Synthesis of Phosphorus-Containing Macrocycles and Cryptands

Anne-Marie Caminade* and Jean Pierre Majoral*

Laboratoire de Chimie de Coordination du CNRS, 205, Route de Narbonne, 31077 Toulouse Cédex, France

Received November 22, 1993 (Revised Manuscript Received March 5, 1994)

Contents

I. Introduction

Despite the fact that the first phosphorus containing macrocycles $[(PNCl_2)_n, n = 5, 6, 7]$ were prepared in 1897 by Stokes,[1] intensive studies in this field only appeared in the middle of the 1970s, several years after the discovery of the complex-forming properties of crown ethers by Pedersen in 1967.[2] Experimental difficulties—multistep procedures, low yields, unstability of the final products, etc.—probably explained the reason why such a research field did not earlier evoke more interest.

Indeed, the preparation of such macrocycles was undertaken in order to increase the efficiency of macrocyclic ligands by introducing into the ring tricoordinated phosphorus atoms or phosphoryl and thiophosphoryl groups which possess a high complex-forming capacity. Tricoordinated phosphorus-containing macrocycles can easily bind to transition metals while alkali metal ions can be trapped with P=O or P=S groups. Moreover, macrocyclic phosphanes can stabilize transition metals in their lowest valence states. Unusual catalytic properties were expected from complexes of this type. Thiophosphoryl macrocycles form weaker complexes with alkali and alkali earth metals than their phosphoryl analogues. Some of them are able to transport transition metals (Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}) through liquid membranes.[3-7]

Since phosphane oxides have been demonstrated to serve as strong hydrogen-bond acceptors, phosphorus-containing macrocycles can be used for molecular recognition, complexation of ammonium salts, anions, etc. Potential applications in homogeneous catalysis and in phase-transfer catalysis can also be pointed out and will probably be in the future the subject of numerous investigations.

Several reviews containing compilations of synthesis[3,4] and/or thermodynamic and kinetic data for cation–macrocycle interactions[5-7] have been published. Most of them are limited to macrocycles possessing P-O or P-C bonds.

In contrast with these reviews, the aim of the present work is to report the preparation of phosphorus-containing macrocycles (nine-membered rings at least) whatever the environment around phosphorus (P-C, P-O, P-N, P-S, P-N-N, P-Si, etc. bonds) and whatever the coordination number of phosphorus (tri-, tetra-, or pentacoordination) are. Macrocycles possessing direct intracyclic phosphorus–metal bonds and macrocycles with phosphorus pendent groups are excluded from this compilation as well as phosphates containing macrocycles and species relevant to biochemistry.

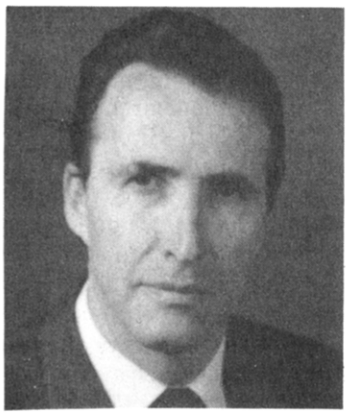
Two almost independent ways of synthesis of phosphorus containing macrocycles can be outlined: that involving classical methods of macrocyclic chemistry and that specific to phosphorus chemistry, i.e. taking into account properties of phosphorus species. Template syntheses of P macrocycles are relatively recent but unfortunately a very few methods have yet been devised to remove the metal from the ring. Complexation properties are not considered here. Rather, we would like to focus on the strategy of the construction of phosphorus macrocycles and cryptands. Three main types of reactions are presented (i) cyclocondensations, the most commonly used reactions, (ii) ring opening essentially of five- and six-membered rings and, (iii) template reactions. In addition a few miscellaneous methods are reported. The preparation of cryptands is described in the final section. The listing of macrocycles characterized by X-ray structural studies is given in Table 10.

II. Cyclocondensations

The term cyclocondensation indicates the condensation between two functionalized species leading to a macrocycle. For example a [2 + 2] cycloadduct is **here**, a compound arising from the cyclocondensation of 2 equiv of each partner.

0009-2665/94/0794-1183$14.00/0

Anne-Marie Caminade is "Chargée de Recherche" at the Centre National de la Recherche Scientifique since 1985 in Dr. J. P. Majoral's group. She was born in Carmaux, France, in 1958. She received her "3ème cycle" doctoral degree in 1984 from the Université Paul Sabatier (Toulouse) with Dr. Max Koenig, on oxidation reactions of unsaturated compounds, and her Doctorat d'Université ("Ph.D.") in 1988 with Dr. J. P. Majoral on the stabilization by complexation of low coordinated phosphorus compounds. She then joined Professor Michael Veith's group in Saarbrücken (Germany), as a postdoctoral fellow of the Alexander von Humboldt Foundation, working on metalla stibanes and -bismuthanes. She is currently working with Dr. Majoral on main group element chemistry, with emphasis on the chemistry of macrocyclic and polymacrocyclic phosphorus species, main group element dendrimers, and hydrazine derivatives. She was awarded a Bronze Medal from the CNRS in 1989.



Jean Pierre Majoral received his Doctorat d'Etat in 1972 from the Université Paul Sabatier of Toulouse. In 1973, he carried out postdoctoral studies with Professor A. R. Katritzky at the University of East Anglia, England. He became Directeur de Recherche at the Centre National de la Recherche Scientifique in 1978 in Toulouse. In 1987 he moved to the Laboratoire de Chimie de Coordination, a CNRS institute, also in Toulouse, where he is currently at the head of a research group. His research interest includes the synthesis and the complexation properties of phosphorus macrocyclic multidentate compounds as well as the preparation and the properties of main group elements containing dendrimers. Emphasis is also made on the studies of interactions between heavier main group elements and group 4 elements (titanium, zirconium, and hafnium) with applications in organic and organometallic chemistry. He has received awards from the French Chemical Society (1990) and from the French Academy of Sciences (1993).

A. Intracyclic C–P–C Linkage

1. Reaction of Dihalogenated Species with Salts

Cyclocondensations involving lithium salts of diphosphines and bis electrophiles with or without phosphino groups, under high dilution conditions, were developed by Kyba and co-workers from 1977 to 1985, allowing the preparation of a wide variety of triligating 11-membered rings **1a–p** and tetraligating 14-membered rings **2a–e**.[8-17] The use of sulfur or arsenic lithium salts instead of diphosphine salts permits the preparation of similar macrocycles with various donor atoms: sulfur, arsenic, phosphorus, but also oxygen and nitrogen (Scheme 1 and Tables 1 and 2). In some cases all the isomers are separated and fully characterized and their stereochemistries are determined or assigned.[9-13,15,17]

The synthesis of macrocycle **2h** requires considerably more strategy and implies a multistep sequences to obtain the linear ligand **3** which can be treated with lithium diisopropylamide affording **2h** (Scheme 2).[7]

The 1,4,10,13-Tetraoxa-7,16-diphosphino-[18]-crown ethers **4a–c** and the 1,4,10,13-Tetrathia-7,16-diphos-

Scheme 1

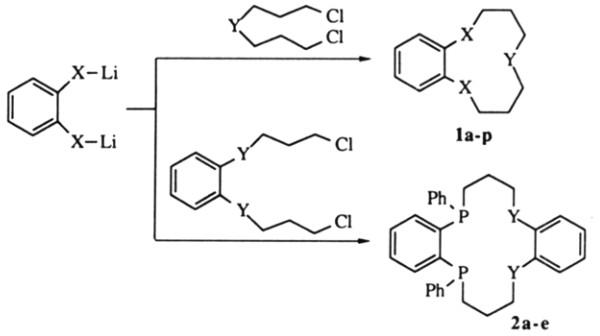
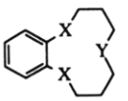
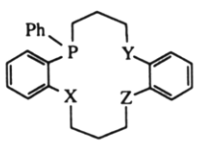


