, and unlike the analogues with tertiary phosphines these do not decompose chemically on standing[532]. The chiral $[Re_2Cl_4(S,S\text{-}Ph_2PCHMeCHMePPh_2)_2]^{0/1+}$ have been prepared, probably as β isomers[533], and a β isomer of $[Re_2Cl_4(dppe)(dppm)]$ has been structurally characterized, which shows how the molecule distorts to relieve the strain caused by the two different diphosphines[534]. In contrast to the complexes of monodentate phosphines, these $[Re_2X_4(L\text{–}L)_2]$ are not cleaved by π-acceptors such as RNC or CO but, as described by Price and Walton[506], form a variety of substitution products.

C. Complexes with Two- or Three-carbon Backbones. Later Transition Metals, Groups VIII–IIB

Compared with the earlier groups, a larger number of diphosphine complexes are known for the Group VIII metals, but the diversity of types is considerably less, reflecting the smaller range of accessible oxidation states and coordination numbers.

The typical carbonyl complexes of iron are the distorted trigonal bipyramidal $[Fe(CO)_3(L\text{–}L)]$ [L–L = dppe, *o*-$C_6H_4(PMe_2)_2$][535,536], but η^1-dppe complexes *trans*-$[Fe(CO)_{5-n}(dppe)_n]$ ($n = 1, 2$) can be made cleanly from $[Fe(CO)_{5-n}(Ph_2PCH{=}CH_2)_n]$ and PPh_2H, and the structure when $n = 1$ confirms the axial monodentate linking of dppe[537]. The synthesis of the homoleptic $[Fe(dppe)_2]$, which in solution is in equilibrium with the metallated $[FeH(o\text{-}C_6H_4PhP(CH_2)_2PPh_2)(dppe)]$ (**67**), has been re-examined[538,539], and its formation by photolysis of $[FeH_2(dppe)_2]$ or $[Fe(C_2H_4)(dppe)_2]$ confirmed. Hydrogen adds to give *cis*-$[FeH_2(dppe)_2]$, and PR_3 generates five-coordinate



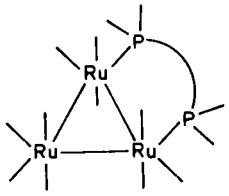
(67)

$[Fe(dppe)_2PR_3]$ (R = OMe, OEt, F). Related systems with $Me_2PCH_2PMe_2$[541], dmpe[540], $Me_2P(CH_2)_3PMe_2$[541] and $Et_2PCH_2CH_2PEt_2$[542] also internally metallate and take up H_2 or N_2. These complexes will metallate arenes, e.g. $[Fe(dppe)_2]$, and benzene gives $[Fe(dppe)_2(Ph)H]$[540]. The sodium naphthalenide reduction of $[M(dmpe)_2Cl_2]$ (M = Fe, Ru, Os) gives $[MH(naphthyl)(dmpe)_2]$, which loses naphthalene on reaction with H_2 or CO to give $[MY(dmpe)_2]$ (Y = CO or H_2)[543], and similarly metallate arenes[544]. The apparently iron(IV) hydrides reported some years ago have been re-examined and are now known to be η^2-H_2 complexes of iron(II), $[Fe(H_2)H(L\text{–}L)_2]^+$ (L–L = dppe, $Et_2PCH_2CH_2PEt_2$) and there are analogous ruthenium complexes[545].

Iron(II) diphosphines can be either high- or low-spin, depending on the ligand set; thus *trans*-$[Fe(dmpe)_2Cl_2]$ is diamagnetic (t_{2g}^6)[546], whereas *trans*-$[Fe(Ph_2PCH{=}CHPPh_2)_2Br_2]$ is high-spin (μ = 5BM, $t_{2g}^4e_g^2$)[547]. Most interestingly the $[Fe(Ph_2PCH{=}CHPPh_2)_2Cl_2]$ and its various solvates (Me_2CO, CH_2Cl_2, etc.) exhibit low-spin↔high-spin cross-overs as a function of temperature, the behaviour varying with the solvate studied, indicating the extreme sensitivity of these effects to solid-state packing factors[547]. X-ray structures of $[Fe(Ph_2PCH{=}CHPPh_2)_2Cl_2].2Me_2CO$ at 295 K (high-spin, μ = 5.1 BM) and 130K (predominantly low-spin, μ = 0.7 BM) reveal a dramatic shortening of *d*(Fe—P) of ca 0.28 Å with the change to the low-spin state[547]. Iron(III) diphosphines are low-spin with one unpaired electron, e.g. *trans*-$[Fe\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]BF_4$[548]. Nitric acid oxidation of *trans*-$[Fe(L\text{–}L)_2X_2]^{0/1+}$ at low temperatures produces dark-green or purple iron(IV) complexes, $[Fe(L\text{–}L)_2X_2](BF_4)_2$ [L–L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$, *o*-$C_6F_4(PMe_2)_2$, dmpe; X = Cl, Br], which are the only known examples of iron(IV) containing neutral donor ligands[48]. The complexes are very unstable, which has prevented X-ray crystallographic studies, but Fe K-edge EXAFS data on $[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^{n+}$ (*n* = 0, 1, 2) revealed that oxidation produces a shortening of *d*(Fe—Cl) but a lengthening of *d*(Fe—P). Electrochemical data show that the iron(IV)–iron(III) redox couple is very similar for complexes of *o*-$C_6H_4(PMe_2)_2$ and *o*-$C_6H_4(AsMe_2)_2$, but that the presence of the electron-withdrawing backbone in *o*-$C_6F_4(PMe_2)_2$ makes the oxidation of the complexes considerably harder[48,549]. An interesting new development is the demonstration that dmpe cleaves the double cubanes $[Mo_2Fe_7S_8(SR)_{12}]^{n+}$ to single cubanes with coordinated dmpe[550], and much further work of this type is expected.

Carbonyl clusters present a variety of coordination sites to diphosphines, and with the development of new routes allowing substitution under mild conditions a range of such complexes have been obtained[258]. The reaction of $[Ru_3(CO)_{12}]$ with dppe thermally gave only poor yields of $[Ru_3(CO)_{10}(dppe)]$, but using an electron-transfer catalyst it is possible to isolate $[Ru_3(CO)_{11}(\eta^1\text{-dppe})]$, $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppe})]$, $[Ru_3(CO)_{10}(dppe)]$ and $[Ru_3(CO)_8(dppe)_2]$. All contain the diphosphine substituted for equatorial carbonyls, and the last two have structures **68** and **69**[551]. However, with *cis*-$Ph_2PCH{=}CHPPh_2$, in addition to $[Ru_3(CO)_{10}(L\text{–}L)]$, $[Ru_2(CO)_6(L\text{–}L)]$ (**70**) is obtained[552]. Under forcing conditions the diphosphine may undergo further reaction, e.g. $KBHBu^s_3$ cleaves a phenyl group from $[Ru_3(CO)_{10}(dppe)]$ and after acidification $[Ru_3(\mu\text{-H})(\mu^3\text{-}PPhCH_2CH_2PPh_2)(CO)_9]$ (**71**) is isolated[553]. The ligand dppm appears to be particularly

prone to fragmentation on ruthenium clusters, and species which have lost a phenyl group, *o*-metallated a phenyl ring or metallated at the central CH_2 are well characterized[553-555], and there are some osmium analogues[556]. From dppe and $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ two isomers of $[Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)]$ are obtained, one containing the dppe chelated to one Ru atom and the other with edge-bridging dppe[557]. Similar isomers are found with $Ph_2PCHMeCH_2PPh_2$, whereas $Ph_2P(CH_2)_nPPh_2$ ($n = 3, 4$) edge-bridge, and for $n = 5$ the ligand bridges two clusters in $[\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)]$[558]. Other clusters afford a range of similar coordination modes, e.g. $[Os_5C(CO)_{15}(\eta^1\text{-dppe})]$[559], whereas in $[Ru_5C(CO)_{13}(Ph_2P(CH_2)_4PPh_2)]$ the diphosphine bridges opposite Ru centres in the base of the square pyramid[560].



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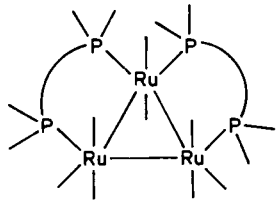

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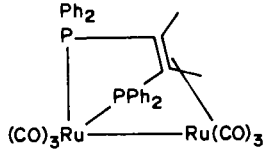

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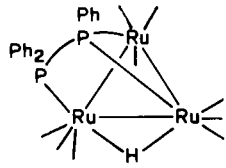

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Attempts to prepare homoleptic complexes of ruthenium(0) with PMe_3 or dmpe are complicated by the tendency for the Ru to metallate the phosphine; however, treatment of $[Ru(dmpe)_2(H)(naphthyl)]$ with PMe_3 affords $[Ru(dmpe)_2PMe_3]$, which is a five-coordinate square pyramidal monomer with apical PMe_3[561]. Another ruthenium(0) complex is the surprisingly stable $[Ru(styrene)(dppm)_2]$, but $[Ru(styrene)(dppe)_2]$ readily loses styrene with concomitant metallation of one phenyl ring on the diphosphine, whereas $Ph_2P(CH_2)_3PPh_2$ gives only the metallated product in these systems[562].

Diphosphines with two-carbon backbones form stable six-coordinate *trans*-$[Ru(L\text{-}L)_2X_2]$[L–L = dmpe, dppe, $CH_2{=}C(PPh_2)_2$, $Ph_2PCH_2CH_2P(C_6H_4F)_2$; X = Cl, Br, I], usually prepared from $RuCl_3{\cdot}nH_2O$ or $[Ru(PPh_3)_3Cl_2]$ and L–L[563-567], and in many cases *cis* isomers can be obtained starting with $[Ru_2(PR_3)_6X_4]$. *cis*-$[Ru(dmpe)_2Cl_2]$ isomerizes photochemically to the *trans* isomer in alcohols, but in stronger donor solvents the products are trans-$[Ru(dmpe)_2ClL]^+$ (L = H_2O or dmso)[566]. With longer backbones six-coordinate *trans*-$[Ru(L\text{-}L)_2X_2]$ are still obtainable [L–L = $Me_2P(CH_2)_3PMe_2$[568], $Ph_2P(CH_2)_3PPh_2$[567] or $Ph_2P(CH_2)_3PMePh$[567]], but in some cases these can be converted into five-coordinate cations $[Ru(L\text{-}L)_2X]^+$ [note, however, that the smallest $Me_2P(CH_2)_3PMe_2$ affords *only* six-coordinate complexes[568]]. The five-coordinate complexes are thought to be trigonal bipyramidal with equatorial halide[567]. *trans*-$[RuHCl(L\text{-}L)_2]$ and *trans*-$[Ru(CO)Cl(L\text{-}L)_2]^+$ are also easily prepared[567,568]. Similar five- and six-coordinate osmium halide complexes can be prepared, e.g. *trans*-$[Os(L\text{-}L)_2Cl_2]$ [L–L = $CH_2{=}C(PPh_2)_2$, $Ph_2P(CH_2)_3PPh_2$][564,569] and

$[Os\{Ph_2P(CH_2)_3PPh_2\}_2Cl]PF_6$. Removal of the chloride from $[M(dppe)_2Cl_2]$ (M = Ru or Os) with $AgSbF_6$ in the presence of CO leads to the dicarbonyls *trans*-$[M(CO)_2(dppe)_2](SbF_6)_2$, which can be reduced to formyl (CHO) complexes[570,571]. Refluxing ruthenium perchlorate solutions with dppe in ethanol yields $[Ru(dppe)_3OClO_3](ClO_4)$, which is believed to contain both chelating and monodentate dppe[572].

Grocott *et al.*[573–575] isolated and characterized (some by X-ray crystallography) various geometric and optical isomers of *cis*- or *trans*-$[Ru(L–L)_2Cl_2]$, $[RuHCl(L–L)_2]$ and $[Ru(CO)_2Cl_2(L–L)]$ with *o*-phenylenebis(phenylmethylphosphine). Several other studies of ruthenium complexes of chiral diphosphines have been carried out, although interest in this area is much less than in the rhodium systems. Examples include $[RuHCl(binap)_2]$, $[Ru_2Cl_4(binap)_2NEt_3]$[576], $[RuCl(C_5H_5)Ph_2PCHRCH_2PPh_2)]$[577] and the binuclear ruthenium(II)–ruthenium(III) complex $[Ru_2Cl_2(L–L)_2(\mu\text{-}Cl)_3]$ (L–L = chiraphos, diop)[578] (see Figure 7 for the structures of some common chiral diphosphines).

Metal—metal bonded complexes are much rarer in halide systems than in earlier groups, but include $[Ru_2Cl_6(Me_2PCH_2PMe_2)_2]$[487]. However, diphosphines cleave the

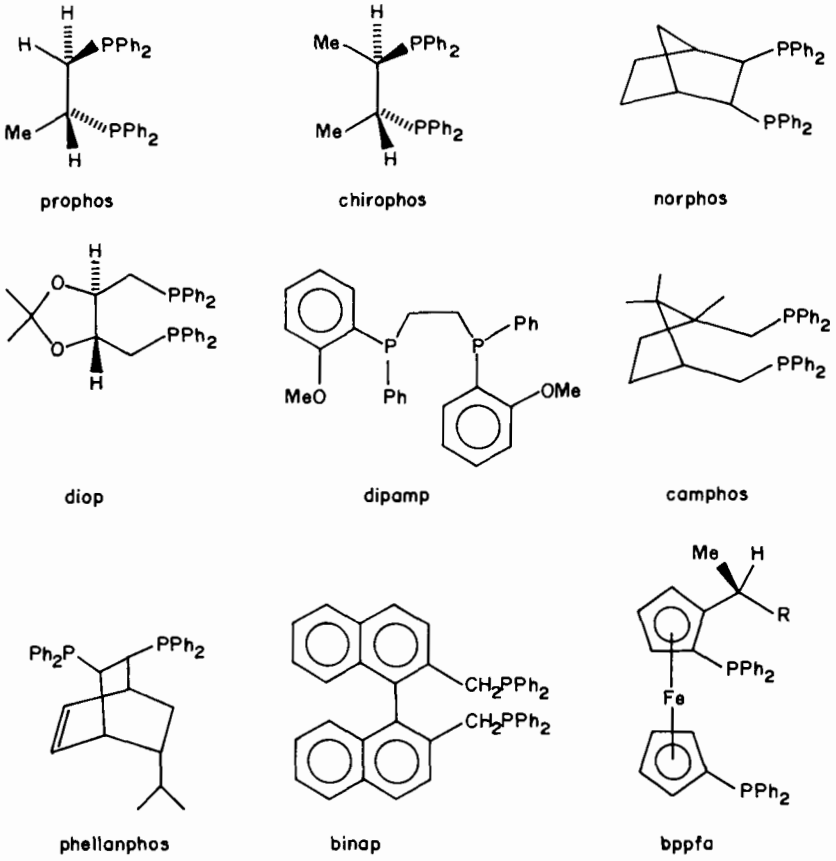
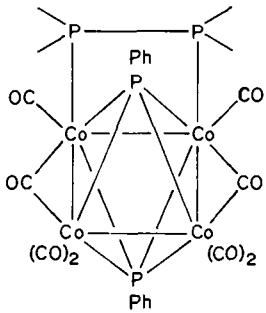


FIGURE 7. Some chiral disphosphines.

Os—Os triple bond in $[Os_2Cl_8]^{2-}$ to give the well known *trans*-$[Os(L{-}L)_2Cl_2]$[292]. Osmium(VI) complexes are the osmyl $[OsO_2(L{-}L)X_2]$ [L–L = *o*-$C_6H_4(PMe_2)_2$, dmpe, dppe, *cis*-$Ph_2PCH{=}CHPPh_2$; X = Cl, Br] which have *trans*-OsO_2 units, and are formed from OsO_4, HX and L–L at low temperatures. Only *o*-$C_6H_4(PMe_2)_2$ has been observed to give a 2:1 complex, $[OsO_2(L{-}L)_2]X_2$[579].