Table 1. Compounds 1a–p



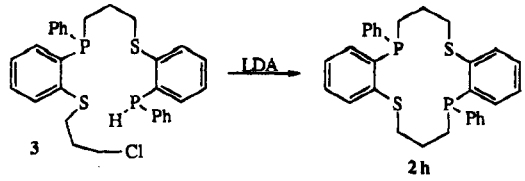
1a–p	X	Y	ref(s)
a	PPh	PPh	8,10–12,14
b	PPh	S	10–12,14
c	PPh	O	11,12
d	PPh	NMe	11,12,14
e	PPh	NPh	11,12
f	PPh	CH_2	11
g	PPh	AsPh	10,12
h	PPh	P(S)(CH_2Naphtyl)	16
i	PPh	P(S)H	16
j	PPh	PH	16
k	PH	S	16
l	PH	NMe	16
m	S	PH	16
n	S	PPh	8,11
o	AsMe	PH	16
p	AsMe	PPh	12

Table 2. Compounds 2a–h

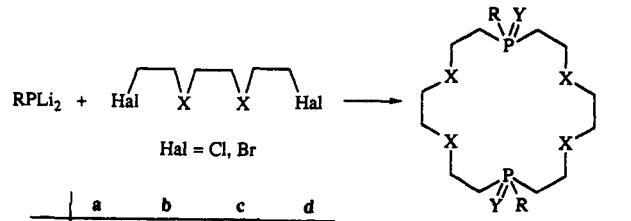


2a–h	X	Y	Z	ref(s)
a	PPh	PPh	PPh	8,9,13,17
b	PPh	S	S	8,13,17
c	PPh	NMe	NMe	13,17
d	PPh	O	O	13,17
e	PPh	AsMe	AsMe	15,17
f	PPh	PPh	S	17
g	S	PPh	S	17
h	S	S	PPh	17

Scheme 2

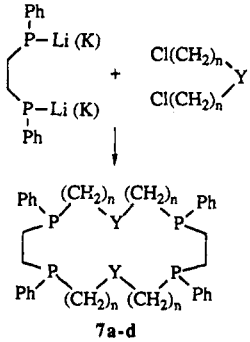


Scheme 3



	a	b	c	d
R	Ph	c-C_6H_{11}	CH_2-Ph	Ph
X	O	O	O	S

Scheme 4

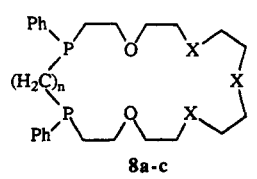


7a-d	n	Y	Refs.
a	2	O	19, 21-24, 26, 27, 29-32
b	2	S	20, 24, 26, 27, 29-32
c	2	N-Pr	24-26, 29, 31, 32
d	3	S	28, 30-32

phino-[18]-crown ether **4d** are accessible in a one-step synthesis by reaction of dilithiophosphides with 1,2-bis(2-chloroethoxy)ethane and 1,2-bis[(2-chloroethyl)-thio]ethane (Scheme 3).[18]

Similar reactions have been done by Ciampolini's group[19-32] who treat dilithiophosphide with bis(dichloroethyl) ether (or the corresponding thio compound). All five possible diastereoisomers of **7a–d** are isolated. The hexadentate phosphorus–nitrogen-containing macrocyclic ligand **7c** is obtained by reacting bis(2-dichloroethyl)propylamine with a stoichiometric amount of the bispotassium salt of 1,2-bis(phenylphosphino)-ethane (Scheme 4).

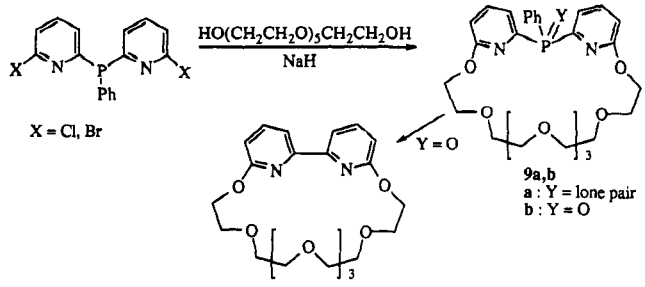
Such an approach is employed to prepare a class of hard/soft dinucleating phosphine macrocycles **8a–c**.[33,34]



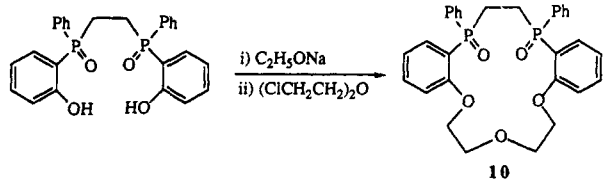
8a-c	a	b	c
X	O	NH	NTs
n	2	3	3

Nucleophilic displacement of halide from phosphine with a glycolate dianion offers the possibility of isolating in good yields (50–60%), a macrocyclic phosphine which was easily oxidized with dilute hydrogen peroxide to the corresponding *P*-oxide **9b**. A surprising phosphorus expulsion reaction takes place when **9b** is treated with sodium hexaethylene glycolate leading to a ring-contracted bipyridyl macrocycle (Scheme 5).[35]

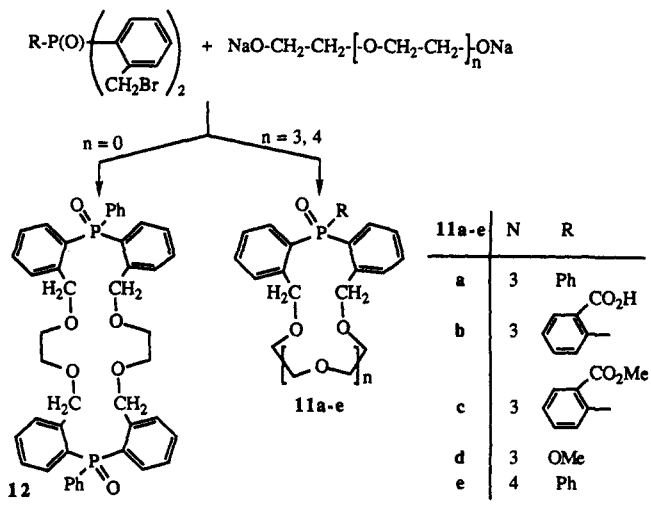
Scheme 5



Scheme 6



Scheme 7

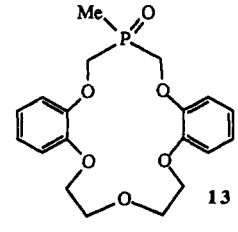


11a-e	N	R
a	3	Ph
b	3	CO_2H
c	3	CO_2Me
d	3	OMe
e	4	Ph

A 15-membered ring **10** is prepared from the sodium salt of ethylenebis[phenyl(*o*-hydroxyphenyl)phosphine] *P,P'*-dioxide and bis(2-chloroethyl) ether (Scheme 6).[36]

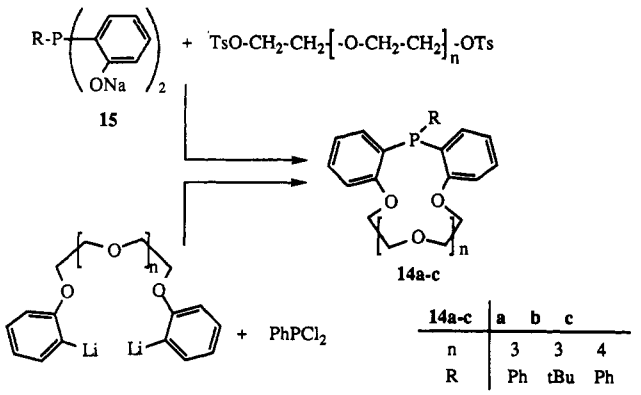
Phosphoryl groups have also been incorporated into the ring systems of macrocyclic polyethers by slowly adding the appropriate ethylene glycol and dibromide [$RP(O)(C_6H_4CH_2Br)_2$] as a mixture in THF to a stirred refluxing suspension of NaH in THF. Depending on the length of the ethylene glycol derivative, [1 + 1] **11a–e** or [2 + 2] **12** cyclocondensation products are isolated (Scheme 7).[37]

An analogous reaction carried out with the diphenyl ethylene glycol salt [*o*-$NaOC_6H_4O(CH_2)_2]_2O$ and $MeP(O)(CH_2Cl)_2$ gives **13**.[38]

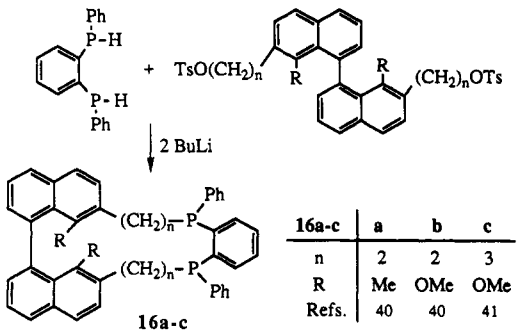


The direct addition of dichlorophenylphosphine to tetraethylene glycol bis(2-lithiophenyl) ether leads to

Scheme 8



Scheme 9



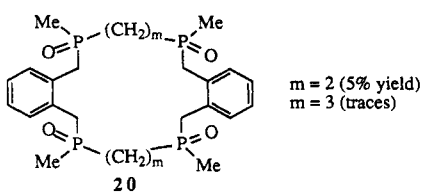
monophospha-crown ethers **14a–c** which are also obtained in the reaction of the disodium salt **15** with ethylene glycol ditosylates (Scheme 8).[39]

Binaphthyl-base 16- and 18-membered rings **16** have been synthesized from the corresponding 1,1′-binaphthyl precursors and *o*-phenylenebis(phenylphosphane) (Scheme 9).[40,41]

Reaction of diisopropyl polymethylenediphosphinate with polymethylene dibromide in the presence of sodium bis(2-methoxyethoxy)aluminum hydride under high dilution conditions affords two isomeric macrocyclic bis(phosphine oxides) **17a–c**. Reduction of these oxides with trichlorosilane yields the diphosphines **18a–c** with overall configuration retention (Scheme 10).[42] The structure of the analogous compound **17d** ($n = m = 4$) was solved by X-ray diffraction studies.[43]

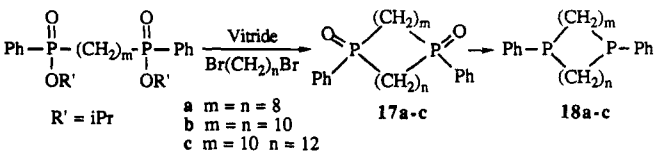
Analogous direct cycloaddition of two dioxophosphide dianions with two molecules of the unsaturated dihalide $ClCH_2CH{=}CHCH_2Cl$ produces unsaturated macrocyclic phosphine tetraoxides **19a,b**. Their reduction with molecular hydrogen is highly selective (Scheme 11).[44a,b]

Similarly, the cycloaddition reaction of the same dianions with α,α'-dichloro-*o*-xylene gives predominantly the [1 + 1] cyclocondensation compounds; [2 + 2] (**20**) and [3 + 3] cycloadducts are also obtained but in significantly lower yield.[45]

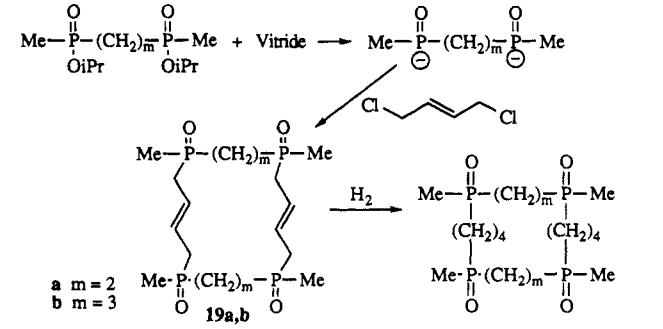


Phosphine oxide dithioether **21** is prepared by allowing the corresponding dithiol to react with 1,4-

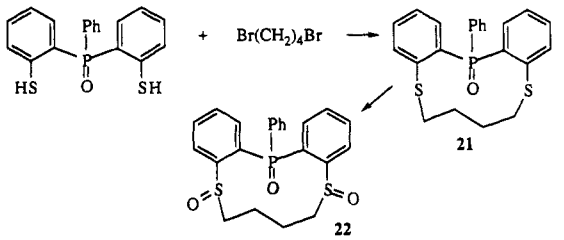
Scheme 10



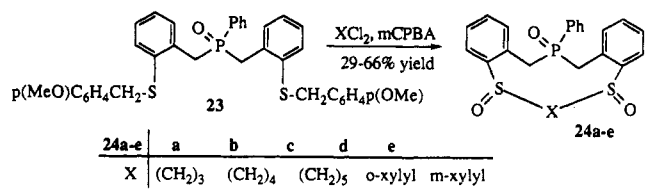
Scheme 11



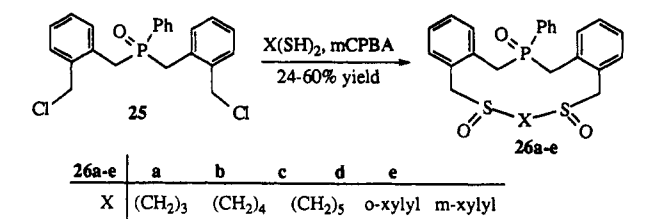
Scheme 12



Scheme 13



Scheme 14

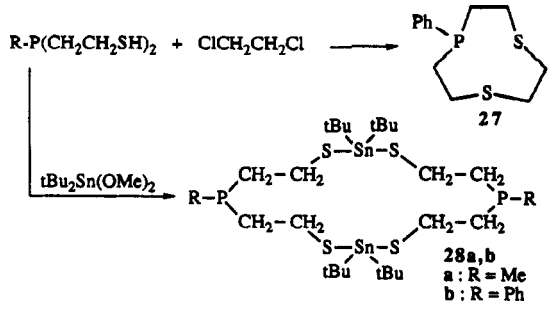


dibromobutane and K_2CO_3 at room temperature; oxidation with H_2O_2 or with *m*-chloroperbenzoic acid produces **22** (dl) (Scheme 12).[46]

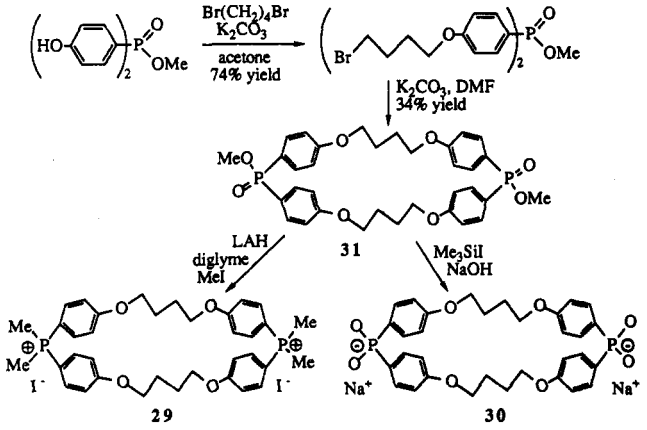
Two other families of macrocyclic phosphine oxide disulfoxides are formed by reacting either the dithio reagent **23** with the appropriate dihalide (formation of compounds **24a–e**, Scheme 13) or the phosphine oxide **25** with the appropriate dithiol (preparation of derivatives **26a–e**, Scheme 14). The final step in the synthesis of each macrocycle is the oxidation of the macrocyclic phosphine oxide dithioester with *m*-chloroperbenzoic acid.[47,48] In all cases, this process yields predominantly one stereoisomer of the desired trioxide.