Good examples of the coordination of diphosphines to clusters are in the reactions of the phosphinidine cluster $[Co_4(CO)_{10}(\mu^4\text{-}PPh)_2]$ with $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4)[580]. Either thermal or electron-transfer catalytic methods gave $[Co_4(CO)_8(\mu\text{-}PPh)_2(L{-}L)]$ (L–L = dppm, dppe) (**72**), but *cis*-$Ph_2PCH{=}CHPPh_2$ chelated to one cobalt atom; longer backbones gave $[Co_4(CO)_9(\mu\text{-}PPh)_2(\eta^1\text{-}L{-}L)]$ ($n = 3, 4$). A similar series of ligands when reacted with cobalt(II) salts in the presence of $NaBH_4$ gave red cobalt(I) hydrides, $[CoH(L{-}L)_2]$, and the structure of the complex with $n = 3$ revealed a trigonal bipyramidal geometry[581]. Curiously, in these reactions *trans*-$Ph_2PCH{=}CHPPh_2$ was hydrogenated to dppe.



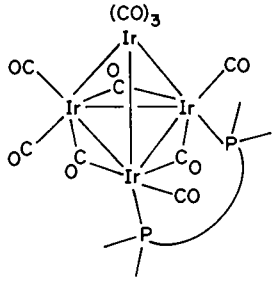
(**72**)

Cobalt(II) halide diphosphine complexes are well known with Co:L–L ratios of 1:1, 1:2 and 3:4. It appears that the complexes with 1:1 stoichiometry for two-carbon backbone ligands are $[Co(L{-}L)_2][CoX_4]$ (X = halides), and the reported tetrahedral 'Co(dppe)Cl_2' has been shown to be a diphosphine dioxide complex[582]. The 1:2 and 3:4 types are $[Co(L{-}L)_2X]X$ and $[Co(L{-}L)_2X]_2[CoX_4]$ containing five-coordinate cations, which may adopt either trigonal bipyramidal or square pyramidal geometries depending on the ligand set involved, and in some cases both isomers may be obtained[583,584]. Genuine tetrahedral $[Co(L{-}L)X_2]$ are formed with longer backboned ligands or with some two-carbon backbone hybrids such as *o*-$C_6H_4(PMe_2)(NMe_2)$[584]. Hybrid ligands were studied in great detail notably by Sacconi and co-workers in investigations of the effect of donor set and ligand geometry on the spin state and structure of the cobalt, and their review[585] remains a valuable source.

Cobalt(III) halo complexes $[Co(L{-}L)_2X_2]^+$ are readily prepared by halogen oxidation or air oxidation (alkyl diphosphines only) of the cobalt(II) complexes. Alkyl-substituted ligands form *trans* isomers [L–L = *o*-$C_6H_4(PMe_2)_2$, dmpe, $Me_2P(CH_2)_3PMe_2$, $Bu^n{}_2P(CH_2)_2PBU^n{}_2$, *o*-$C_6F_4(PMe_2)_2$][49,586] by air oxidation, and *cis* isomers are usually formed from $[Co(CO_3)(L{-}L)_2]^+$ and HX. Generally the *cis* isomers are less stable and are converted to the *trans* form on photolysis or in cobalt(II)-catalysed reactions. Phenyl-substituted bidentates [*o*-$C_6H_4(PPh_2)_2$, *cis*-$Ph_2PCH{=}CHPPh_2$] appear to give only *trans* isomers[587], which may reflect their greater steric bulk, or alternatively the much easier reduction to cobalt(II) which provides a facile isomerization mechanism. Yellow cobalt(III) peroxo complexes *cis*-$[Co(O_2)(L{-}L)_2]BF_4$ [L–L = dmpe, $Me_2P(CH_2)_3PMe_2$] are obtained by oxygenation of the cobalt(I) species, and both have

been structurally characterized[588]. A red dimer $[Co_2(dmpe)_4(\mu\text{-}O_2)(dmso)_2]^{4+}$ is also obtainable. Tris(diphosphine) complexes $[Co(L\text{–}L)_3](BF_4)_3$ [L–L = *o*-$C_6H_4(PMe_2)_2$, dmpe, *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$] are obtainable by air oxidation of the ligand–cobalt(II) acetate mixture followed by addition of HBF_4, or from $[Co(L\text{–}L)_2X_2]^+$, $AgBF_4$ and L–L[589]. These complexes were characterized by UV–visible and ^{59}Co NMR spectroscopy.

The reactions of $[Ir_4(CO)_{11}Br]^-$ with diphosphines [dmpe, *cis*-$Ph_2PCH{=}CHPPh_2$, dppe, $Ph_2P(CH_2)_nPPh_2$, $n = 3, 4$] yields a variety of substituted derivatives of $[Ir_4(CO)_{12}]$ including $[\{Ir_4(CO)_{11}\}_2(\mu\text{-L–L})]$ [L–L = $Ph_2P(CH_2)_nPPh_2$, where the diphosphine occupies one axial site on each Ir_4 tetrahedron], $[Ir_4(CO)_{10}(L\text{–}L)]$ [L–L = dppe, dmpe, $Ph_2PCH{=}CHPPh_2$ and $Ph_2P(CH_2)_nPPh_2$], which are fluxional in solution[590]. For the latter various isomers are possible; thus with dppe the structure is **73**, $Ph_2PCH{=}CHPPh_2$ and dmpe form both **73** and **74**, and for longer backbones **75** is found[590]. An $[Ir_4(CO)_8(Ph_2PCH{=}CHPPh_2)_2]$ which metallates to $[Ir_4(CO)_7H(o\text{-}C_6H_4PhPCH{=}CHPPh_2)(Ph_2PCH{=}CHPPh_2)]$ has also been isolated[591]. The structure of $[Ir_4(CO)_{10}\{(+)\text{-diop}\}]$ is of type **73**[592], but that of $[Rh_6(CO)_{10}\{(-)\text{-diop}\}_3]$ is unclear[593]. A dinuclear carbonyl of rhodium is $[Rh_2(CO)_4(Ph_2P(CH_2)_4PPh_2)_3]^{2+}$, which contains two five-coordinate rhodium centres linked with a single diphosphine bridge[594].



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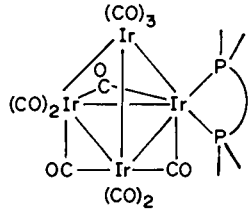

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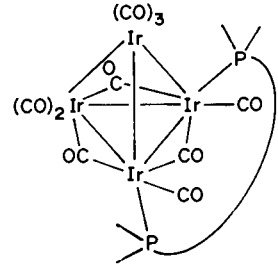
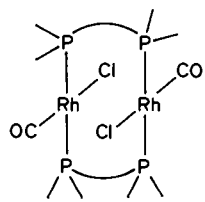


(75)

The reaction of $[\{Rh(cod)Cl\}_2]$ with $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) under CO produces $[\{Rh(L\text{–}L)Cl(CO)\}_m]$, which for $n = 2$ (dppe) is a chelated monomer, but for $n = 1, 3$ or 4 the complexes are dimeric (**76**)[595]. The *cis*-$Ph_2PCH{=}CHPPh_2$ complex was formulated as $[Rh(L\text{–}L)_2][Rh(CO)_2Cl_2]$. Excess diphosphine gave $[Rh(dppe)_2]Cl$, but for longer backbones the products were $[Rh(L\text{–}L)_2(CO)]Cl$. Addition of Co and oxidative addition of HX, O_2 and H_2 to $[Rh(Ph_2P(CH_2)_nPPh_2)_2]^+$ ($n = 1$–3) and $[Rh(PhMeP(CH_2)_3PPhMe)_2]^+$ have been reported, the reactivities showing a dependence on the backbone length[596,597]. Similarly, the diphosphines $Ph_2P(CH_2)_nPPh_2$ form $[\{Ir(L\text{–}L)(CO)Cl\}_m]$ complexes which are ligand bridged dimers for $n = 1$ or 3, a trimer for $n = 4$, whilst for $n = 2$ the formulation proposed was $[Ir(L\text{–}L)_2[Ir(CO)_2Cl_2]$[598].



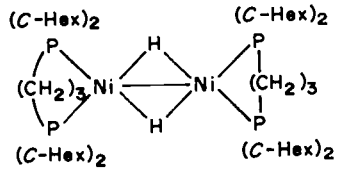
(76)

Subsequently, it was shown that mononuclear [Ir(dppe)(CO)X] can be formed from $[Ir(CO)_2X_2]^-$ and dppe at low temperatures[599,600], and oxidative additions to these and to the dinuclear $[\{Ir(Ph_2P(CH_2)_3PPh_2)(CO)Cl\}_2]$ were studied[599-601]. As can be seen, there is a marked tendency for rhodium(I) and iridium(I) to adopt a *trans* arrangement of the phosphorus donors, necessitating bridging behaviour of the ligands, and only for $n = 2$ is the tendency for chelation sufficient for monomers with *cis* phosphorus donors to be easily obtained.

The electrochemical reduction of $[Rh(dppe)_2]^+$ has produced considerable disagreement in the literature, but the chemical reduction with sodium naphthalenide has been shown to proceed stepwise, giving the paramagnetic $[Rh(dppe)_2]$ and then $[Rh(dppe)_2]^-$[602]. Oxidation of $[Ir(dppe)_2(CO)]^+$ to iridium(III) cations with halogens, HX, HBF_4, etc., has been studied[603]. Treatment of $[Ir(dppe)_2]Cl$ with MeLi gives the five-coordinate trigonal bipyramid $[Ir(dppe)_2Me]$[604]. NMR studies suggest that in solutions of $[Rh(Ph_2P(CH_2)_nPPh_2)_2]^+$ ($n = 3,4$) several species are present, but an X-ray study of the material with $n = 4$ showed a distorted planar RhP_4 core with chelating diphosphines[605].

Studies of asymmetric diphosphines (see Figure 7 for the formulae of some common ligands) bonded to rhodium(I) and their catalytic reactions is an increasingly popular area of research. The precursor complex is usually of the type $[Rh(diphosphine)(diene)]^+$, which is then treated in solution with the substrate. This work has been reviewed[22,606,607]; representative examples with emphasis on the phosphine complex are refs 608–612. Finally in this section, we note the polyhydrides $[Ir_2H_5(Ph_2P(CH_2)_3PPh_2)_2]^+$ and $[Ir_3H_7(Ph_2P(CH_2)_3PPh_2)_3]^{2+}$, formed from $[Ir(CoD)(L\text{–}L)]^+$ and H_2 in methanol[613]. They both contain one chelated diphosphine per iridium atom, with the units held together by bridging hydrides.

Diphosphine complexes of divalent nickel, palladium and platinum are among the most familiar examples and, although some recent new work has appeared, the most interesting developments in this triad concern the lower and higher oxidation state complexes. A re-examination of the nickel(0)–dmpe system showed that in addition to $[Ni(dmpe)_2]$, small amounts of a dimer formulated as $[(dmpe)Ni(\mu\text{-dmpe})_2Ni(dmpe)]$ are present[614]. An unusual dimer with an Ni—Ni bond is the hydride **77**[615]. Nickel(II) halide complexes of two-carbon backbone diphosphines include both 1:1 and 1:2 stoichiometries. The former are planar diamagnetic materials, e.g. $[Ni(dppe)Cl_2]$[616], and $[Ni(cis\text{-}Ph_2PCH{=}CRPR'R'')X_2]$ obtained *in situ* from PHR′R″ and $[Ni(Ph_2PC{\equiv}CR)_2X_2]$ (R = CF_3, Ph, Bu^t; R′, R″ = Ph, Et)[617]. The 1:2 complexes $[Ni(L\text{–}L)_2X]X$ are diamagnetic and, depending on the system, may be five-coordinate or exhibit 4↔5 coordination equilibria in solution. Ligands of the type $o\text{-}C_6H_4[P(alkyl)_2]_2$ form only 1:2 complexes, which are either planar or very tetragonally distorted (diamagnetic) octahedral in the solid state, but unusually $o\text{-}C_6F_4(PMe_2)_2$ gives two isomers of the nickel(II) chloride complex, an orange planar and a green octahedral form[549]. If the anion has only weak coordinating ability (BF_4, ClO_4, I_3) then planar $[Ni(L\text{–}L)_2]^{2+}$ are isolated[618]. Complexes of $Ph_2P(CH_2)_3PPh_2$ are known to exhibit planar↔tetrahedral isomerism in solution, but are exclusively planar in the solid state; however, with $Ph_2PCH_2SiMe_2CH_2PPh_2$ orange

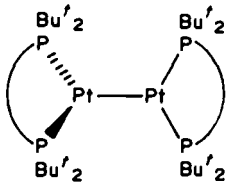


(77)

planar and violet tetrahedral forms of $[Ni(L–L)(NO_3)_2]$ have been isolated, the first examples of allogons with a diphosphine[619]. Chiral diphosphine complexes including those of diop, trans-1,2-$(Ph_2P)_2$-cyclo-C_5H_8 and norphos have been structurally characterized[620,621]. Detailed ^1H NMR studies[622] of $[Ni(L–L)_2](PF_6)_2$ and $[Ni(L–L)_2Cl]PF_6$ [L–L = o-$C_6H_4(PPhMe)_2$] have shown that the diphosphines do not readily exchange, in contrast to the arsenic analogue where ligand redistribution between metal centres is facile, but that fast exchange of the coordinated chloride is observed.

Oxidation of $[Ni(L–L)X_2]$ with NOX or X_2 (X = Cl, Br) forms olive-green $[Ni(L–L)Cl_3]$ and brown $[Ni(L–L)Br_3]$ [L–L = dmpe, dppe, $Ph_2P(CH_2)_3PPh_2$, o-C_6H_4-$(PPh_2)_2$. *cis*-$Ph_2PCH{=}CHPPh_2$], which are paramagnetic with one unpaired electron as expected for low-spin nickel(III)[623]. The X-ray structure of $[Ni(dppe)Br_3]$·toluene shows a distorted square pyramidal molecule with a long apical Ni—Br bond. Air or halogen oxidation of $[Ni(L–L)_2X]X$ [L–L = o-$C_6H_4(PMe_2)_2$, o-$C_6F_4(PMe_2)_2$, dmpe; X = Cl or Br] produces pale green (Cl) or orange (Br) *trans*-$[Ni(L–L)_2X_2]^+$, and detailed X-ray, ESR and UV–visible studies of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]PF_6$ have been reported[624–627]. Attempts to produce nickel(III) iodo complexes have given only nickel(II) polyiodides[618]. For the ligands o-$C_6H_4(PMe_2)_2$, o-$C_6F_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)(PMe_2)$ and dmpe (Cl only), further oxidation with HNO_3–HX yields unstable nickel(IV) complexes $[Ni(L–L)_2X_2](ClO_4)_2$. The products are dark green or violet, and decompose back to nickel(III) in a few hours at room temperature, which prevents single-crystal X-ray studies. However, detailed spectroscopic and nickel K-edge EXAFS data have been obtained, and support the nickel(IV) formulation[49].

Reduction of $[Pt(L–L)Cl_2]$ (L–L = $Bu^t_2P(CH_2)_3PBu^t_2$) with sodium amalgam generates a deep red platinum(0) complex $[\{Pt(L–L)\}_2]$ which has the structure **78**[627]. The Pt—Pt bond is easily broken on reaction with CO, H_2 or chlorinated solvents to give *cis*-$[Pt(L–L)Y_2]$ (Y = CO, H or Cl, respectively). Similar reactions with slightly less bulky diphosphines, e.g. $R_2P(CH_2)_2PR_2$ (R = Bu^t or menthyl) produce *cis*-dihydrides. There are related dinuclear hydrides $[Pt_2H_3(L–L)_2]^+$ [L–L = dppe, $Ph_2P(CH_2)_nPPh_2$, n = 3, 4, *cis*-$Ph_2PCH{=}CHPPh_2$, $Bu^t_2P(CH_2)_3PBu^t_2$][628–30] which probably have structure **79**. Treatment of $[Pt(L–L)(C_2H_4)]$ [L–L = $(c\text{-Hex})_2P(CH_2)_nP(c\text{-Hex})_2$, n = 2–4] with H_2 gives *cis*-dihydrides[631].



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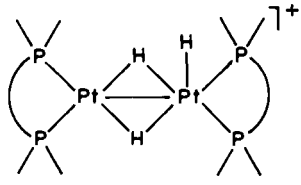

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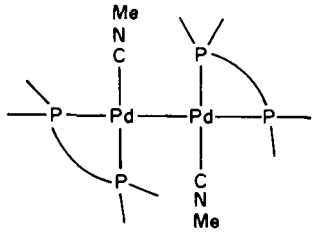
Binuclear palladium(I) complexes, $[Pd_2(L–L)_2(MeNC)_2](PF_6)_2$ [L–L = $Ph_2P(CH_2)_nPPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$] are formed from $[Pd_2(MeNC)_6](PF_6)_2$ and the ligands, and are thought to have structure **80** with an unbridged Pd—Pd bond[632]. What was thought to be a homoleptic 'Pt(dppe)' species has been found on further study to be a dinuclear platinum(I) complex of the metallated diphosphine **81**[633].

Planar $[M(L–L)X_2]$ (M = Pd, Pt) are known with many ligands and the majority with two or three-carbon backbones are chelated monomers. Sanger[598] showed that under some conditions ligand bridged forms $[M_2(\mu\text{-L–L})_2X_4]$ can be obtained for L–L = $Ph_2P(CH_2)_3PPh_2$ and M = Pt, and for both metals with *cis*-$Ph_2PCH{=}CHPPh_2$, although with dppm and dppe only monomers with chelating diphosphines were isolated. Under reflux in *N*,*N*-dimethylformamide the dimers rearrange into chelated monomers,



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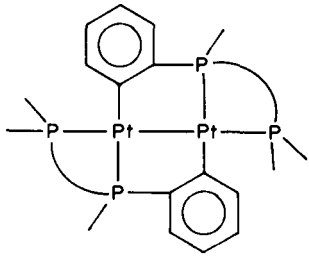
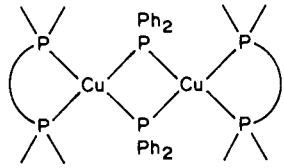


(81)

the two forms being easily distinguished by their ^{31}P NMR spectra[634]. X-ray studies are now available for several series of complexes allowing detailed comparisons to be made of the effects of changing the metal centre, e.g. $[M(dppe)Cl_2]$ (M = Ni, Pd, Pt)[616,635], $[M\{(+)\text{-diop}\}Cl_2]$[636] where the Ni complex is tetrahedral but the other two are planar and $[M(Ph_2P(CH_2)_3PPh_2)Cl_2]$[637] and $[M(dppe)_2]Cl_2$ (M = Pd or Pt only)[635]. Although the differences in bond lengths for comparable complexes are small with palladium and platinum, it does appear that palladium has a greater affinity for the halogen and platinum for the phosphorus[637]. Electronic and circular dichroism spectra have been reported and assigned for complexes of $Et_2PCH_2CH_2PEt_2$[638]. A number of studies of complexes of chiral diphosphines are available including chiraphos, R-prophos and R-phenphos[639]. Detailed ^1H NMR studies[640] of planar $[M(L\text{–}L)_2]^{2+}$ and square pyramidal $[M(L\text{–}L)_2Cl]^+$ [M = Pd, Pt; L–L = *o*-$C_6H_4(PPhMe)_2$] have been carried out; the planar complexes are kinetically stable, but the five-coordinate complexes undergo rapid halide exchange. Various $[Pt(L\text{–}L)(PR_3)Cl]^+$ (L–L = dppe, dmpe, dppm) ions are produced from $[Pt(L\text{–}L)Cl_2]$ and PR_3, and have been studied by ^{31}P NMR spectroscopy; in some cases $[Pt(L\text{–}L)(PR_3)_2]^{2+}$ are also obtainable[641].

Octahedral palladium(IV) complexes $[Pd(L\text{–}L)Cl_4]$ (L–L = dppe, dmpe) and $[Pd(dmpe)Br_4]$ are formed by halogen oxidation of the corresponding palladium(II) complexes, but $[Pd(dppe)Br_2]$ is not oxidized[642], and they reductively eliminate halogen on gentle heating. *trans*-$[Pd(L\text{–}L)_2X_2](ClO_4)_2$ [L–L = dmpe, *o*-$C_6H_4(PMe_2)_2$; X = Cl, Br] are obtained by nitric acid–HX oxidation of $[Pd(L\text{–}L)_2X_2]$, and precipitation with perchloric acid, but for phenyl diphosphine complexes the halogen oxidation of $[Pd(L\text{–}L)_2X_2]$ removes one ligand, forming $[Pd(L\text{–}L)X_4]$[642]. Although iodine converts several $[Pd(L\text{–}L)I_2]$ complexes to materials of composition $[Pd(L\text{–}L)I_4]$ an X-ray study of [Pd(*cis*-$Ph_2PCH{=}CHPPh_2)I_4$] showed it to be a palladium(II) polyiodide[643]. In contrast to the unstable palladium(IV) complexes, platinum(IV) compounds of types $[Pt(L\text{–}L)X_4]$ (L–L = dmpe, dppe, *cis*-$Ph_2PCH{=}CHPPh_2$) and $[Pt(L\text{–}L)_2X_2](ClO_4)_2$ [L–L = dmpe, *o*-$C_6H_4(PMe_2)_2$] are readily obtained and are thermally stable[644]. Characterization of these complexes by ^{195}Pt NMR spectroscopy has been achieved[634]. However, materials of composition $[Pt(L\text{–}L)I_4]$ appear to contain platinum(II)[634].

In Group 1B, the majority of recent work concerns gold diphosphines, although some studies of copper and silver complexes have been published. An unusual copper cluster is the yellow dodecahedral $[Cu_8(Ph_2P(CH_2)_3PPh_2)_4H_8]$ formed from $[\{CuOBu^t\}_4]$ and the diphosphine under hydrogen[645]. Copper(II) halides are reduced by phosphines, but copper(I) complexes include the tetrahedral $[Cu(L\text{–}L)_2]Cl$ (L–L = $Et_2PCH_2CH_2PEt_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, dppe) and the unusual $[(CuCl)_2(dppe)_3]$[646,647]. However, [CuMe] cleaves dppe to give the phosphido-bridged dimer **82**, which has a planar Cu_2P_2 core[648]. Silver complexes $[Ag(L\text{–}L)_2](NO_3)$ [L–L = dppe, $Et_2PCH_2CH_2PEt_2$, $Ph_2PCH_2CH_2PEt_2$, $Ph_2P(CH_2)_3PPh_2$] have been studied in solution by NMR using the $^{109}Ag\{^{31}P\}$ INEPT technique[649].



(82)

For gold(I) it is possible to prepare linear [ClAu(L–L)AuCl] which have bridging diphosphines [L–L = dppe, $Ph_2P(CH_2)_nPPh_2$, $n = 3,4$, $Et_2PCH_2CH_2PEt_2$, *cis*-$Ph_2PCH{=}CHPPh_2$][650,651], the structures being confirmed by X-ray studies of $[(AuCl)_2\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 2, 3$)[652,653], and tetrahedral $[Au(L–L)_2]^+$ [L–L = dppe, $Ph_2P(CH_2)_3PPh_2$, *o*-$C_6H_4(PPhMe)_2$, $Et_2PCH_2CH_2PEt_2$][651,654,655] with $[Au(dppe)_2]Cl$ having been the subject of two independent X-ray studies[654,656]. Ligand exchange in complexes of *o*-$C_6H_4(PPhMe)_2$ is sufficiently slow for *meso* and *rac* forms to be separated by crystallization[655].

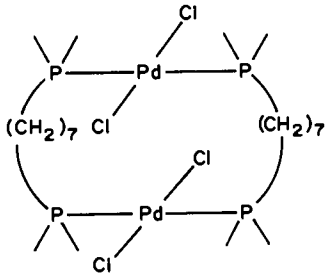
Little new work on the zinc group has been carried out, although notable are the electrochemical reduction of $[Hg(L–L)X_2]$[657] and the X-ray structure determination of $[Hg(cis\text{-}Ph_2PCH{=}CHPPh_2)Br_2]$[446].

D. Diphosphines with Longer Backbones

As demonstrated in the preceeding section, diphosphines with two or three carbon backbones chelate to metal centres in most cases, although with suitable substrates both monodentate and bridging bidentate behaviour can occur. As the backbone is lengthened, the tendency to occupy *cis* positions on a metal centre decreases and bridging behaviour becomes more likely. Further increase in the backbone length may make it possible for the ligand to chelate *trans* to a metal. Although studies of these longer backbonded ligands are of relatively recent origin, several short articles have reviewed developments[20,658–660], and only some examples are given below.

Shaw[20,659] used ligands with bulky terminal substituents such as $Bu^t_2P(CH_2)_nPBu^t_2$ ($n = 5$–10, 12), or $Bu^t_2P(CH_2)_nC{\equiv}C(CH_2)_nPBu^t_2$, and prepared large chelate ring complexes with normal oxidation state platinum metal halides. It was proposed that the presence of bulky substituents made favourable conformational and entropy contributions to the stability of these rings. *Trans* chelation requires a carbon backbone length of ca 9–12 atoms, shorter backbones leading to dimers such as **83**[661]. For the ligand $Bu^t_2P(CH_2)_5PBu^t_2$ the phosphorus atoms bind *trans* to the metal centre but the backbone is now so close to the metal that the central carbon, C(3), is metallated to give a P—C—P tridentate (**84**), examples being found with platinum(II), palladium(II), rhodium(III) and iridium(III)[659,661–664]. In other cases the backbone may be converted by reaction at the metal centre into an olefin group or a carbene, e.g. $[PtCl(Bu^t_2PCH_2CH_2C{=}CHCH_2PBu^t_2)]$[665]. When smaller terminal groups are used, the chemistry is different. Despite the eight-membered ring, $Ph_2P(CH_2)_5PPh_2$ chelates *cis* to platinum(II) in $[Pt(Ph_2P(CH_2)_5PPh_2)Cl_2]$[666]. McAuliffe and coworkers showed that bulky terminal groups were not essential components if the ligands were to chelate *trans* to the metal centre[660,667,668]. From $Ph_2P(CH_2)_nPPh_2$ ($n = 6$–16) they obtained *cis*-$[\{Pt(L–L)Cl_2\}_n]$ from K_2PtCl_4 and *trans*-$[\{Pt(L–L)Cl_2\}_n]$ from $K[Pt(C_2H_4)Cl_3]$ as starting materials; molecular weight and ^{31}P NMR studies showed that in solution both monomers and dimers were present, the proportions varying with the ring size, and that the maximun amount of *trans* chelation occurred in the 15-membered ring $[Ph_2P(CH_2)_{12}PPh_2]$. Subsequently these studies were extended to palladium(II) where *cis* dimers occur with

eight- or ten-carbon backbones and *trans* chelation for twelve-carbon backbones[668]. More recently, labile gold(I) complexes of these ligands have been reported[669]. Other workers observed that when $Ph_2P(CH_2)_6PPh_2$ reacted with iridium(I) or rhodium(I) centres the two central methylene groups were dehydrogenated to an olefinic linkage which coordinated to the metal (**85**)[670,671], and a similar reaction was observed for the ligand $Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$[672].



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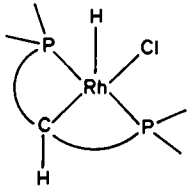

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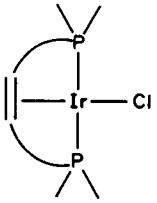

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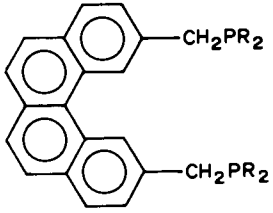


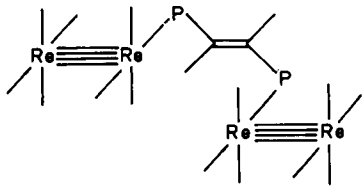
(**86**)

A different approach to *trans* chelation was taken by Venanzi, who designed ligands of type **86**, 2,11-bis(di-R-phosphinomethyl)phenanthrenes (R = usually Ph, but can also be Bu^t, *c*-Hex), which have a rigid backbone of suitable dimensions to span *trans* positions on a planar metal ion[658]. *Trans*-chelated planar complexes of nickel(II), palladium(II), platinum(II), rhodium(I) and iridium(I)[673-676] were obtained and also *trans*-chelated complexes of octahedral iridium(III)[676]. In $[M(CO)_3(L\text{–}L)]$ (M = Fe, Ru) these ligands span *trans* axial positions of a trigonal bipyramid[677], whereas in the three-coordinate silver(I) complexes [Ag(L–L)X] (X = Cl, Br, I) the metal is trigonally coordinated with wide P—Ag—P angles[678,679]. However, it was subsequently shown that even these ligands can chelate *cis* to a metal under certain conditions, as in *cis*-$[Pt(L\text{–}L)Cl_2]$ and *cis*-$[PtH(L\text{–}L(PPh_3))]^+$[680].

E. Diphosphines which Cannot Chelate

Some diphosphines have steric properties which make it impossible for then to chelate to a metal centre, and hence their coordination modes are limited to monodentate or bridging bidentate. Although this property would seem to make them ideal for assembling bimetallic species, relatively little work has been done in this area. One such ligand is *trans*-$Ph_2PCH{=}CHPPh_2$, which may singly bridge metal centres as in $[(CO)_5V(\mu\text{-}Ph_2PCH{=}CHPPh_2)V(CO)_5]^{2-}$[471] or $[\{Re_2Cl_7\}_2(Ph_2PCH{=}CHPPh_2)]^{2-}$[681] (**87**). In $[Mo_2(CO)_8(\mu\text{-}Ph_2PCH{=}CHPPh_2)_2]$ the ligands bridge as in **88** to produce a ten-

membered ring[682]. Bis(diphenylphosphino)acetylene behaves similarly in $[Cl_2Pd(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2PtCl_2]$[683], and a new ligand of this type is $m\text{-}C_6H_4(PPh_2)_2$ for which dinuclear platinum(II) and palladium(II) complexes have been reported[684].



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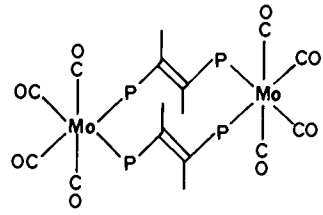

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VI. COMPLEXES OF MULTIDENTATE PHOSPHINES

Tri- and tetra-phosphines are now widely used as ligands and several are commercially available, but in contrast studies of hexaphosphines and phosphinomacrocycles have been limited to the efforts of a small number of research groups. There are many multidentates in which one or more of the phosphorus donors have been replaced by AsR_2, SR, OR, $CH{=}CH_2$, etc., and the disparate electronic properties of the donors in such ligands can produce a particularly complicated coordination chemistry. Regrettably, owing to limitations of space, mixed donors will not be treated in this chapter. Previous reviews of multidentate phosphine complexes have been organized either in terms of the metal[34], or have adopted a classification based on ligand denticity[29,37]. Three other articles which contain much data on these ligands, mostly with 3d transition elements, are notable[18,40,585]. The chemistry of polydentate phosphines depends both on the number of donors and on the interdonor linkages, and how these accommodate to the demands of the metal substrate (or fail to meet them). At one extreme the coordination chemistry may differ only in degree from that of the equivalent number of mono- or bi-dentate ligands, whilst at the other the chemistry of the polydentate may have no equivalent among ligands of lower denticity. In the description that follows the approach has been to discuss the characteristic types of coordination behaviour found for the main polyphosphines, and in contrast to Sections IV and V the organization is not based on the Periodic Table.

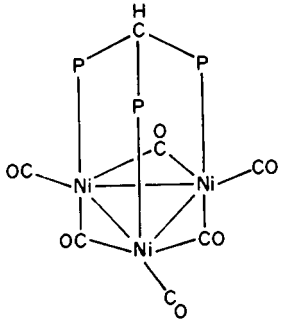
A. Triphosphines

There are two basic types of triphosphine, the 'linear' $R_2P{\cdots}P(R){\cdots}PR_2$, and the 'tripod' $RC(\cdots PR_2)_3$.

The simplest tripod type is exemplified by tris(diphenylphosphino)methane, $HC(PPh_2)_3$, which has introduced by Osborn[686] as a ligand which was sterically capable of binding to a triangular face of a metal cluster. The geometry of the ligand is such that it chelates to a single metal centre with difficulty, and the only structurally characterized example of this appears to be $[Fe(C_5H_5)\{HC(PPh_2)_3\}]PF_6$[685], produced by photolysis of a mixture of the ligand and $[Fe(C_5H_5)(p\text{-xylene})]^+$. The strain in the system is evident from the ease with which ring opening occurs.