1-Phenyl-1-phospha-4,7-dithiacyclononane (**27**) is obtained from the corresponding phosphine $PhP(CH_2CH_2SH)_2$ and dichloroethane,[49] whereas the reaction

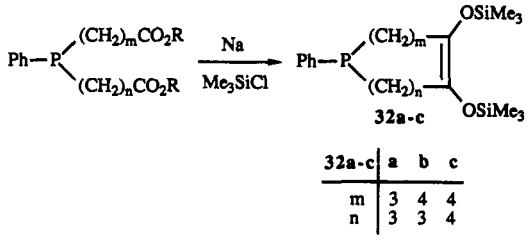
Scheme 15



Scheme 16



Scheme 17



32a-c	a	b	c
m	3	4	4
n	3	3	4

with di-*tert*-butyltin dimethoxide yields a mixture of compounds from which the cyclic dimers **28a,b** are isolated (Scheme 15).[50] When treated with sulfur or selenium, they give rise to the corresponding thioxo or selenoxo derivatives.[50]

Macrocyclic salts **29** and **30** are prepared in high yields from the common intermediate neutral species **31** (Scheme 16).[51]

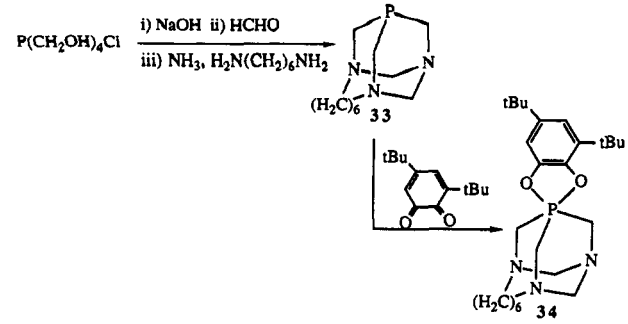
Acyloin condensations of phosphine $C_6H_5P[(CH_2)_m CO_2R][(CH_2)_nCO_2R]$ in the presence of trimethylsilyl chloride give rise to the expected bis(trimethylsiloxy)-phosphacycloalkenes **32a–c** in poor yields (14–23%) (Scheme 17).[52]

The 1,3,10-triaza-12-phospha[8.3.1.1^{3,12}]tricyclopentadecane **33** is obtained by reacting the tetrakis(hydroxymethyl)phosphonium salt $[P(CH_2OH)_4Cl]$ with aqueous formaldehyde and hexamethylenediamine in basic media.[53] Addition of α-quinone leads to the corresponding P^V derivative **34** (Scheme 18).[54]

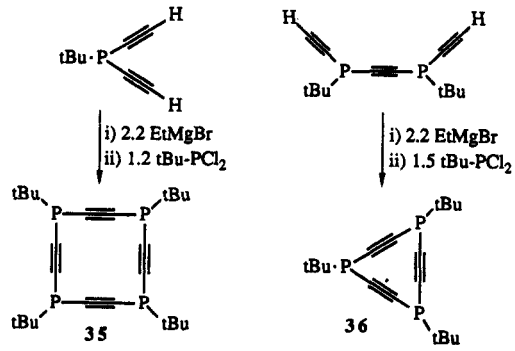
Macrocycles comprising alternating phosphorus atoms and alkyne units **35** and **36** are elegantly prepared by treatment of *tert*-butyldiethynylphosphine or 3,6-di-*tert*-butyl-3,6-diphospha-1,4,7-octatriyne with ethylmagnesium bromide followed by addition of *tert*-butyldichlorophosphine (Scheme 19).[55]

Reaction of a 1:4 (molar) mixture of tetrakis[[(phenylsodio)phosphino]methyl]methane (**37**) and CS_2 in

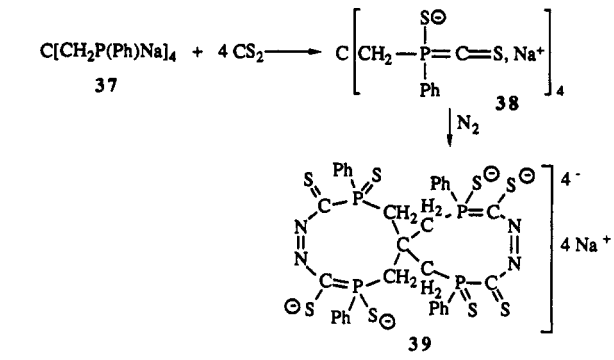
Scheme 18



Scheme 19



Scheme 20



THF at 60 °C under argon gives tetrasodium neopentanetetrayltetrakis[phenyl(thiocarbonyl)phosphoranethiolate] (**38**). This product absorbs molecular nitrogen giving a complex **39**. This complex is also formed directly and more rapidly by analogous reaction of **37** with CS_2 under nitrogen (Scheme 20).[56]

2. Phosphonium Salts

The first macrocycles **40a,b** were prepared by reacting 2,2′-biphenylylenebis(diethylphosphine) with 1,3-dibromopropane[57] or *o*-xylylene dibromide (Scheme 21).[58]

The synthesis was developed later on by several groups[18,59–66] for the formation of macrocycles possessing two or four phosphorus atoms in the ring. Various diphosphines and dihalides are used (Table 3). Indeed, two main processes are employed: reaction of a diphosphine with dihaloalkanes or alkenes[18,59–61,64] (method A) or linking of a ω,ω'-dihalo alkyl bisphosphonium salt with bisphosphine (method B) (Scheme 22).[62–64] On the basis of the same principle a recurrent method for controlled synthesis of polyheteroatomic tri- or tetracoordinated diphosphorus macrocycles is also described.[62,63] This procedure allows the stepwise introduction of different bridges between the phos-

Scheme 21

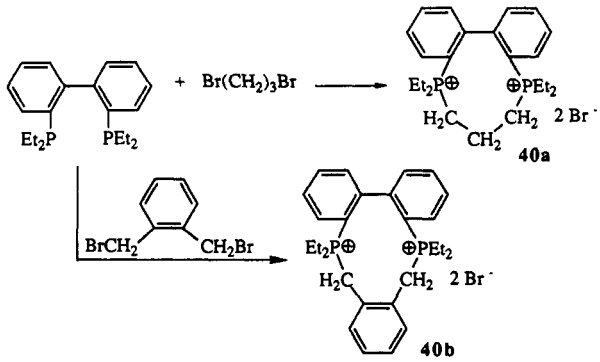
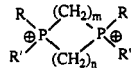
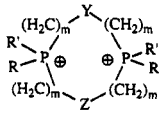
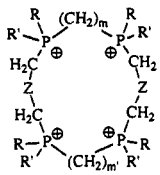
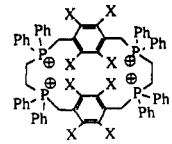
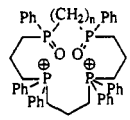
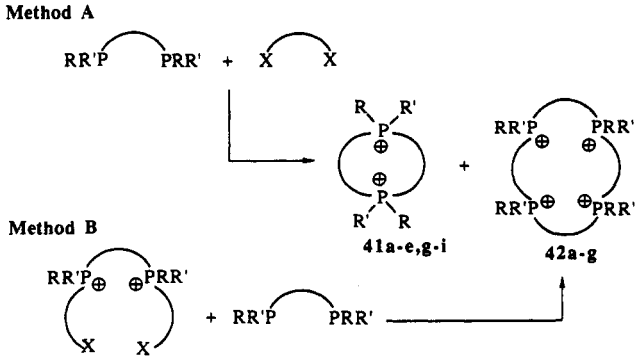


Table 3. Phosphonium Salts 41–43

Compound								Method	Refs.
	**41**	**R**	**R'**	**m**	**n**				
	a	Bz	Bz	2	5			A	61
	b	Bz	Bz	3	4			A	61
	c	Bz	Bz	4	4			A	61
	d	Bz	Ph	4	4			A	61
	e	Bz	Bz	4	5			A	61
	f	Et	Et	4	4				67
	41	**R**	**R'**	**Y**	**Z**	**m**			
	g	Ph	Ph	O	O	3		A	63
	h	Ph	Ph	O		3		A	63
	i	Ph	Ph			3		A	62, 63
	j	Me	Ph	O	O	3			63
	k	Me	Ph	$O(CH_2)_2O$	$O(CH_2)_2O$	2			18
	l	Bz	Bz	$O(CH_2)_2O$	$O(CH_2)_2O$	2		A	18
	**42**	**R**	**R'**	**m**	**m'**	**Z**			
	a	Bz	Bz	3	3	CH_2		A	61
	b	Bz	Ph	3	3	CH_2		A, B	59, 61
	c	Bz	Bz	3	3	$(CH_2)_2$		A	61
	d	Bz	Bz	4	2	$(CH_2)_2$		B	61
	e	Bz	Bz	4	4	$(CH_2)_2$		A, B	59, 61
	f	Ph	Ph	2	2	CH=CH		A	64, 66
	g	Ph	Ph	2	2	$(CH_2)_2$			64
	**42**	**X**							
	h	Cl						A	60
	i	H						A	60
	j	Me						A	60
	**43**	**n**							
	a	2						A	65
	b	3						A	65

Scheme 22



phorus atom through selective phosphonium salts formation and cleavage. Generally use of dilution does not improve the yields.