The face bridging mode of binding to the triangular face of a metal cluster is illustrated in $[M_4(CO)_9\{HCPPh_2)_3\}]$ (M = Co, Rh, Ir), which have been fully characterized[686-688]. The ligand stabilizes the cluster unit against degradation to mononuclear species by carbon monoxide at high temperatures and pressures. However, in other systems the ligand itself may fragment, for example on reaction with $[Ru_3(CO)_{12}]$ the capped

$[Ru_3(CO)_9\{HC(PPh_2)_3\}]$ is a minor product, and other species incorporating fragments of the ligand include $[Ru_3(CO)_9\{Ph_2PCHP(Ph)\}(C_6H_4PPh)]$, $[Ru_2(CO)_5Ph\{(Ph_2P)_2CHPPh\}]$, $[Ru_2(CO)_4(dppm)Cl(PPh_2)]$ and $[Ru_2H(CO)_4(Ph_2PCHPPh_2)(PhPC_6H_4)]$[689]. The ligand also has an ability to 'assemble' clusters from mononuclear starting materials, e.g. $[Ni(CO)_4]$ produces $[Ni_3(CO)_6\{HC(PPh)_3\}]$ (**89**)[690], and $[Ir_4(CO)_9\{HC(PPh_2)_3\}]$ is formed in poor yield from $[Ir(CO)_2Cl(p\text{-toluidine})]$, although in the latter reaction fragmentation to $[Ir_3(CO)_6(Ph)(\mu^3\text{-}PPh_2)(dppm)]$ also occurs[691]. In other systems the ligand may coordinate as a monodentate, $[Fe(CO)_4\{HC(PPh_2)_3\}]$, or bidentate, *cis*-$[Mo(CO)_4\{HC(PPh_2)_3\}]$[692], and the uncoordinated PPh_2 group(s) in such complexes may be bound to a second metal centre to form homo- or hetero-nuclear systems, $[Fe(CO)_3\{HC(PPh_2)_3\}Fe(CO)_4]$[692] or $[RhFe(CO)_5\{HC(PPh_2)_3\}]$[693] (**90**).



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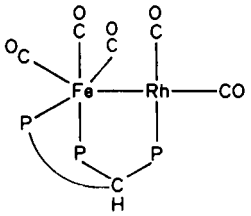
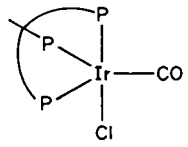
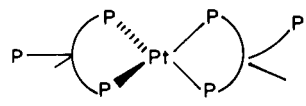


(**90**)

The commonest tripod tridentate, 1,1,1-tris(diphenylphosphinomethyl)ethane $[MeC(CH_2PPh_2)_3$, tdpme][40], has approximate C_{3v} symmetry which prevents it chelating *mer* to an octahedral metal centre, and its usual binding modes are facial to an octahedron, or occupying three positions in a distorted five-coordinate geometry. The ligand is also known bound as a bidentate, and very rarely it may be monodentate. In $[(AuCl)_3(tdpme)]$ each phosphorus is bound to a separate gold atom[694]. Typical carbonyl complexes are $[V(CO)_{6-n}(tdpme)]^-$ ($n = 1, 2, 3$) in which the ligand is bound by one, two or all three phosphorus donors, respectively[695]. Manganese carbonyl derivatives are *fac*-$[Mn(CO)_3(tdpme)]^+$ and $[Mn(CO)_3Cl(tdpme)]$[696]. However, five-coordinate trigonal bipyramids with tdpme occupying one axial and two equatorial sites are found in $[Ru(CO)_2(tdpme)]$[697] and $[Ir(CO)Cl(tdpme)]$[696] (**91**), both of which are oxidized by halogens or HX to six-coordinate *fac* octahedral species. Octahedral rhodium(III) hydrides *fac*-$[RhH_3(tdpme)]$ are obtained by reducing rhodium trichloride–tdpme with sodium borohydride, and two hydrides are displaced by CO to give five-coordinate $[Rh(CO)H(tdpme)]$[699]. This ready switching between five- and six-coordinate metal centres is characteristic of the ligand. Typical of the binding to an early transition metal are the moisture sensitive *fac*-$[Cr(tdpme)X_3]$ (X = Cl, Br)[700] and $[Cr(tdpme)_2](BF_4)_3$ provides a rare example of two ligands bound to one octahedral metal centre[499]. Bis(bidentate) behaviour is present in $[Pt(tdpme)_2]$ (**92**)[701].

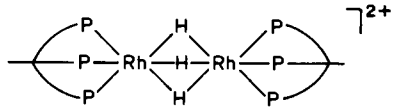


(**91**)



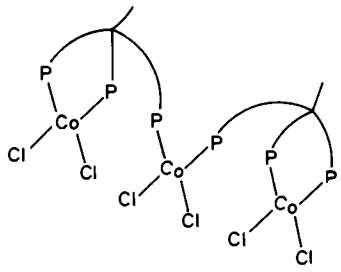
(**92**)

The alkyl-substituted $MeC(CH_2PMe_2)_3$ is a better donor and is smaller than tdpme. It has been little studied but several chromium complexes[702] provide examples of two coordination modes, and their increased stability over those of tdpme is evident. In *fac*-$[CrCl_3\{MeC(CH_2PMe_2)_3\}]$, prepared from $[Cr(thf)_3Cl_3]$, it is tridentate, but in *trans*-$[CrCl_2\{MeC(CH_2PMe_2)_3\}_2]$ it binds as a bidentate, and when the latter is reduced by Na–Hg to chromium(0) (in $[Cr\{MeC(CH_2PMe_2)_3\}_2]$), *fac* tridentate coordination returns. Reduction of the chromium(III) complex with $LiBHEt_3$ generates the seven-coordinate hydride $[CrH\{MeC(CH_2PMe_2)_3\}_2]^+$[703]. Binuclear complexes with triple hydride bridges have been characterized for Co, Fe and Rh, e.g. $[(tdpme)Rh(\mu\text{-}H)_3Rh(tdpme)]^{2+}$ (**93**), which can be reduced stepwise electrochemically[704], and mixed metal derivatives $[(tdpme)Rh(\mu\text{-}H)_3M(tdpme)]^{n+}$ (M = Co, Ni) can be made by combining $[RhH_3(tdpme)]$ and an $[M(tdpme)]^{n+}$ unit[705]. Binuclear complexes with halide bridges are formed by cobalt and iron, and the geometry is exemplified in the complex of $MeC(CH_2PEt_2)_3$, $[\{MeC(CH_2PEt_2)_3\}Fe(\mu\text{-}Cl)_3Fe\{MeC(CH_2PEt_2)_3\}]^+$, which an X-ray study showed is a confacial bioctahedron[706]. Sacconi and coworkers[707,708] have demonstrated that (tdpme) M moieties are capable of binding a range of novel main group ligands such as P_3, As_3 or Te_2 in mono- or bi-nuclear complexes such as $[(tdpme)Co(P_3)]$ and $[\{MeC(CH_2PEt_2)_3\}Fe(P_3)Co(tdpme)](PF_6)_2$.

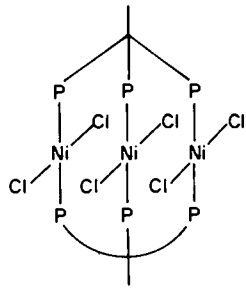


(**93**)

All of the tripods discussed above produce six-membered chelate rings, but recent studies have shown that increasing the chain length or altering the steric properties, e.g. in $MeC(CH_2PEt_2)_3$, can produce some unusual effects. Thus, in contrast to tdpme, which gives dinuclear $[(tdpme)Co(\mu\text{-}Cl)_2Co(tdpme)](BPh_4)_2$, the ligand $MeC(CH_2PPh_2)_2(CH_2CH_2PPh_2)$ (L) gives a $[Co_3L_2Cl_6]$ stoichiometry containing three separate tetrahedrally coordinated cobalt centres (**94**), the bridges to the central cobalt being made by the longer arms of the chelates[709]. With nickel(II) tdpme affords $[Ni(tdpme)X_2]$, which are probably planar (P_2X_2)[40], but $MeC(CH_2CH_2PPh_2)_3$ gives the trimer **95**[709]. A new ligand with silicon at the apex in $Bu^tSi(CH_2PMe_2)_3$ (L′) has recently been synthesized, and preliminary studies show it to form novel complexes with early transition metals, including seven-coordinate $[Ti(CO)_4L']$ and $[V(CO)_3HL']$[710].

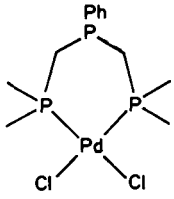


(**94**)

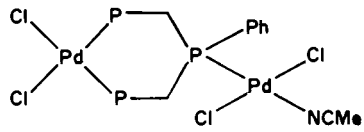


(**95**)

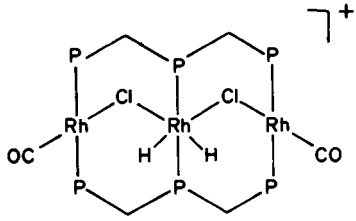
Linear tridentates $R_2PCH_2P(R)CH_2PR_2$ would form fused four-membered rings if all three phosphorus atoms chelated to metal centres, and the strain involved rules out this mode of coordination. The ligands can bind as bidentates via the terminal phosphorus atoms, producing unstrained six-membered rings. Examples of this are the tetrahedral $[Ni\{(Me_2PCH_2)_2PMe\}_2]$[711], the planar $[Pd\{(Ph_2PCH_2)_2PPh\}Cl_2]$ (**96**) and *cis* octahedral $[M(CO)_4\{(Ph_2PCH_2)_2PPh\}]$ (M = Cr, Mo, W)[712]. The central 'free' phosphorus in such systems bind to a second metal centre, as when **96** reacts with $[Pd(MeCN)_2Cl_2]$ to produce **97**[713] The major interest in this type of ligand has derived from the ability to bridge bi- or tri-nuclear species exemplified by $[Rh_3\{(Ph_2PCH_2)_2PPh\}_2(CO)_3Cl_2]^+$ or $[Rh_3\{(Ph_2PCH_2)_2PPh\}_2(H)_2Cl_2(CO)_2]^+$ (**98**), where each phosphorus of the ligand is bound to a different rhodium atom[714–716]. In $[Rh_2(CO)_2\{(Me_2PCH_2)_2PMe\}_2](BPh_4)_2$



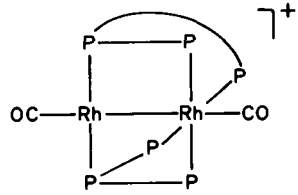
(**96**)



(**97**)



(**98**)



(**99**)

there are six- and four-coordinate centres (**99**)[716], and in $[Re_2Cl_3\{(Ph_2PCH_2)_2PPh\}_2]PF_6$ the ligands bridge the Re—Re bond binding by the central phosphorus to one metal and by the terminals to the other[717].

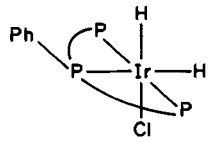
The commercially available $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ (triphos) has been much studied and complexes with most of the transition metals are known. It has no strong stereochemical preference and can bind as a chelating bidentate via one terminal and the central phosphorus, or as a tridentate, and unlike tdpme is capable of coordinating *mer* or *fac* to an octahedral metal centre or of occupying three positions in a square plane or the base of a square pyramid. It may also bridge or even bind as a monodentate, although like other two-carbon backbone ligands its preferred mode is as a chelating ligand.

Using variations of the method of adding a P—H bond of a secondary phosphine to an olefinic phosphine, Keiter *et al.*[718] prepared all possible isomers of $[(triphos)\{W(CO)_5\}_n]$ ($n = 1$–3). More conventional routes with substitution into the metal carbonyl anion were used to prepare *cis*-$[V(CO)_4(triphos)]^-$ and *mer*$[V(CO)_3(triphos)]^-$[719], although with more bulky analogues (*c*-Hex)$P(CH_2CH_2PPh_2)_2$ or $PhP\{CH_2CH_2P(c\text{-Hex})_2\}_2$ the substitution stops after removal of two carbonyl groups[720]. X-ray structures of $[M(CO)_3(triphos)]$ (M = Cr, Mo) show them to be *fac* isomers[721]. Typical examples of

triphos binding as a tridentate to 3d metals are *mer*-$[CrX_3(triphos)]$[700], $[Cr(triphos)_2[(BF_4)_3$[499], *fac*-$[CoX_3(triphos)]$[587] and square planar $[Ni(triphos)X]BPh_4$[722], but in $[Fe(triphos)_2Cl_2]$ the ligand functions as a bidentate and the iron(II) is high-spin[546]. There is an interesting comparison between the geometries about the cobalt(I) in $[Co(triphos)\{P(OMe)_3\}_2](BF_4)$ and $[Co(\{PhP(CH_2CH_2CH_2PPh_2)_2\}(CO)\{P(OMe)_3\}]BF_4$ in that the former is distorted trigonal bipyramidal, but the latter is a square-pyramid[723].

The two fused five-membered rings in chelated triphos are strained when bound to a large metal ion, and $RP\{(CH_2)_3PR_2\}_2$ ligands have been prepared to overcome this effect[724], e.g. in the platinum(II) complexes $[PtLX]^+$ and $[PtL(PEt_3)]^{2+}$ [725], and there are complexes of unsymmetrical tridentates such as $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$ or $(c\text{-Hex})_2P(CH_2)_3P(Ph)(CH_2)_3P(c\text{-Hex})_2$[726].

Bidentate coordination of several triphosphines is found in $[PtMe_2(triphosphine)]$ complexes[727]. Other heavy metal complexes are *mer*-$[Pt(triphos)Cl_3]^+$[634] and $[RuLCl_2]$ and $[Ru(CO)_2L]$ [$L = PhP\{(CH_2)_3P(c\text{-Hex})_2\}_2$], both of which are five-coordinate[728]. The planar $[IrCl\{PhP((CH_2)_3PPh_2)_2\}]$ oxidatively adds H_2 and HCl to give $[IrH_2ClL]$ and $[IrHCl_2L]$, respectively, and with CO gives sequentially the five-coordinate carbonyls [Ir(CO)ClL] and $[Ir(CO)_2L]Cl$[729]. In low-symmetry complexes the orientation of the central R group of a linear tridentate can lead to diastereoisomers, although the effect has often been ignored. An X-ray study of *mer-cis*-$[IrH_2Cl\{PhP(CH_2CH_2CH_2P(c\text{-Hex})_2)_2\}]$ (**100**) showed the phenyl group to be *syn* to the axial hydride[730].



(100)

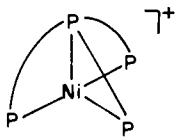
B. Tetraphosphines

There are three basic types of tetradentate, tripods $P(\text{——}PR_2)_3$, linear $R_2P\text{——}P(R)\text{——}P(R)\text{——}PR_2$ and spirocyclic $C(CH_2PR_2)_4$. This last type can coordinate a maximum of three phosphorus donors to one metal centre due to steric constraints as in $[Co(CO)_2\{C(CH_2PPh_2)_4\}][Co(CO)_4]$[731], and these ligands have been little used.

The first tripod tetraphosphine was Venanzi's QP, $(o\text{-}C_6H_4PPh_2)_3P$[18,40], but recent studies have mostly used the alkane backboned $P(CH_2CH_2PPh_2)_3$ (tet-2). Many complexes of this ligand have been prepared, particularly with the Group VIII metals, and detailed comparisons of its cobalt and nickel complexes with those of related ligands such as $N(CH_2CH_2PPh_2)_3$ have been made[40]. The ligand tends to impose trigonal bipyramidal geometry when this is acceptable to the electronic properties of the metal; examples are high-spin iron(II) in $[Fe(tet\text{-}2)Br]PF_6$[732], low-spin nickel(II) in $[Ni(tet\text{-}2)\{P(OMe)_3\}](BF_4)_2$ and cobalt(I) in $[Co(tet\text{-}2)\{P(OMe)_3\}]BF_4$[733], although the cobalt(II) complex $[Co(tet\text{-}2)Br]PF_6$ is square pyramidal, probably owing to the Jahn–Teller distortion in the d^7 ion[40].

The nickel(I) complex $[Ni(tet\text{-}2)](ClO_4)$ has the very rare trigonal pyramidal geometry **101**[734]. Usually the ligand binds as a tetradentate but in the chromium(III) complex *mer*-$[CrCl_3(tet\text{-}2)]$ it is present as a tridentate as the hard metal prefers to coordinate the chlorines (**102**)[700]. If, however, the third halogen is removed by $AgBF_4$ then tetradentate binding is possible, $[CrX_2(tet\text{-}2)]BF_4$ (X = Cl, Br, I) (**103**)[700]. The cobalt(III) complexes are *cis*-octahedral $[Co(tet\text{-}2)X_2]ClO_4$, again due to the preference of the metal

for six coordination[587]. Platinum(II) is trigonal bipyramidal in $[Pt(tet\text{-}2)X]^+$ and $[Pt(tet\text{-}2)(PR_3)]^{2+}$[634,735].