Scheme 23

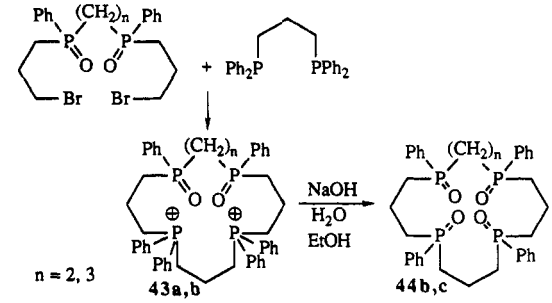
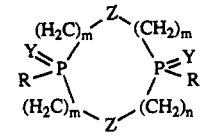
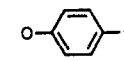


Table 4. Compounds 44 and 45

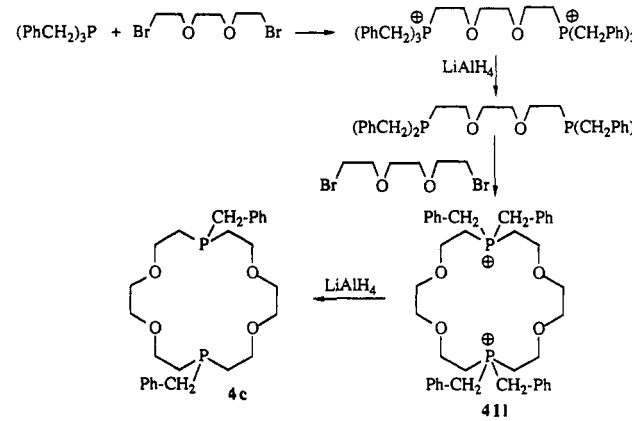


44 Y = O
45 Y = lone pair

44	*m*	*n*	R	Z	ref(s)
a	3	3	Ph	O	63
b	3	2	Ph	PhP(O)	65
c	3	2	Ph	PhP(O)	59,65
d	3	3	Ph		62
e	4	4	Bz	BzP(O)	59

45	*m*	*n*	R	O	ref
a	3	3	Ph	O	63
b	3	3	Ph	PhP	59
c	4	4	Bz	BzP	59

Scheme 24

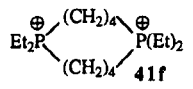


A slightly different methodology, via a bridge protection, leads after alkaline hydrolysis to homologous phosphine tetraoxides **44** and to phosphines **45** after reduction (Scheme 23).[65]

Cyclic phosphonium salts with a benzyl group attached to phosphorus could be cleaved in good yields to the corresponding cyclic phosphines **45** by use of $LiAlH_4$. Other cyclic phosphonium salts[61] can be transformed into the corresponding oxides **44** by hydrolysis in basic medium (Table 4).[63,65]

A multistep synthesis starting from tribenzylphosphine allows the preparation of tetraoxa diphosphino crown ethers (Scheme 24).[18]

The phosphinophosphonium salt $(C_2H_5)_2PP(C_2H_5)_3I^-$ was claimed to react with THF to give the macrocyclic dication **41f**.[67]



41f

B. Intracyclic N–P–N Linkage

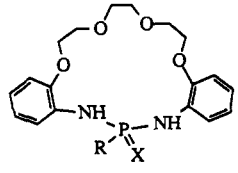
It is claimed that nine-membered rings **46a–l** are obtained by reacting either p-$MeC_6H_4P(O)(OH)_2$[68] or various phenoxydichlorophosphines[69] with bis(2-aminophenyl) disulfide (Scheme 25).

A one-step high-yield synthesis of a macrocyclic ligand containing phosphorus and nitrogen donor atoms **48** is based upon the derivatization of cyclam (**47**, Scheme 26).[70]

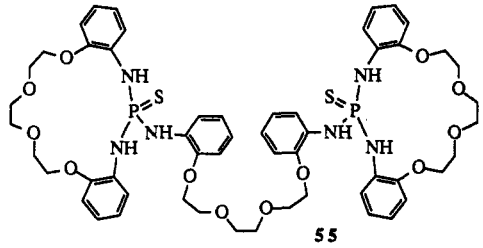
An efficient synthesis of rigidified macrocyclic phosphoramides, the preorganized ligands **49** and **50** incorporating a diaminophosphine group in a polyether macrocycle, is proposed by Dutasta and Simon[71,72] according to Schemes 27 and 28.

Rigidification of **51** can be accomplished by substitution on the nitrogen atoms to give compound **52** (Scheme 29).[73]

The use of hexamethylphosphoric triamide instead of $C_6H_5P(NMe_2)_2$ in the reaction with triethylene glycol bis(*o*-aminophenyl) ether followed by addition of sulfur gives **53** (*cis* and *trans* isomers) based on the P_2N_2 diphosphazane ring (Scheme 30).[74] In the course of this reaction the macrocycles **54a,b** and the bismacrocycle **55** are isolated.



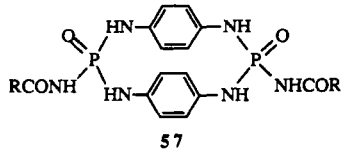
54a R = NMe_2, X = S
54b R = H, X = O



55

The synthesis of a cyclic bis(diaminodiphenylphosphonium salt) namely the 2,2,7,7-tetraphenyldecahydro-1,3,6,8,2,7-tetraazadiphosphecine-2,7-diium dibromide (**56**) consists in the successive reactions of chlorodiphenylphosphine with bromine and then with 1,2-ethanediamine (Scheme 31).[75]

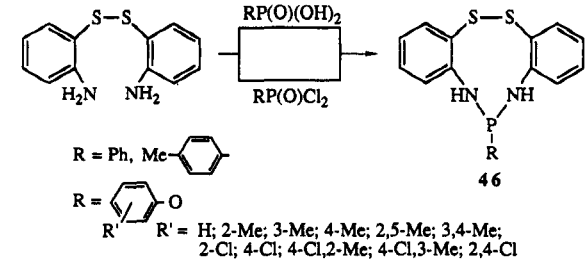
Treatment of $RCONHP(O)Cl_2$ with p-phenylenediamine affords the expected [2 + 2] cyclocondensation product **57**.[76]



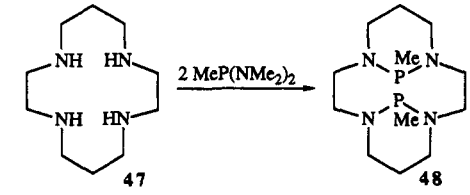
57

Cyclization of $(CH_2)_n(CH_2NHMe)_2$ (n = 4) with $(R_2N)_2POEt$ (R = Me, Et) gives 40–63% yield of 1,3,2-diazaphosphacycloalkane (**58**, Scheme 32).[77]