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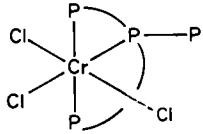

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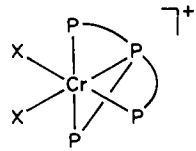
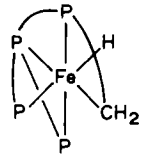


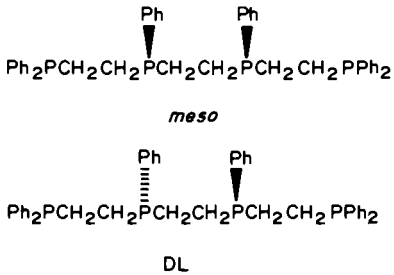
(103)

The ligand $P(CH_2CH_2CH_2PMe_2)_3$ with three-carbon backbones has been studied more recently, and here the longer chains and the smaller steric requirements and good donor power of the terminal groups combine to produce six coordination in the examples studied, *cis*-$[FeX_2\{P(CH_2CH_2CH_2PMe_2)_3\}]$ and *cis*-$[RuX_2\{P(CH_2CH_2CH_2PMe_2)_3\}]$ (X = Cl, Br; X_2 = HX)[736–739]. Reduction of the dichlorides with $LiAlH_4$ produces *cis*-dihydrides for both iron and ruthenium[737,738], and on photolysis in benzene the iron complex metallates a methyl group to give **104** (cf. dmpe or PMe_3), but the ruthenium forms $[Ru(Ph)H\{P(CH_2CH_2CH_2PMe_2)_3\}]$[740,741].



(104)

Linear tetraphosphine chemistry is largely confined to $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$ (tet-1), which like the linear tridentates has no strong stereochemical preference. It can bind between one and four donors to metal carbonyl derivatives. The central P(Ph) groups in the coordinated ligand are asymmetric centres and hence *meso*- and DL-diastereoisomers are to be expected (**105**). In practice the picture is confused, most workers have not observed (or looked for?) these isomers, and their presence in samples of the commercially obtained ligand from different sources is unclear; one form is much less easily isolated from the preparation[742]. Brown and Canning[743] separated the isomers by fractional crystallization from a sample of ligand previously heated to 200 °C under argon, and prepared rhodium(I) complexes from the separate diastereoisomers. They concluded that the higher melting form of the ligand was probably the *meso* form, and showed that different reactivities were exhibited by complexes of the different isomers. The ligand can bind to an octahedral metal centre to give $[M(tet\text{-}1)X_2]^{n+}$ around the equatorial plane (*trans* isomer) or axial–equatorial to give two *cis* isomers (*cis*-α and *cis*-β (**106**)), although the steric constraints of the *meso* form preclude it forming *cis*-α geometry[587]. Both *cis* isomers have been characterized by NMR for $[Rh(tet\text{-}1)O_2]^+$, DL-in the *cis*-α and *meso* in the *cis*-β form[743], and in $[Co(tet\text{-}1)X_2]^+$ the *cis*-β form appears to be present[587]. In $[RuCl_2(tet\text{-}1)]$ *trans* geometry and *syn*-phenyl groups (*meso*) were revealed by an X-ray study[744]. Five-coordinate complexes are readily formed, and an example is the singlet↔triplet spin cross-over system $[Fe(tet\text{-}1)Br]BPh_4$, which has $\mu = 0.87$ BM at 86 K and $\mu = 2.26$ BM at 376 K[745]. It is reduced by $NaBH_4$ under nitrogen to $[FeH(N_2)(tet\text{-}1)]Br$ and under helium to $[FeH(tet\text{-}1)]Br$, and an X-ray study of the former showed a *trans* structure containing *meso*-tet-1[746].



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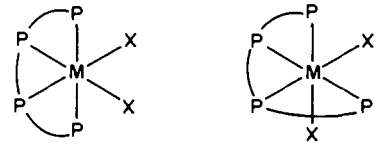
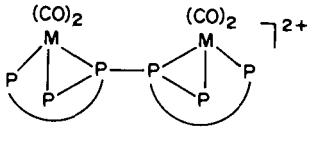


(106)

Methyl-substituted tetraphosphines, e.g. $Me_2P(CH_2)_3P(Me)(CH_2)_nP(Me)(CH_2)_3PMe_2$ ($n = 2$, 3), have been prepared by Stelzer and co-workers[140,747–749], and complexes with nickel(II), palladium(II), platinum(II) and zinc(II) have been studied. The isomers present were deduced by a combination of X-ray crystallography and detailed NMR studies.

C. Hexaphosphines

Hexaphosphines such as $(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2$ usually bind less than six donors to a metal centre, e.g. $[V(CO)_{6-n}L]^-$ ($n = 1$–3)[750], although they can bind as bis(tridentates) in, for example, $[\{Cr(CO)_3\}_2L]$[751]. The ligand with a single central methylene group, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$, was designed to form binuclear complexes with direct metal–metal interactions[752]. However, it can also adopt other conformations in $[Co_2(CO)_4L]^{2+}$ (**107**) and in planar $[Pt_2Cl_2L]^{2+}$[753] and *mer*-octahedral $[Cr_2Cl_6L]$[754], whilst in $[Fe(CO)ClL]^+$ it binds as a tetradentate (**108**)[755].



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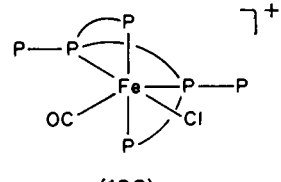
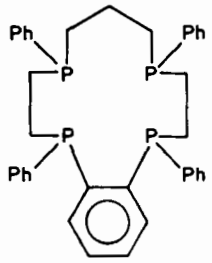


(108)

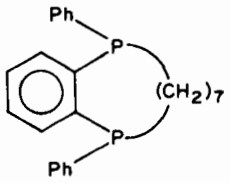
D. Phosphinomacrocycles

Phosphorus macrocycles are synthetically very challenging to produce, and appeared later than N, O or S analogues. There are now a variety of macrocyclic ligands with P_2O_2, P_2S_2, P_2N_2, P_3O_3, etc., donor sets[23], but we shall restrict coverage here to ligands containing only phosphorus. An unusual example is $P(CH_2)_3P(CH_2)_3P(CH_2)_3$, obtained by polymerization of the allylphosphine complex of molybdenum carbonyl $[Mo(CO)_3(H_2PCH_2CH{=}CH_2)_3]$, and obtained as the *fac*-$[Mo(CO)_3L]$ complex[756]. A more conventionally obtained P_4 ligand is **109**, which forms planar complexes with nickel(II), $[NiL]X_2$ (X = Cl, NCS, BF_4)[757]. Kyba *et al.*[758] prepared cobalt(II) complexes of the P_2 macrocycle **110**, which exist in two forms, $[CoL_2X_2]$, octahedral with long Co—X bonds, and $[CoL_2]X_2$, which are planar. Nickel(II) complexes of the 14-membered ring P_4 macrocycle *o*-$C_6H_4PPh(CH_2)_3PPhC_6H_4PPh(CH_2)_3PPh$, were reported together with $P_{4-x}S_x$ analogues, although the details of the former as sparse[759]. Stelzer and coworkers[760,761] used template syntheses to obtain tetraphosphine macrocycles, in

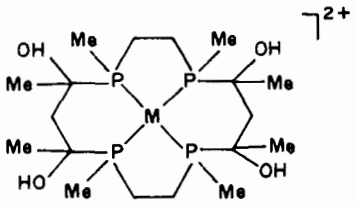
essence by condensation of a diketone with metal complexes of a disecondary phosphine $[M(HMeP(CH_2)_nPMeH)_2]^{2+}$ (M = Ni or Pd) to obtain complexes such as **111** or **112**. However, the ligand does not seem to be removable from the metal once formed. Cyclization of $[Pd(HMePCH_2CH_2PHMe)_2]^{2+}$ by *o*-xylylene dichloride gave three diastereoisomers of **113** with 16-membered rings[762]. The ligand can be displaced with KCN, and subsequently complexed to other metals such as nickel(II) or platinum(II). An X-ray study of [Pd(**113**)Cl]Cl, which is square pyramidal, was also reported[762]. The original papers should be consulted for details of the diastereoisomers present.



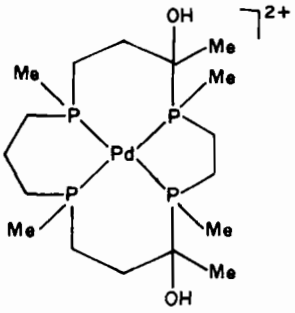
(**109**)



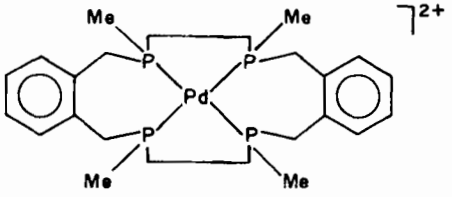
(**110**)



(**111**)



(**112**)



(**113**)

Finally, mention is made of polymer-supported phosphines and their metal complexes, which could be considered to be the ultimate multidentates(!). Much interest in such systems arises from attempts to combine the selectivity of homogeneous catalysts with ease of separation of products and catalyst. A recent monograph[763] and chapter in Volume 4 of this series[764] have been devoted to materials of this type and should be consulted for details.

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The Chemistry of Organophosphorus Compounds
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CHAPTER **16**

Biochemistry of phosphines

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I. INTRODUCTION

Although organophosphines of all structural types covered in this volume have been widely reported in the literature, only a few have so far been the subject of studies of interaction with biological systems and our knowledge of their biochemistry is at present very limited. Nevertheless, there is growing interest in this area, largely owing to the prospect of finding material with pharmacological activity. This lack of biochemical information is a reflection of the limited occurrence of phosphines, whether naturally or as a result of man's activities, their uses and the chemical properties of phosphorus in the trivalent state. Although the role of pentavalent phosphorus in biology has been thoroughly investigated, it provides little which is relevant to the study of phosphines. A limited insight can be gained from a comparative study of the nearest neighbour elements in Group V of the Periodic Table.

The organic amines are widely distributed in nature and many are pharmacologically active. Natural amines comprise many neurotransmitters, hormones, neuromodulators and bacteriocides, the last being the basis for many synthetic amine drugs. Although there is some interest in phosphorus analogues of nitrogen-containing drugs, there are some important differences between the two elements. For example, the action of phosphines as transition metal ligands receives attention later in this chapter, but unlike phosphorus, trivalent nitrogen has no low-lying vacant d orbitals to participate in back-donation from the metal and cannot strengthen such ligand bonding to the same extent. The other neighbour in Group V, arsenic, has also been used biochemically. Trivalent arsenic, by virtue of its combination with protein sulphydryl groups, is a good inhibitor of enzymes in which an active-site SH group is essential. This property explains the toxicity of arsenic compounds which act on the enzymes of respiration and glycolysis. Indeed, trivalent arsenic compounds were used as parasiticides before the advent of modern antibiotics. The

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general toxicity of arsenicals has limited their therapeutic use in recent years and the possibilities of phosphorus analogues may become attractive.

The most comprehensive body of biochemical data on the phosphines has come from a series of studies on the parent unsubstituted molecule, phosphine itself. Much of this results from the use of phosphine as an important fumigant in agriculture and the need to prolong its use against such increasing threats as pest resistance. Although in some respects, for example physical properties, phosphine is atypical of the organophosphines, certain aspects of its biochemistry can be extrapolated to the substituted derivatives. This chapter therefore begins with a review of phosphine and leads on to the organophosphines. As far as is possible, in both cases the discussion proceeds through a general coverage of the toxic and toxicological effects on whole organisms to a more detailed study of events at the molecular level, but in neither case is the story yet complete.

II. PHOSPHINE

The interaction of phosphines with biological material occurs in only a limited number of situations. Phosphine itself occurs rarely in nature, being that transient component of marsh gas known as 'Will o' the Wisp'. Recently it has been reported that this component may be more significant in the earth's phosphorus cycle than previously thought. Devai *et al.*[1] have found that phosphine may account for 25–50% of the phosphorus deficit in sewage tanks and sediments of shallow waters. Their evidence indicates that anaerobic bacterial reduction of orthophosphate is responsible for the generation of phosphine in these situations. Extra-terrestrially, phosphine is present as the major source of phosphorus in the atmosphere of the planet Jupiter. There is some suggestion that the presence of phosphine in the atmospheres of the great planets and in our own prebiotic atmosphere may have played a role in the evolution of organic molecules[2]. From experiments using electric discharges through mixtures of methane, nitrogen and phosphine, it was concluded that phosphine may promote the formation of amino acids. The identification of bacteria which were able to use hypophosphite as a precursor of phosphate indicates that phosphine may have directly played a part in biological evolution and it is possible that some bacteria can utilize phosphine directly[3], although we have been unable to confirm this in the literature.

Phosphine is manufactured for use as a chemical reagent, a dopant in the electronics industry and an agricultural fumigant. With the exception of the last of these uses, biological interactions are likely to be restricted to accidental exposure of workers. This applies also to the incidental evolution of the gas from phosphorus furnaces, and from impurities in ferrosilicon, or during steel pickling, machining of spheroidal graphite iron and other metallurgical processes.

In agriculture phosphine is used as a fumigant, primarily for the disinfestation of stored commodities. The gas is evolved, by the action of atmospheric moisture, from a range of formulations consisting usually of aluminium or magnesium phosphide. The principal biological targests for such treatments are arthropod pests of stored agricultural food commodities. These include grain weevils, flour beetles, mill moths and mites. Preparations of calcium or zinc phosphide are used as rodenticides and it is generally believed that toxicity is due to the hydrolysis of phosphide to phosphine by the gastric acids[4]. In mammals, acute phosphine poisoning is accompanied by a wide variety of symptoms including tremors, fatigue, drowsiness, nausea and severe gastric pain, followed by convulsions or coma. Depression of the central nervous system and irritation of the lungs have also been reported. In insects the primary symptoms of phosphine poisoning are those of respiratory inhibition. Exposure of insects to phosphine results in a rapid decrease in oxygen consumption[5,6] followed by paralysis and death. A number of studies relate to the mechanism of toxicity of phosphine in both insects and mammals. Most of these

studies relate to the biological effects of the reductive capacity of phosphine or its reaction with the heavy metal components of the cell. Phosphine is toxic to all aerobic organisms and toxicity is very dependent on the availability of oxygen. In atmospheres low in oxygen insects accumulate little gas, whereas in oxygen-rich atmospheres their respiration is stimulated and gas uptake increased, resulting in enhanced toxicity. In those organisms which can tolerate some degree of anoxia, uptake of phosphine and toxicity is much reduced[7]. The close relationship between oxidative biology, phosphine accumulation and toxicity have led to consideration of respiratory biochemistry as a major toxic lesion for phosphine. Other suggested targets include a non-specific reduction of tissue components, for example protein disulphide groups, a general lowering of oxygen tension by the reaction of phosphine with oxygenated cytoplasm, the disruption of cellular systems which protect against the harmful effects of free radicals[8,9] and the reaction of phosphine with activated carbonyl groups in proteins[10].

The biochemical processes of respiration are carried out in subcellular organelles called mitochondria, where chemical energy stored in the form of adenosine triphosphate (ATP) is produced from adenosine diphosphate (ADP) and inorganic phosphate through a complex series of electron-transfer reactions mediated by a number of cofactors and enzymes[11].

Suitable 'fuel' molecules from the catabolism of glucose, such as pyruvate, donate H^+ to nicotinamide adenine dinucleotide (NAD). The NADH is oxidized in discrete steps first via a flavoprotein succinate dehydrogenase and a non-haem iron protein, coenzyme Q, and then a series of haem-containing cytochrome proteins to the ultimate electron acceptor, molecular oxygen. It is this oxygen that is consumed in the respiratory process with the overall result that it is reduced to water, thus regenerating NAD and by the conservation of energy ATP is formed. The final cytochrome in the chain is the cytochrome a–a3 complex or cytochrome c oxidase, which contains a copper prosthetic group in addition to a haem centre. This overall process of 'oxidative phosphorylation' can readily be assessed *in vitro* in aqueous suspensions of intact mitochondria by measuring their oxygen consumption either in the 'resting' state when supplied with appropriate substrate or in the 'stimulated' state in the presence of substrate and ADP.

Nakakita *et al.*[12] showed that phosphine inhibited oxygen uptake by rat liver mitochondria *in vitro*. The resting respiration of these mitochondria was less sensitive to phosphine inhibition than ADP-stimulated oxygen consumption, and it was postulated that this was due to an increase in permeability of the mitochondrial membrane in the presence of ADP, allowing greater penetration of phosphine. Phosphine has also been shown to inhibit oxidative phosphorylation in mitochondria isolated from mouse liver, housefly flight muscle and granary weevil tissue[13], and from tissues of susceptible and phosphine-resistant strains of the lesser grain borer *Rhyzopertha dominica*[6]. Chefurka *et al.*[13] found that both stimulated and resting mitochondrial respiration was inhibited by micromolar concentrations of phosphine, with total inhibition occurring at 250 μM. ADP-stimulated respiration was found to be more sensitive to inhibition than resting and it was suggested that phosphine might stabilize a high-energy intermediate by interacting with energy-transfer reactions. By using suitable artificial electron acceptors which allow parts of the electron-transfer chain to be bypassed, Chefurka *et al.* were able to investigate the effect of phosphine on the individual reactions of oxidative phosphorylation. They found that the inhibitory action of phosphine was expressed at site 3 of ATP synthesis, that is, the portion of the electron-transport chain between cytochromes a–a 3 and molecular oxygen. These studies indicated that phosphine acted by preventing the flow of electrons to molecular oxygen via the cytochrome a–a3 complex.

The inhibitory action of phosphine at this site in the electron-transport chain in both insect and mammalian mitochondria led inevitably to the suggestion that phosphine, like hydrogen cyanide, is an inhibitor of cytochrome c oxidase, thus preventing the re-

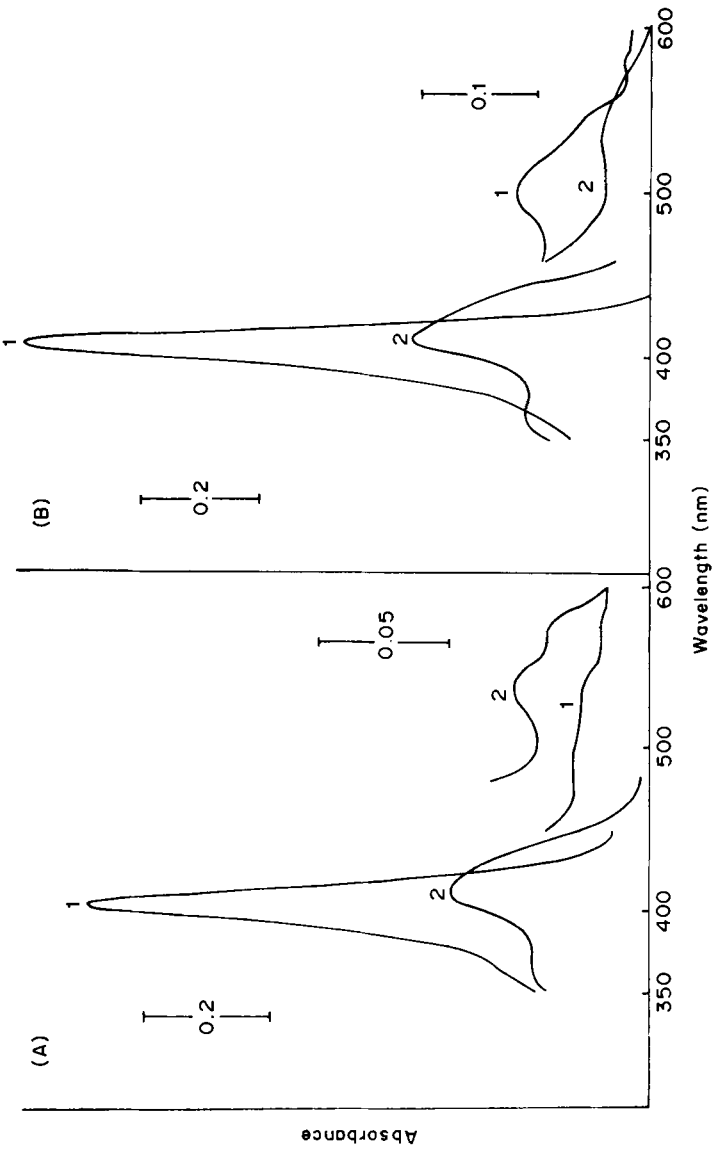


FIGURE 1. Effect of phosphine on the UV–visible spectrum of (A) haemoglobin and (B) myoglobin peaks: 1 = untreated oxidized protein; 2 = exposed to 0.6 mg l^{-1} phosphine for 4 h at 20 °C.

oxidation of cytochrome c. This would cause a blockage of electron flow with a resulting failure to synthesize ATP. Since ATP is the major high-energy compound used in biochemical processes requiring the utilization of energy, the biological consequences of inhibiting its synthesis are catastrophic for the organism.

Cytochrome c oxidase has both haem and copper-containing prosthetic groups which are likely candidates for reaction with phosphine bearing in mind its reaction with heavy metals and its property of complexing with haemoglobin *in vitro* in the presence of oxygen[14]. We have found that phosphine causes spectral changes in both haemoglobin and myoglobin *in vitro* (Fig. 1). The absorption peaks observed in native oxidized haemoglobin are at 406, 500, 538 and 568 nm. Phosphine decreased the intensity of the 406-nm peak with a slight shift to 408–412 nm. The peaks at 500 and 568 nm are abolished, with a concomitant increase in the height of the 538 nm peak. A similar phenomenon is observed with myoglobin. These changes are similar to those observed on addition of dithionite but take place over a period of hours and are indicative of a slow deoxygenation of the haem iron (III).

Nakakita[15] showed that phosphine had an effect on the UV and visible absorption spectra of mitochondria isolated from maize and from rat liver. Difference spectra obtained from mitochondria incubated with phosphine compared with untreated mitochondria exhibited peaks at 602, 445 and 551 nm. These peaks correspond to the α and γ absorption bands of cytochrome c oxidase and the α band of cytochrome c, respectively. The two peaks due to the interaction of phosphine on cytochrome c oxidase were slightly shifted from those seen at 605 and 443 nm when hydrogen cyanide reacts with this enzyme. Mitochondria held in an anaerobic state also showed peaks at 605 and 443 nm, confirming the oxygen-starvation effects of cyanide on cytochrome c oxidase. These results therefore suggested that the action of phosphine on mitochondria is not the same as that of cyanide or anoxia. Indeed, Price and Walter[16] have shown that the disruption of respiratory metabolism in insects treated with phosphine *in vivo* differs from the effects of anoxia or cyanide poisoning. Exposure of the lesser grain borer *Rhyzopertha dominica* to HCN or anoxia resulted in tissue accumulation of pyruvate and a depletion of ATP, indicating that the normal pathway for pyruvate oxidation via the electron transport chain was blocked. Phosphine treatment produced no such accumulation of pyruvate, although ATP was still depleted.

The *in vitro* effects of phosphine on purified cytochrome c and cytochrome c oxidase were further studied by Kashi and Chefurka[17]. They found that the difference spectrum of phosphine-treated cytochrome c oxidase was identical with that produced by reduction of the cytochrome with dithionite. The position and intensity of the α absorption bands were characteristic. In the Soret region the peak at 418–420 nm progressively decreased with increasing phosphine concentration and was accompanied by the appearance of a band at 444 nm. Circular dichroic (CD) spectra in this region showed a drastic reduction of the major extremum normally seen in the oxidized form at 427 nm, with a concomitant appearance of a new extremum at 440 nm. In the visible region the absorption peak characteristic of the oxidized form at 597–599 nm shifted to 603 nm and increased in intensity with increasing phosphine concentration. CD spectra confirmed these observations, showing a shift of the extrema at 566 and 603 nm to longer wavelengths with an associated increase in amplitude. These results suggested that, like dithionite, phosphine produces a change in valency of the haem moiety. However, since the absorption band at 418 nm was never completely replaced by the 444-nm band by phosphine treatment and only disappeared on addition of dithionite, it was concluded that the cytochrome a component of the cytochrome a–a3 complex was the more sensitive component to phosphine, since it is this component which contains the haem moiety. The changes induced by phosphine were consistent with a conformational change in the prosthetic group induced by a change in the valency of the haem iron. The absence of significant absorption or CD changes in the UV region of cytochrome c oxidase, where peaks due to

peptide bonding or aromatic amino acids would occur, was taken as evidence that phosphine has little effect on the polypeptide chains of the protein. Reductive changes due to phosphine were also found in cytochrome c but the concentration of phosphine required together with the time taken for spectral changes to occur indicated that cytochrome c oxidase is more sensitive than cytochrome c.

The effects of phosphine on cytochrome c oxidase and cytochrome c *in vitro* have been clearly demonstrated. However, working with insects that had received a lethal exposure to phosphine, Price[6,18] was unable to detect inhibitory effects on their mitochondria or cytochrome c oxidase. He suggested that although these mitochondrial cytochromes were sensitive to inhibition by phosphine *in vitro*, they were protected from such effects *in vivo* by being inside the mitochondrial outer membrane which is selectively permeable. The lethal biochemical lesion of phosphine may therefore be elsewhere.

The spectral studies discussed previously indicated that phosphine binds to the haem group of cytochrome c and cytochrome c oxidase. A number of studies have shown that both phosphine and organophosphines (see later) are good ligands for haem groups in general. Trimborn and Klimmer[14] found that phosphine reacted with haemoglobin only in the presence of oxygen. They described oxyhaemoglobin being converted 'through a series of iron (III) compounds to a verdichromogen-like substance'. However, from *in vivo* studies on rats, Klimmer[19] discounted the reaction of phosphine with haem as a cause of phosphine toxicity since the blood of poisoned animals contained only oxyhaemoglobin, although some 'brown colouration' was noted in the blood of animals dosed with particularly high levels of the gas.

Catalase, a haem-containing enzyme which catalyses the reduction of hydrogen peroxide to water, has also been found to be affected by phosphine. Rohrlich and Meuser[20] reported inhibition of catalase from wheat fumigated with phosphine, and Bond[21] detected a 54% reduction in catalase activity in granary weevils exposed to the gas. Price *et al.*[8] showed that exposure of a susceptible strain of the lesser grain borer *Rhyzopertha dominica* to phosphine reduced their catalase activity. Price and Dance[22] confirmed this effect with three species of stored product beetles but they found that when homogenates of these insects were exposed to high (1 mM) concentrations of phosphine *in vitro* no significant inhibition of catalase was detectable, from which it may be inferred that catalase is not the primary toxic lesion. Indeed, phosphine when added to catalase does not produce the characteristic haem reduction spectrum seen with cytochrome c and cytochrome c oxidase. Catalase differs from these other haemproteins in that the iron (III) of the catalase haem group is not accessible to reduction. Reaction with critically placed SH groups of catalase is also ruled out since it has none. These features of the enzyme explain the lack of effect of phosphine on it *in vitro*. Hence the inhibitory effect of phosphine on catalase *in vivo* is likely to be an indirect effect.

The importance of catalase as a biochemical lesion is complicated by the uncertainty of the physiological role of the enzyme. There is a growing opinion that catalase is important in the scavenging of oxygen free radicals generated during electron-transfer reactions. The intolerance of obligate anaerobes to oxygen and the phenomenon of hyperbaric oxygen toxicity in aerobes have been associated with the absence or overloading of catalase. Phosphine uptake and toxicity is closely related to oxygen availability. The gas is non-toxic to anaerobes and toxic to insects only in the presence of oxygen[7]. Atmospheres enriched with oxygen enhance the toxicity of phosphine to insects and increase its uptake by insects[21]. However the role of catalase in phosphine toxicity may be questioned since, when catalase levels in insects were reduced to a level similar to that produced by lethal exposure to phosphine, by feeding with 3-amino-1,2,4-triazole, no mortality resulted[16]. When these insects with artificially low levels of catalase were treated with phosphine a further decrease in their catalase activity was obtained but there was no increase in mortality compared with insects that had not been treated with the aminotriazole.

In attempting to explain the observed inhibition of catalase by phosphine, Nakakita and Kuroda[9] proposed that phosphine combines with a cellular factor and reacts with oxygen in solution, producing the superoxide radical. The detoxication of the radical by superoxide dismutase would produce hydrogen peroxide which would, by virtue of the lowered catalase activity caused by phosphine treatment, be damaging to the cell. There is no direct evidence for this hypothesis, although they demonstrated a factor in the soluble fraction of *Tribolium castaneum* cells that absorbed oxygen and phosphine. They proposed that this factor is responsible for the uptake of phosphine into the insect body. Recent studies in our laboratory have confirmed these findings but have indicated that other species of insect do not possess this factor but are able to absorb phosphine and are poisoned by it. Further, it seems possible that the oxygen-absorbing component seen by Nakakita and Kuroda is an artefact of the combination of insect and buffer used. We have evidence to suggest that the oxygen absorption property of *Tribolium* cytosol is due to the reaction of the precursors of defensive quinones found in abundance in this species with amine groups both in the cytosol and particularly in the Tris–glycine buffer used. Indeed, the reaction has been documented[23] and we have found that a solution containing methyl-1,4-hydroquinone, a precursor of methyl-1,4-benzoquinone which is a major component of the defensive secretions of this insect, shows oxygen-absorbing properties when mixed with Tris–glycine buffer. With regard to accumulation of phosphine, however, there were indications of a high molecular weight component in the cytosol of both quinone-containing and non quinone-containing insects which binds or reacts with phosphine, since gel permeation chromatography of cytosol from insects treated with $^{32}PH_3$ suggest that ^{32}P is associated with a > 5k dalton component. There is also evidence however, that event this may be an artefact of the techniques used.

Bearing in mind the large number of haem and other metallo-enzymes in biological systems, the ligand properties of phosphine may well have wider implications than previously thought. This may in turn be related to the nucleophilic action of phosphine particularly with respect to carbonyl groups[24], especially in compounds which take part in vital metabolic pathways, such as coenzyme A[10], and its general reductive action on strategically placed disulphide groups. Phosphine can react in aqueous solution with cystine, breaking the disulphide bonds to form cysteine[25] and, in comparison with data on organophosphines discussed in the following section, it seems likely that these disulphide-cleaving reactions may play a part in the toxic actions of phosphine.

III. ORGANOPHOSPHINES

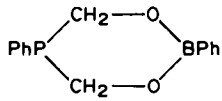
Organic phosphines are primarily manufactured for use as chemical intermediates in synthetic processes, but some phosphines themselves are used as mineral oil additives and increasingly as pharmaceuticals.

Although organic phosphines are widely used as intermediate compounds in the chemical industry, their deliberate interaction with biological systems has, until recently, been very limited and thus has received little study. Interest has been stimulated by the discoveries of therapeutic uses of some phosphine compounds, particularly in the treatment of rheumatism and certain forms of carcinoma. The potential environmental hazards of certain phosphines have been considered sufficient for the US Department of the Interior to include tributylphosphine, trioctylphosphine and tridodecylphosphine in routine screens of toxicity and repellancy to a number of wild and domestic animal species[26,27].

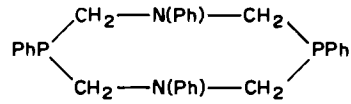
The great effort required to examine the toxicological effects of the vast number of potential chemical hazards has prompted some studies into the validity of predicting such effects in a related series of chemicals. The inhalation toxicity of phosphine, phenylphosphine and triphenylphosphine in rats was examined by Waritz and Brown[28].

The symptoms of poisoning by all three compounds were similar and considered to be those of classic respiratory inhibition. No gross histopathogical changes were observed in a wide range of tissues from chronically and acutely poisoned rats. The LC_{50} for a 4-h exposure was found to be 0.015, 0.171 and 12.5 mg l^{-1} for phosphine, phenylphosphine and triphenylphosphine, respectively. They concluded that whilst acute inhalation toxicity followed a pattern, the chronic effects could not be predicted either from experimental data or the position of the chemical in the series.

As part of a search for new compounds with antimicrobial activity, studies of oxyalkyl and aminoalkyl derivatives of organophosphorus compounds focused on phosphines[29]. The compounds, which ranged in oral LD_{50} for mice from 240 to 800 mg kg^{-1}, were tested for toxicity against colonies of the bacteria *Escherichia coli* and *Staphylococcus aureus* and the fungi *Trichophyton rubrum*, *T. mentagrophytes*, *Microsporum canis* and *Candida albicans*. The minimum toxic concentration for the fungi varied considerably even between the two *Trichophyton* species. Of the phosphines tested, 1,4-diphenyl-1-bora-2,6-dioxa-4-phosphorinane (**1**), bis(hydroxymethyl)phenylphosphine, 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclo-octane (**2**) and tris(toluidinomethyl)phosphine were the most active against the fungi, with minimum toxic concentrations of 0.6–2.0 mM. Activity against the bacteria was generally weaker.