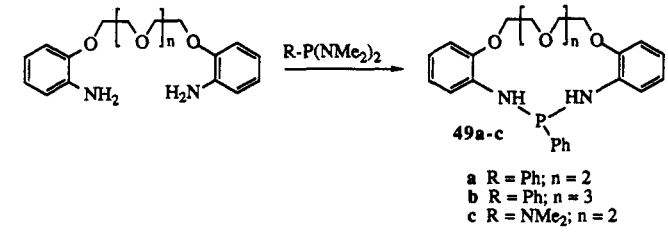
Scheme 25



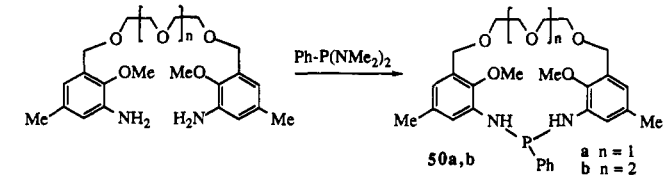
Scheme 26



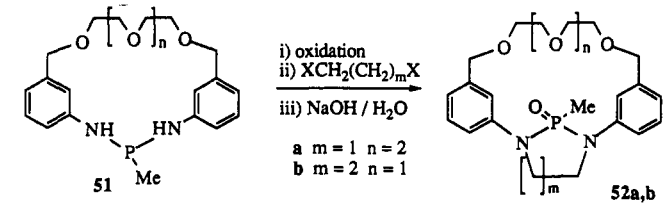
Scheme 27



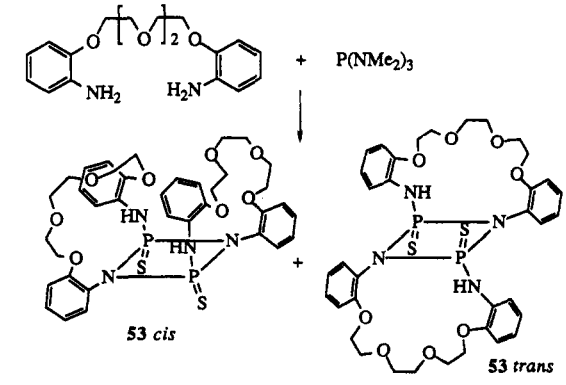
Scheme 28



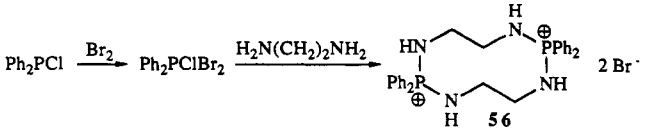
Scheme 29



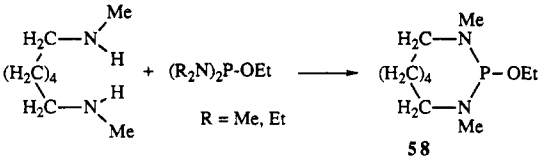
Scheme 30



Scheme 31



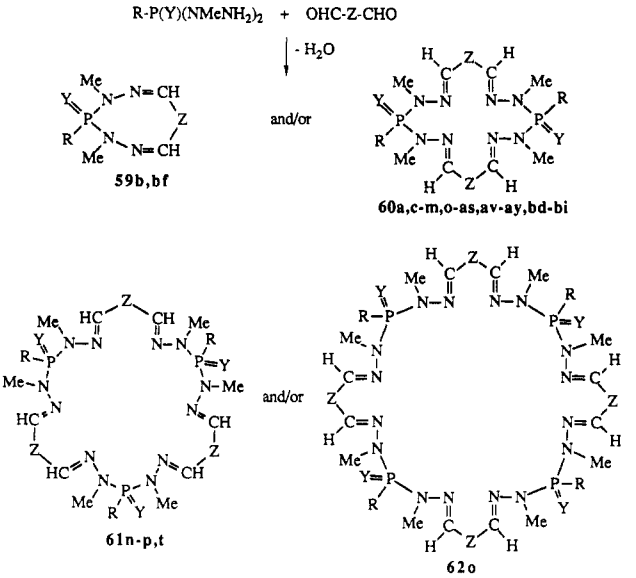
Scheme 32



C. Intracyclic N–N–P–N–N Linkage

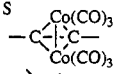
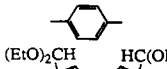
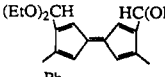
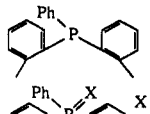
A one-step high yield method of preparing various macrocycles involves the addition of phospho dihydrazides of general formula $RP(Y)[N(CH_3)NH_2]_2$ with dialdehydes (Scheme 33). Macrocycles can be formed from [1 + 1],[78,79] [2 + 2],[79–89] [3 + 3],[79,82,85,89,90] or even [4 + 4][89,90] cyclocondensation reactions. The reaction proceeds in very mild conditions (room temperature, stirring for 1–5 h). No high dilution is required. More than 100 compounds were formed in which phosphorus can be tri-, tetra-, or pentacoordinated. Two to six phosphorus atoms can be included in the macrocyclic chain which can possess up to 20 heteroatoms. Beside N–N–P–N–N linkages, O–P–O, C–P–C, and O–P–N linkages can be introduced in the macrocyclic chain. Mass spectrometry and X-ray structure determinations[82,89] show that most of these macrocycles arise from [2 + 2] cyclocondensation reactions (Table 5).

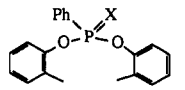
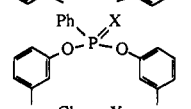
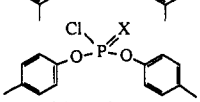
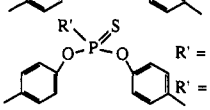
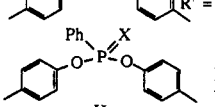
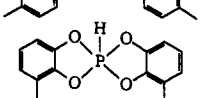
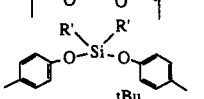
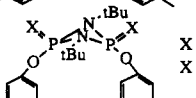
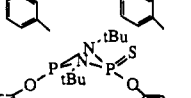
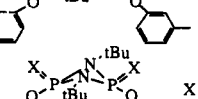
Scheme 33



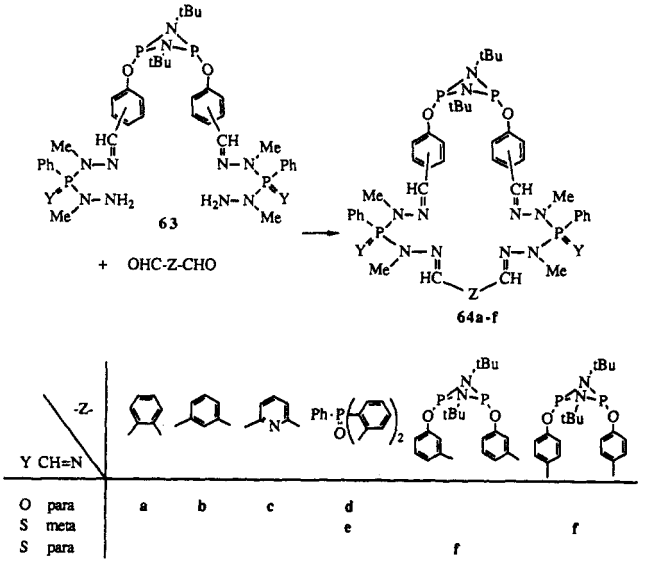
Analogous reactions carried out with the tetraphospho dihydrazides **63** and various dialdehydes led only to [1 + 1] cyclocondensations (Scheme 34).[79,88]