(1)



(2)

One of the early examples of pharmacologically active trivalent phosphorus compounds was 3-dimethylaminopropyldiphenylphosphine (**3**), which was synthesised by Wiley and Godwin[30] as part of a synthetic programme to evaluate phosphorus analogues of classic nitrogen-containing drugs. Compound **3** was found to be toxic to mice, causing reduction in spontaneous activity accompanied by tremors and convulsions. This was interpreted as signifying inhibition of the central nervous system, but this may only be true in the widest sense since these symptoms are identical with those of phosphine itself, which appears to be primarily a respiratory inhibitor. It may be, of course, that respiration in nervous tissue is the most critical lesion.

Wiley *et al*[31] investigated the metabolism of **3** and diphenylmethylphosphine (**4**) *in vitro* using rat liver microsomes. In addition, they studied the reaction of these compounds with glutathione and with cysteine, biologically important thiol-containing compounds which are known to take part in conjugation reactions with xenobiotics. They found that the phosphines reacted in buffer alone but that reaction was much increased by the presence of microsomes and NADP, the required cofactor for microsomal oxidation involving the cytochrome P450 electron-transport system. The biological transformation of **3** and **4** was found to be dependent on NADP and inhibited by carbon monoxide and occurred mainly in the microsomal fraction of liver homogenates. These are features characteristic of metabolic transformations mediated by the cytochrome P450 system. Considerable non-enzymic activity occurred in the presence of boiled homogenate and it was suggested that free thiols were released by boiling, which then reacted with the phosphines. Indeed, **3** and **4** reacted readily in aqueous solution with glutathione or cysteine to form the corresponding phosphine sulphides. This proposed reaction was subsequently discounted as the explanation of the non-enzymic reactions with boiled homogenate, since the only metabolite detected was the corresponding phosphine oxide, the same product as was formed by incubation with the active microsomal preparations. Reaction of the phosphines with exposed thiols as an intermediate step was ruled out since the reaction did

not diminish in the presence of reagents that block SH groups. The reaction products of microsomal oxidation of **3** and **4** were the phosphine oxide together with, in the case of **3**, the *N*,*P*-dioxide.

The fact that metabolism of **3** resulted in no product oxidized solely at the nitrogen atom was taken as indicative that trivalent phosphorus is more susceptible than nitrogen to microsomal oxidation. It was suggested that this may be due to the fact that aromatic rings do not lower the nucleophilicity of phosphines as they do with amines, since the phosphorus lone pair electrons are not so readily delocalized. As a result, trivalent phosphorus may be more susceptible to electrophilic attack.

In studies designed to investigate the nature of ligand binding to cytochrome P450, Mansuy *et al.*[32] compared the binding properties of mercaptide and phosphine ligands. The interactions of tri-*n*-butylphosphine (**5**), triphenylphosphine (**6**) and diethylphenylphosphine (**7**) with cytochrome P450 were investigated using UV–visible spectrophotometry. Compounds **5** and **7** bound to oxidized rat liver P450, giving a characteristic spectrum with split peaks in the Soret region at 377 and 453–455 nm. The EPR spectrum showed that about 83% of both iron (II) and iron (III) P450 had bound the phosphines, a very high proportion compared with the 10–20% binding with sulphydryl ligands. Compound **6** did not show a binding spectrum with the cytochrome but merely produced a small difference spectrum peak at 388 nm, interpreted as beng due to the formation of an enzyme–substrate complex. Steric hindrance in the haem region was suggested as the reason for the lack of binding of this compound. This study showed that some organic phosphines bind to P450 and is indicative of one of the properties shared by these compounds and the parent compound, phosphine, viz. that of reaction with haem proteins having sulphydryl groups proximal to the haem group which influence ligand binding.

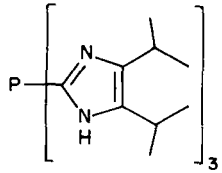
Smyser and Hodgson[33] investigated the oxidation of diethylphenylphosphine, (**7**) by the other main xenobiotic oxidative detoxication pathway, flavin adenine dinucleotide-containing (FAD) monooxygenase. The phosphine acted as a substrate for this electron-transporting system and the phosphine oxide was the sole oxidation product. FAD monooxygenases had previously been implicated only in *N*- or *S*-oxidation of organophosphorus compounds. In addition to an enzymic reaction there was considerable non-enzymic conversion of the phosphine, and this is similar to the findings of Wiley *et al.*[31] using the P450 microsomal system. The ability of the phosphine to act as a good substrate in these system led Smyser *et al.*[34] to re-evaluate the role of P450 in *P*-oxidation. They found that cytochrome P450-linked monooxygenases could catalyse the *P*-oxidation of diethylphenylphosphine, which bound to induced and non-induced microsomal P450 producing electronic difference spectra with peaks at 373 and 458 nm. These results were similar to those of Mansuy *et al.*[32] The binding of the phosphine to the microsomes competitively inhibited the P450-catalysed demethylation of *p*-nitroanisole. The affinity of P450 microsomes for **7** as measured by the Michaelis constant (K_m) was 18 μM compared with 2.5 μM for FAD microsomes. The sole product of the reaction was the phosphine oxide, which itself had no inhibitory effect on the demethylation of *p*-nitroanisole. It was concluded from this and the earlier studies using FAD systems that since the affinity of FAD-containing monooxygenases for trivalent phosphorus compounds was much greater than the P450 systems, oxidation to the phosphine oxide is more readily achieved by the former. The biological role of FAD monooxygenases in the metabolism of trivalent phosphorus compounds may therefore be more important than that of P450 systems, other things being equal. They also suggested that because of the greater affinity of the FAD monooxygenase for the phosphine, impurities of these microsomes in P450 preparations might account for the non-enzymic activity detected in boiled homogenates, if only a small quantity of the FAD enzyme survived the boiling. It is common for short periods of boiling to denature membrane-bound enzymes incompletely.

Both FAD and P450 monooxygenases are complex membrane-bound enzymes which

are easily inactivated during isolation. Cytochrome P450CAM is a soluble bacterial monooxygenase that is more amenable to experimentation and was used by Dawson *et al.*[35] as a model for the membrane P450s of higher animals. P450CAM catalyses the hydroxylation of camphor, and the binding of phosphine ligands was studied as part of an investigation into the role of cysteine SH groups in the ligand-binding reactions of P450. Complexes of P450 with **7** were studied and it was found that low-spin hyperporphyrin spectra were obtained with peaks at 345, 460, 555 and 581 nm. The generation of hyperporphyrin spectra is generally interpreted in terms of the electron distribution patterns in relation to the cysteine residues which act as axial ligands in the protohaeme moiety. Dawson *et al.*[35] pointed out that hyperporphyrin-type spectra are also obtained on addition of **7** to sperm whale myoglobin, which contains no cysteine or potential cysteine (cystine) residues which could act as axial ligands. It was suggested that the characteristic binding spectra of phosphines with P450 are due to the coordination of the phosphine as an axial ligand. This phenomenon also occurs with horseradish peroxidase and appears to be due to the formation of complexes in which the phosphine phosphorus and an imidazole nitrogen atom of a proximal histidine residue are the axial ligands. In these cases the characteristic spectra with peaks at ca 373, 427 and 537 nm show a single Soret peak which is less red-shifted than those of proteins with endogenous thiolate ligands. In the case of chloroperoxidase, which chemical analysis has suggested also has no free cysteine residues available for haem ligation[36], a classic hyperporphyrin binding spectrum was nevertheless obtained with bis(hydroxymethyl)methylphosphine. The Soret peak of the native iron(III) enzyme at 399 nm was split and shifted to 376 and 450 nm, whilst the visible peaks at 514, 544, 590 and 650 nm were merged into a low-spin peak at 553 nm. With the iron(II) enzyme a single red-shifted Soret peak at 457 nm was obtained with a splitting of the visible peak at 553 to 551 and 578 nm. This suggested that phosphines are multifunctional ligands to both the iron(II) and iron(III) forms of haem. Also, since the formation of a true hyperporphyrin spectrum requires the presence of thiolate ligands, it was concluded that such ligands must be present in chloroperoxidase, despite there being no evidence for critically placed cysteine residues.

The binding of phosphines to haem proteins has led to the use of phosphines in the study of model haem systems. Connor and Straub[37] examined a number of complexes between phosphines and haemochromes as models of haem protein properties. The electronic spectrum of bis(tri-*n*-butylphosphine)tetrakis(*p*-methoxyphenyl)porphinatoiron(II), showed a Soret peak resembling the 446-nm peak of cytochrome P450 and the 443-nm peak of the chloroperoxidase, indicating that phosphine phosphorus atoms were able to act as axial ligands in haemochrome systems. Ruf *et al.*[38] used a low-temperature mixing process with a variety of ligands including phosphines to examine the nature of the sixth ligand of a model haem system with mercaptide as the fifth ligand. The phosphine **7** was the only potential ligand other than another mercaptide which produced a clear hyperporhyrin spectrum. Peaks were at 380 nm with red-shifted Soret peaks at 450–475 nm.

The use of phosphine groups in model metalloenzyme studies was also examined by McAuliffe *et al.*[39], who found that a number of phosphine complexes containing manganese(II), which is isoelectronic with iron(III), were good models of biological oxygen carriers. The complexes with the general formula $[MnLX_2]$, where X is an anion and L a tertiary phosphine, showed similar oxygenation–deoxygenation kinetics to natural haemoprotein oxygen carriers such as myoglobin. Brown *et al.*[40] used tris(imidazole)phosphine ligands with zinc or cobalt (**8**) as models of the metalloenzyme carbonic anhydrase. The synthetic complexes had similar structural spectroscopic and catalytic properties to the native enzyme, although there was no evidence for a metal-coordinated complex in solution. In order to improve this, they studied a slightly more flexible ligand in which the imidazole was separated from the phosphine by a



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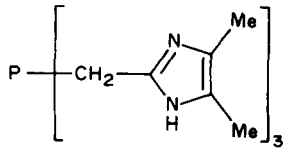
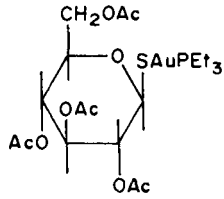


(9)

methylene group (**9**). This enabled them to obtain evidence to indicate a pH-dependent metal association with zinc or cobalt but, owing to the instability of the compound, they had to substitute the phosphine oxide for the phosphine. Although phosphine metal complexes have been useful in models of carbonic anhydrase, it appears that the actual ligand is an imidazole nitrogen atom and not the phosphine phosphorus.

In recent years, much interest has been stimulated by the investigation of the pharmacological activity of phosphine–gold complexes[41]. Whilst gold(I) thiomalate has been used for many years in the treatment of arthritis and rheumatism, attempts have been made to improve the uptake of gold into the cell by using 'soft' ligands attached to the gold. These studies led to the development of the thioglucose derivative of triethylphosphine gold(I), auranofin (**10**). This compound is now being used for the treatment of arthritis



(10)

and has been shown to have antitumour activity. After administration of the compound, over 80% of serum gold is found bound to albumin. Malik and Sadler[42] used ^{31}P NMR to probe the reaction of three orally active gold(I) phosphine compounds with bovine serum albumin (BSA). BSA was incubated with various concentrations of triethylphosphinegold(I) chloride (**11**), bis(triethylphosphine)gold(I) chloride (**12**) and auranofin. The NMR spectra of the resulting mixtures indicated that the Au—P bond was not broken on binding to BSA and that the primary reaction was an attack on the S—S bridges of the protein by the gold. It was suggested that the cleavage of S—S bonds may induce denaturation of the albumin, giving rise to the enhanced catabolism of serum albumin.

Malik *et al.*[43,44] studied the interaction of triethylphosphinegold(II) chloride with components of human blood using ^{31}P NMR. When added to whole blood, the phosphine readily bound to erythrocytes, producing two new resonance peaks at 40.2 and 42.2 ppm. Cysteine residues in oxyhaemoglobin and the tripeptide glutathione were considered to be the most likely reaction sites, with the probable displacement of the Cl^- of the phosphine by the S^- of cysteine. It was also suggested that the reaction with oxyhaemoglobin could release hydrogen peroxide, the detoxication of which via glutathione peroxidase might be hampered owing to its own reaction with the triethylphosphinegold(I) chloride. Indeed, purified oxyhaemoglobin and glutathione were both found to react *in vitro* with **11**, producing NMR peaks reminiscent of those found in the reaction of the compound with whole blood. The bisphosphine analogue **12** is ionic in aqueous solution and reacts very strongly with whole blood, causing it to solidify.

This effect was shown to be due to the reaction with albumin. They postulated that the reaction might start with the electrophilic attack of one of the phosphorus atoms on the disulphide linkage. However, the spectroscopic evidence did not show the actual order of the reaction steps and it could be helpful to regard it as starting with the attack of a sulphur atom on the gold to displace a phosphorus ligand, this being analagous to the displacement of Cl^- in the reaction with **12**. Alternatively, of course, these two steps could be concerted. The overall reaction becomes

$$[Au(PEt_3)_2]^+ + RSSR + H_2O \longrightarrow [(RS)\,AuPEt_3] + RSH + OPEt_3 + H^+ \quad (1)$$

Otiko and Sadler[45] showed that **11** reacted with the haem protein cytochrome c. The reaction in aqueous medium at neutral pH produced a change in spin state of the normally low-spin iron(III). The electronic spectrum of the resulting high-spin species was characterized by the shift of the Soret peak from 409 to 411 nm and by a time-dependant appearance of a peak at 596 nm. They implicated the nitrogen atom of histidine and the sulphur atoms of cysteine and methionine as gold binding sites. The penetrative properties of the molecule conferred by the phosphine moiety appeared to provide access for the gold to crucial binding sites proximal to the haem portion of the cytochrome. This resulted in perturbation of the haem conformation and the change in spin state.

Grootveld *et al.*[46] examined the reaction of **11**, triethylphosphinegold(I) nitrate and auranofin with other haem proteins: myoglobin, haemoglobin and the bacterial cytochrome cytochrome b_{562}. The reaction of cytochrome b_{562} with **11** was rapid and characterized by the formation of a high-spin species with a visible absorption peak at 610 nm.The Soret peak was shifted from 416 to 392 nm. The addition of 24 molar equivalents of **11** completely converted the iron(III) cytochrome b_{562} to the high-spin state. With haemoglobin the Soret band was shifted from 410 to 400 nm and a new peak at 630 nm was produced. On addition of 30 molar equivalents of the phosphine to haemoglobin, a new, deep-green species was formed with absorption maxima at 564, 596 and 710 nm with a Soret peak at 400 nm. EPR studies showed that this compound was also a high-spin species. Similar changes were observed with myoglobin, although higher concentrations of **11** were required to produce the spectral changes. There was some evidence that the autoxidation of haemoglobin, and presumably also myoglobin, produced superoxide. It was suggested that the observed changes were due to the binding of $AuPEt_3^+$ to a nitrogen atom of one of the histidine residues coordinated to the haem. Reaction with an adjacent cysteine residue was not considered important in this particular reaction since blocking of this sulphydryl group with *N*-ethylmaleimide did not abolish the reaction. The evidence for the $AuPEt_3^+$ being the only active species was that only compounds of this cation with weakly bound anion ligands such as Cl^- and NO_3^- were active. Auranofin, with a strong thiol ligand, did not produce the spin state changes and neither did the non-phosphine gold—thiol compound aurothiomalate. However, it was considered that this phenomenon might be important in the pharmacological action of auranofin, since acid hydrolysis in the stomach could lead to the production of **11** and thus $AuPEt_3^+$. No mention was made of the earlier work by the same group of workers[43,44] showing that **11** reacts strongly with SH groups of cysteine in blood to form $[(RS)AuPEt_3]$ complexes with proteins, but it was acknowledged that many haem proteins would be protected from the autoxidative reactions by virtue of the high affinity of $AuPEt_3$ for thiolates. No indications were given as to whether any of the ^{31}P NMR changes reported in blood components were found in the haem proteins studied.