Table 5. Compounds 59–62

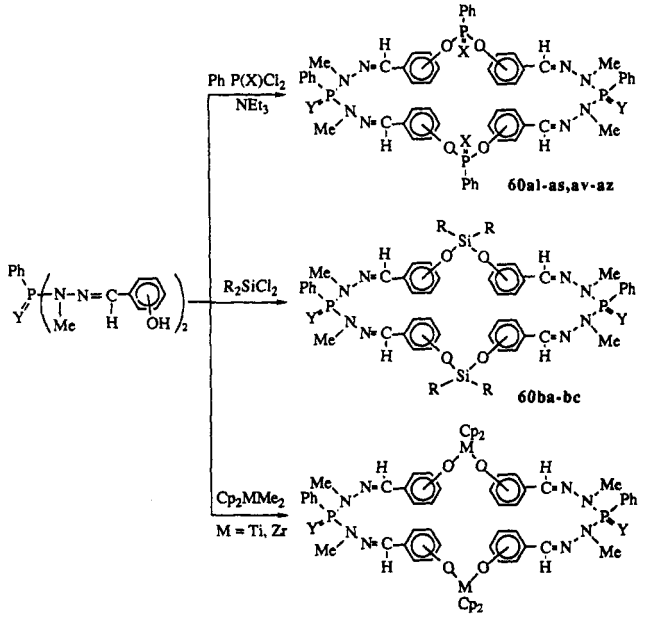
-Z- \ Y / R	O Me$_2$N	O Ph	O Ph-O	S Cl	S Ph	S Ph-O
—C≡C—					60a[79,81,82,85]	
PhP(S)[NMeN=CH-C≡C]$_2$		59b[79,81,82,85]				
		60c[79,81,82,85]			60d[79,81,82,85]	
		60e[79,83]	60f[83]		60g[79,83]	
		60h[79,81,85,93]		60i[79]	60j[79-82,85]	
		60k[79,81,82,85]			60l[79,81,82,85]	
					60m[79-82,85]	
		61n[89,90]	60o[89] 61o[89] 62o[89,90]			
			60p[89] 61p[89]			
	60q[80-82]	60r[79-82,85]	60s[80-82,85]		60t[79-82,85] 61t[79,82,85]	60u[80-82,85]
		60v[87]	60w[87]			
	60x[81,82]	60y[79,81,82,85]		60z[79]	60aa[79-82,85]	
		60ab[79,83,85]			60ac[79,83,85]	
		60ad[79,84]			60ae[79,84]	
 X = O X = S X = Se		60af[79,84] 60ah[79,84] 60aj[79,84]			60ag[79,84] 60ai[79,84] 60ak[79,84]	

-Z- \ Y / R	O Ph	S Cl	S Ph
 X = O X = S	60am[79,86]		60al[79,86]
 X = O X = S	60ao[79,86]		60an[79,86]
 X = O X = S		60ap[79] 60ar[79]	60aq[79,86] 60as[79,86]
 R' = NMe-NH$_2$ R' = CHO			60at[86] 60au[86]
 X = O X = S	60av[79,86] 60ax[79,86]		60aw[79,86] 60ay[79,86]
			60az[79,86]
 R' = Me R' = Ph	60ba[91,92] 60bc[91,92]		60bb[91,92]
 X = lone pair X = S			60bd[78,79,88] 60be[78,79,88]
			59bf[78] 60bf[78]
 X = lone pair X = S	60bg[78,79,88]		60bh[78,79,88] 60bi[78,79,88]

Scheme 34



Scheme 35



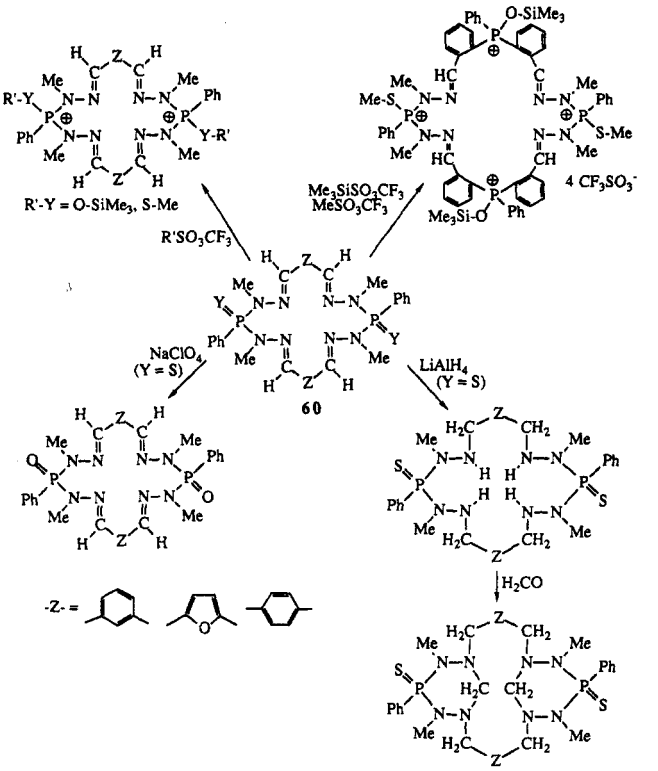
Another general way of synthesizing macrocycles containing P–N–N linkages consists in the reaction of hydroxyphenyl functionalized phospho dihydrazones with $RP(X)Cl_2$,[79,86] R_2SiCl_2,[91,92] Cp_2ZrMe_2,[91] or Cp_2TiMe_2:[91] [2 + 2] cycloadducts are exclusively formed (Scheme 35).

Most of the macrocycles **56–62, 64** are stable enough to be submitted to different chemical procedures: modification of the cavity size (Scheme 36),[79,81,85,93] formation of di-[85,93] or tetraphosphonium salts (Scheme 36),[84] P=S → P=O transformation (Scheme 36),[85,93] or substitution reactions (Scheme 37).[86]

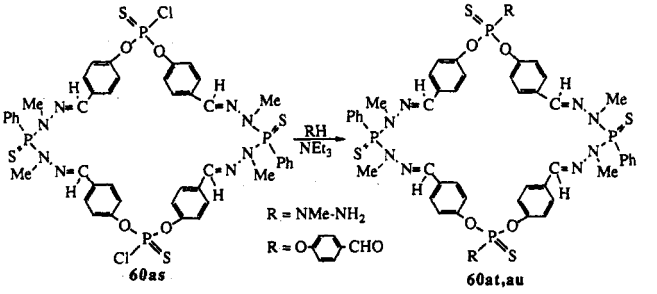
Addition of 2 equiv of aqueous formaldehyde to a di(tetraazaphosphorine) gives rise to the tetracyclic structure **65** (Scheme 38).[94]

Phospho dihydrazides $(C_6H_5O)P(S)(NHNH_2)_2$ react with dichlorohexamethyltrisiloxane to give mixtures of eight-, nine-, and 10-membered rings **66a–c** (Scheme 39).[95]

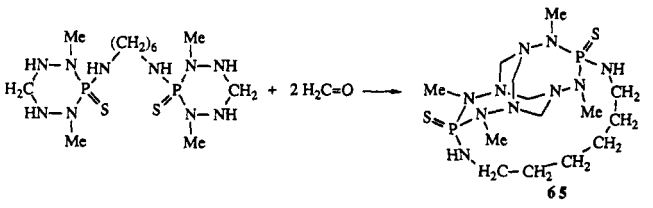
Scheme 36



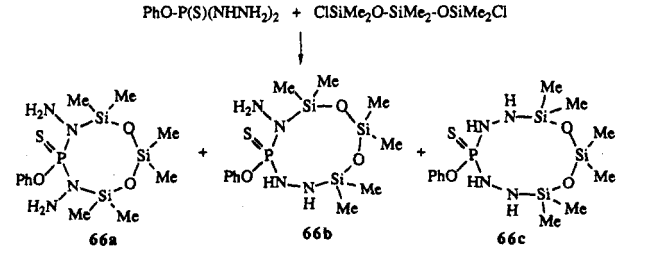
Scheme 37



Scheme 38



Scheme 39



D. Intracyclic O–P–O Linkage

1. Reactions Involving Chlorophosphines

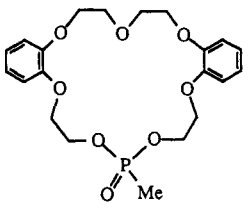
Macrocyclic polyethers containing phosphonyl, phosphoryl, thiophosphoryl, iminophosphoryl groups are