Using radiolabelling methodology, Ecker *et al.*[47] examined the reactions of the gold and phosphine moieties of auranofin with BSA, transferrin (a metal-transporting protein using tyrosine–metal binding), histidine-rich glycoprotein and metallothionein (a cysteine-rich metal-binding protein). It was shown that about 50% of orally administered auranofin was able to survive acid hydrolysis in the gut and thus would be available as the parent

compound for reaction with serum albumin. Auranofin was able to penetrate artificial liposomes containing BSA, suggesting that the lipohilic properties of the molecule to which the PEt_3 contributes would enable the drug to enter hydrophobic membrane environments where gold ligation could take place. When auranofin was added in stoichiometric ratios to BSA, 60% of both the gold and the triethylphosphine were found to be bound to BSA. Calculations indicated that this was exactly equivalent to the number of free sulphydryl groups available. The remaining 40% of radioactivity was due to unreacted auranofin, hence the reaction did not involve the dissociation of the gold from the phosphine. By way of confirmation, almost 60% of the 'leaving group', tetraacetylthioglucose (TATG), was detected as free TATG-SH. These results indicated that the only reaction of auranofin with BSA is with the SH group of Cys-34, which is the only cysteine residue of BSA not to exist totally as a bridged disulphide. The purified preparation used in this study contained 60% titratable Cys-34 SH groups. The reaction appeared to be thiol ligation of the $AuPEt_3^+$ to BSA to form [BSA—S—$AuPEt_3$], releasing stoichiometric amounts of TATG-SH. There was no reaction with histidine-rich glycoprotein or with transferrin, which indicates that other amino acid–metal ligands such as histidine or tyrosine are not involved in the reaction of auranofin with serum proteins. Auranofin reacted with the cysteine-rich metallothionein but only when its prosthetic cadmium and zinc groups had been removed.

The reactions of auranofin with BSA were further studied by Coffer *et al.*[48] using ^{31}P NMR, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS). Cys-34 was found to be the sole binding site for auranofin but using **11** there appeared to be a larger amount of bound gold than would be equivalent to the free SH sites available. In addition, when the complex was chromatographed by gel filtration there was a 'tailing' of gold eluting after the high molecular weight complex. It was suggested that there are other weak binding sites for **11** in BSA which take no part in the reaction between BSA and auranofin. ^{31}P NMR spectra indicated that there was a rapid exchange of material with the weak binding sites which appeared to be topographically remote from the Cys-34 position in the protein. It was postulated that these sites might be imidazole, lysine, carboxylate or thioether groups. This is in agreement with the findings of Grootveld *et al.*[46] in explaining the formation of the high-spin derivatives of haem proteins by compounds of $AuPEt_3^+$ with weakly associated anions but not with auranofin. This difference in binding has been used to explain the differences in observed biological activity of **11** and auranofin. Compound **11** has anti-rheumatoid activity only on injection and it causes severe gastrointestinal irritation. Auranofin is active orally and appears to be fairly resistant to hydrolysis in the gut to the reactive $AuPEt_3^+$ ion.

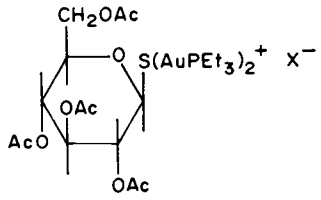
In a study of the biochemical effects of a number of anti-inflammatory drugs on membrane processes, Chan and Minta[49] found that only gold sodium thiomalate and auranofin inhibited the activity of membrane-bound and purified Na/K-ATPase. Whereas the presence of the gold appeared to be essential, neither of the free ligands they tested, sodium thiomalate and triethylphosphine, was individually effective. The inhibitory action of the gold-containing drugs was abolished by their preincubation with dithiothreitol. This compound is commonly used to prevent enzyme SH groups from forming S—S bridges. The effect of the reagent would be to free the sulphur ligand from the gold. The abolition of inhibitory activity in this experiment might thus result from the reaction of the gold with the excess of SH groups of the dithiothreitol as compared with the Na/K-ATPase.

Evidence that gold reacts with SH groups is supported by Caltabiano *et al.*[50], who demonstrated that pharmacological levels of auranofin induced the biosynthesis of two so-called stress proteins, which are known to be induced by other chemicals which react with SH groups such as iodoacetate and arsenite. In addition to stimulating the production of

these proteins in cultured cells, oral administration of auranofin to rats induced stress protein synthesis in peritoneal exudate cells. The role of these proteins in terms of either their physiological function or their action in auranofin pharmacology remains to be elucidated.

In addition to the anti-rheumatic activity of auranofin, micromolar concentrations were found to be cytotoxic to tumour cells in culture. Its activity was found to be very restricted, probably owing to the high affinity of the compound for the thiols in serum albumin.

In view of the reported ability of some gold compounds to inhibit DNA, RNA and protein synthesis, Allaudeen *et al.*[51] examined the effect of auranofin and a number of related compounds on DNA replication. Whereas auranofin itself had little effect on DNA polymerase from a number of sources, **11** at a concentration of 5 μM showed inhibitory activity of between 5 and 85%, depending on the enzyme source. In an attempt to combine the biological advantages of auranofin with the pharmacological properties of the chloride, they studied two further complexes, which are effectively addition compounds of these two molecules: 2,3,4,6-tetraacetyl-β-D-glucopyranosyl-bis[(triethylphosphine)aurio]sulphonium chloride (**13**) and the nitrate (**14**). These



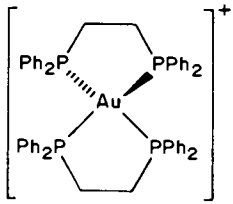
(**13**) X = Cl

(**14**) X = NO_3

compounds were as effective inhibitors of DNA polymerase as the chloride **11**. It was suggested that the interference with DNA replication was due to the interaction of the compounds with the enzyme's thiols. Structure–activity studies indicated that both the phosphine and the gold moieties were required for good pharmacological activity.

Auranofin and similar compounds bind strongly to thiol groups and this property has been suggested as the reason for the very limited antineoplastic activity of auranofin *in vivo*. Thus compounds which retain anti-tumour activity whilst having reduced affinity for serum thiols might be more promising.

It was found that bis[(diphenylphosphine)ethane]gold (**15**), a tetrahedrally co-ordinated chelated complex formed by reaction of bis(diphenylphosphine)ethane (dppe)

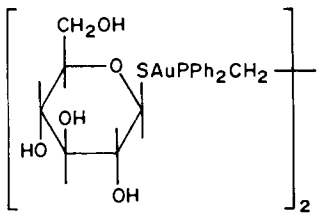


(**15**)

(**16**) with [$(AuCl)_2$dppe] (**17**), was not thiol-reactive and was highly cytotoxic to a range of animal tumours, (see ref. 41 for a review). It was suggested that the low thiol reactivity allowed the gold to reach critical binding sites, possibly on DNA bases. Reactivity towards

natural metal ions in cells was also considered to be a possible factor in the pharmacology of dppe derivatives. The bisphosphineethane itself (**16**) was found to have anti-tumour activity *in vivo* but its metal complexes, particularly with copper or gold, are much more potent[52]. The bis{chlorogold(I)} complex **17** and a bis{trichlorogold(III)} complex were 7.5 and 17 times more active, respectively, than the phosphine alone. The same study also showed that the presence of simple salts of some transition metals could modulate the cytotoxicity of **16** against melanoma cells in culture. Copper and gold salts enhanced its cytotoxicity whereas zinc, cobalt, magnesium, manganese, iron(II) and cadmium were all ineffective. Nickel appeared to be antagonistic, abolishing antitumour activity at 0.1 mM. It was suggested that the presence of copper(II) salts prevented the oxidation of the phosphine to the non-toxic oxide and that the balance between endogenous transition metals and **16** may be important in mediating the pharmacology of the phosphine *in vivo*. *In vivo* dosing of mice with copper and gold salts together with **16** showed that whilst the overall toxicity of the phosphine was enhanced by the metal salts, there was no increase in anti-tumour activity at clinically useful (i.e. sublethal) doses.

The effects of **16** and some of its metal complexes on DNA polymerase were also assessed since previous studies had shown that some gold compounds inhibited this enzyme and that other antitumour drugs with metal ligand properties interfered directly with DNA synthesis. The phosphine itself, either alone or with transition metal salts, was generally without effect, with the exception of mixtures of $CuCl_2$ or $CuSO_4$ with the phosphine, which were inhibitory. The chlorogold(I) complex **17** inhibited the enzyme at concentrations as low as 2.5 μM. This effect, which was measured on purified DNA polymerase, could also be demonstrated *in situ* on the polymerase of cultured KB melanoma cells. Mirabelli *et al.*[53] examined some of the pharmacological properties of one of the bisphosphinegold compounds. They found that μ[1,2-bis(diphenylphosphine)-ethane]bis[(1-thio-β-D-glucopyranosato-*S*)gold(I), [$(AuTG_2)$dppe] (**18**), was a potent



(**18**)

cytotoxin against melanoma, colon carcinoma and leukaemia cells *in vitro*. Detailed examination of the effects of this compound on cell division indicated that it induced a specific block on mitosis, suggesting that it interfered directly with DNA or its metabolism. Compound **18** was also found to inhibit the incorporation of thymidine into DNA, uridine into RNA and leucine into protein. This points to a direct effect of **18** on DNA synthesis, in turn inhibiting RNA duplication and protein translation. The effects on DNA were correlated with the dose-dependent ability of **18** to cause single-strand breaks in DNA. It was found that the dose of **18** required to produce 50% inhibition of growth of L1210 leukaemia cells caused DNA breaks equivalent to 300 rad of X-radiation.

The biological usefulness of gold–phosphine compounds has been further exploited in the development of gold cluster labelled antibodies. Hainfield[54] used a cluster of eleven gold atoms surrounded by a shell of seven triphenylphosphines in which each phenyl ring bears an amino group, one of which is used for covalent bonding to the antibody and the remainder of which impart water solubility to the complex. This electron-dense probe is suitable for the electron microscopic study of antibody binding and has advantages

over other probes in being relatively small in molecular size and stable in biological systems.

A number of phosphine complexes with technetium-99 have been studied as replacements for thallium-201 chloride in the field of cardiac scintigraphy. This is a vital tool in the diagnosis of heart disease, and is based on the imaging of the heart using introduced radioisotopes. The method is currently limited by the resolution with which the heart can be distinguished from other proximal organs such as the liver. It appears that the lipophilicity conferred by the phosphine and the tissue-binding properties of technetium combine to make such compounds useful in this respect.

The reaction between [^{99}Tc] pertechnetate and 1,2-bis(dimethylphosphino)ethane (dmpe) under appropriate conditions of pH produces two complex cations with myocardial affinity[55]. These are $[^{99}Tc(dmpe)_2Cl]^{2+}$ (**19**) and $[^{99}Tc(dmpe)_3]^{+}$ (**20**). The results of Syhre *et al.*[55] indicated that the technetium(I) cation **20** bound much more strongly to human serum albumin, and was more lipophilic than **19**. After injection into rats, the tissue levels of **20** were found to be higher than those of **19** and there was prolonged retention in the myocardium. However, the advantage of higher cardiac retention by the technetium(I) ion **20** was outweighed by a higher uptake into other tissues and slow release from the blood, presumably owing to its affinity for albumin. Thus it was concluded that in the first 20–30 min after injection the technetium(III) cation was the more useful. Munze *et al.*[56] concluded that both technetium(I) and technetium(III) were useful probes but that the non-specific biokinetic parameters such as lipophilicity and metabolic elimination imposed on the complex by the phosphine moiety were important to the future usefulness of technetium and thus parameters such as steric effects, molecular size, liphophilicity and protein binding could be modified in attempts to improve the resolution of these problems.

One of the major properties that emerges from the study of the interactions of phosphines with biological molecules is their reaction with protein sulphydryl groups. This reaction has been known for a considerable time and has been exploited in both biochemistry and industry. The ability of tertiary phosphines to cleave S—S bonds in keratin was known in the early 1950s, and later Levison *et al.*[57] reported that tris(hydroxymethyl)phosphine and tris(carboxyethyl)phosphine could reduce the S—S bonds in human gammaglobulin to a greater extent than the commonly used reagent mercaptoethanol. In addition, and pertinent in retrospect, was the observation that tris(hydroxymethyl)phosphine was capable of inactivating human rheumatoid factor *in vitro* but only at concentrations in excess of 0.1 mM. The use of organic phosphines for routine cleavage of protein S—S bonds was favoured by Ruegg and Rudinger[58]. Unlike conventional sulphydryl reagents such as mercaptoethanol, dithiothreitol (Cleland's reagent) and dithioerythritol, which require 100–1000-fold excess for complete cleavage of S—S to SH, only 10-fold excesses of some phosphines were required. Tributylphosphine was found to be more reactive that either of the phosphines used by Levison *et al.* and the reaction with protein disulphides appeared to be more predictable and more specific than with 'classic' reagents. It was found that the reaction required a 1:1 molar ratio of tributylphosphine to S—S group. Using vasopressin, insulin and human serum albumin, it was found that a 5–20% excess of the phosphine allowed complete S—S to SH reduction. The reaction is rapid and specific, producing no other detectable modification of the protein. This property has been exploited in the use of simple tertiary alkyl phosphines in the cosmetics industry as hair-waving agents. Tris(3-hydroxypropyl)phosphine and tris(3-hydroxybutyl)phosphine were developed as odourless alternatives to mercaptide reagents for this purpose[59]. The rationale behind their use is that disulphide bonds, which determine the tertiary structure of the keratin, are cleaved by the phosphine, the bonds being reformed after curling the hair and removal of the phosphine.

IV. CONCLUSION

Phosphine itself is a reducing agent. When present in solution with those haem proteins in which the haem iron readily undergoes reversible oxidation and reduction, it arrests the iron in the iron(II) state. One of the proteins which is most sensitive in this respect to phosphine *in vitro* is cytochrome c oxidase, but data from *in vivo* studies are equivocal in implicating this enzyme as the major target site of phosphine action. In contrast, catalase a haem enzyme which is not readily reduced, has been implicated in phosphine action *in vivo* but undergoes no valence change *in vitro* and is not itself inhibited by the gas. There are many biochemical processes which rely on repetitive redox reactions which may be adversely affected by phosphine and remain to be studied. Phosphine can slowly reduce S—S linkages which stabilize the tertiary structure of many proteins. It may also react with free SH groups which form an essential part of the active sites of many enzymes. In these respects phosphine shares common properties with its organo derivatives, which are known to participate in similar reactions.

In attempting to summarize the biochemical actions of the organophosphines, we are constrained by the limited number of structural types of biochemical targets investigated. With only a few exceptions, all of the phosphines studied so far have been acyclic tertiary derivatives with either alkyl or aryl groups. The organic moieties of the phosphine influence the properties of the molecule in three separate ways. They impart lipophilicity, may enhance the nucleophilicity of the phosphorus and may affect the access of the phosphorus to reactive sites through steric effects. There are insufficient data on primary and secondary derivatives, alkoxy derivatives or cyclophosphines to define fully the extent of these influences. In those derivatives for which there are data, the role of the phosphorus atom is structurally important in enabling an organic moiety to which it is covalently bonded to be connected to a 'soft' metal cation. The metal ion may either be joined to the phosphine prior to introduction into a biological system, such as gold or technetium, or be that to which the phosphine may be joined following introduction into a biological system such as the iron of haemochromes. The criterion shared by the metal ions to which the 'soft' phosphorus is connected seems to be, predictably, that they are 'soft' and in a low valence state.

Despite the increase in studies on the interaction of organophosphines with biological systems, the exact biochemical role of the phosphorus atom remains to be elucidated. In the case of the anti-arthritic and neoplastic compounds, it appears that some of the parent phosphines are active even though they are not complexed to metal, but activity is greatly enhanced by the presence of gold in the molecule. Simple alkylphosphines share with the unsubstituted compound the ability to cleave S—S bonds, and tris(hydroxymethyl)phosphine inactivates human rheumatoid factor at relatively high concentrations. Bis(diphenylphosphine)ethane itself is anti-neoplastic but its metal complexes are more effective. Berners-Price and Sadler[41] suggested that the potent oxygen-accepting properties of tertiary phosphines may be important in their biochemical actions. Reactions with metals in cells could generate free radicals, which are known to be highly disruptive to membrane organisation on which the whole delicate balance of biological energy transfer, solute transport and cell communication is dependent. It is interesting that the pharmacological action of the phosphines is not exhibited by their oxides and it may be that the metal protects the phosphorus from oxidation, which appears to be accomplished readily by both FAD and P450 monooxygenase systems. The subtle balance between the need to protect the phosphine phosphorus atom from oxidation before it reaches the biochemical target and the release of its reducing power at that site is indicative of the fascinating complexity of the interaction between phosphines and biological systems, much of which remains to be investigated.

V. REFERENCES

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