Table 6. Compounds 67a–q

R \ X	n 1 lone pair	1 O	1 S	1 NSO_2Ph	2 O	2 S
H		b[115]				
Me		c[96,109–113]	g[105,106,109]		j[101]	p[99,101,105]
Et					k[101]	
Ph		d[109,112]		h[97,98]	l[99,101,103]	q[99,101]
Ph–O		e[109]			m[99,101]	
Ad					n[99,104]	
Ad–O	a[114,116]					
N=PPh_3		f[97,98,100]		i[97,98]		
N(–$(CH_2)_2CN$)(–$(CH_2)_2Cl$)					o[102]	

prepared by treatment of disodium salts of open-chain polyethers with $RPCl_2$, $RP(X)Cl_2$, $R_3P{=}NP(O)Cl_2$ (Table 6, Scheme 40).[96–106]

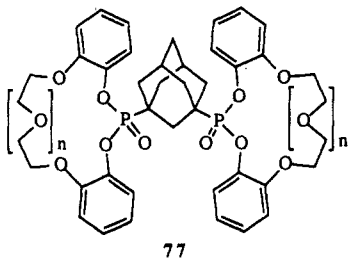
Phosphorus crown ether **69**[107,108] is similarly obtained from $CH_3P(O)(OCH_2CH_2Cl)_2$.



69

Analogous reactions are undertaken starting directly from polyethylene glycols or related species which are reacted with di- or trihalogenated phosphorus compounds in the presence of base: derivatives of type **67** and compounds **68a,c** are thus prepared (Table 6).[109–116] Extension of this method allows the synthesis of macrocycles **70**,[117,118] **71**,[119] **72**,[120] **73**,[121] **74**,[122–124] **75**,[125] and **76**[116,126,127] (Chart 1). The reaction of P-functionalized macrocycles **67b** and **76** with amines allows the preparation of other macrocyclic species.[115,127]

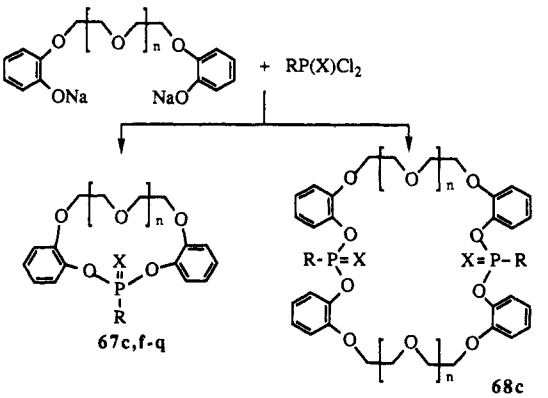
The macrobicyclic derivative **77** is formed in 46% yield by cyclizing *o*-$NaOC_6H_4O(CH_2CH_2O)_nC_6H_4ONa$-*o* ($n$ = 2, 3) with adamantanediphosphonic dichloride.[116,128]



77

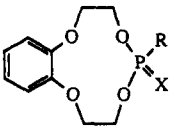
When *p-tert*-butylcalix[6]arene **78** is treated with cesium fluoride and then with ethyl phosphorodichloridite, an ethyl phosphate substituent is introduced onto the lower rim of the calix[6]arene. The new macrocyclic compound **79** has a single ethyl phosphate spanning two adjacent phenolic oxygens of the calix[6]arene.[129] When the same reaction is carried out in the presence of potassium hydride, a stronger base than cesium fluoride, a second ethyl phosphate substituent can be introduced onto the lower rim of the calixarene affording the derivative **80**. Treatment of *p-tert*-butylcalix[6]arene with $ClP(O)(OEt)_2$ followed by

Scheme 40



67c,f-q **68c**

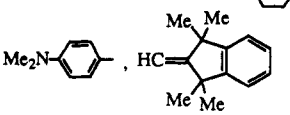
Chart 1

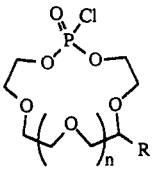


70

X = lone pair, O, S, Se, O_2N–N, CF_3SO_2–N

R = Me, Ph, CH_2CH_2Cl, EtO, PhO,  ,

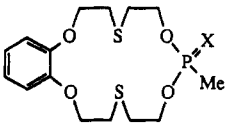




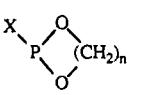
71

n = 1 R = H, $CH_3(CH_2)_7$

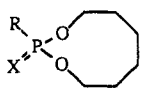
n = 2 R = H, $CH_3(CH_2)_7$, $CH_3(CH_2)_9$, $CH_3(CH_2)_{15}$



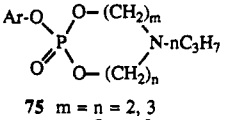
72 X = O, S



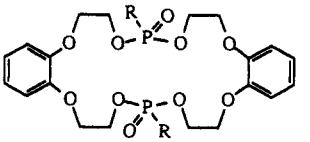
73 n = 6, 10
X = Cl, F



74 R = Cl, Ph, OPh
X = O, S



75 m = n = 2, 3
m = 2 n = 3
Ar = Ph, *p*-ClC_6H_4, *m*-cresyl



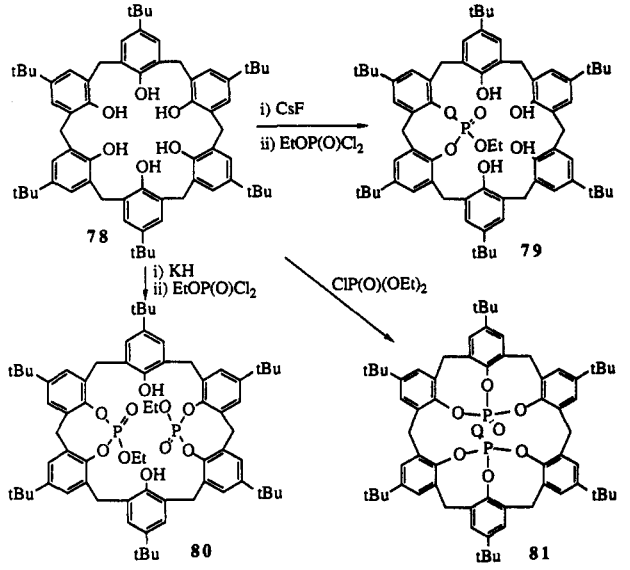
76 R = H, Me, AdNH, PhNH, OH, CH_2OH, $CH(OH)CCl_3$

heating of the resulting isolated product under vacuum at 330 °C yields **81** in 47% yield (Scheme 41).[130]

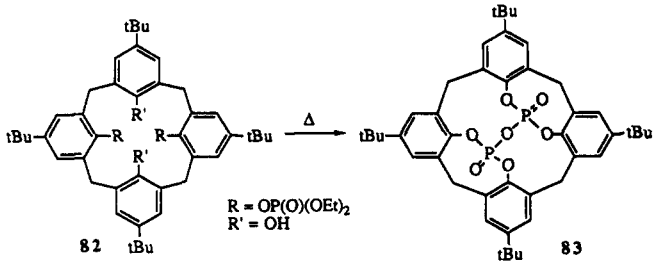
Pyrolysis of poly(dialkyl phosphate) ester derivatives of calixarene results in multiple bridges. Heating of bis(diethyl phosphate) calixarene **82** at 230 °C under vacuum leads to the formation of pyrophosphate **83** in which two phosphorus atoms are each bridging two proximal phenoxy groups (Scheme 42).[130]

Condensation of PCl_3 with (*R,R*)-tartaric acid gives rise to the macrocycle **84** possessing two pentacoordinated phosphorus atoms. The triethylammonium salt **86** of the corresponding hydroxyphosphorane **85** is also isolated.[131–134] Treatment of the phosphorane **84** with-

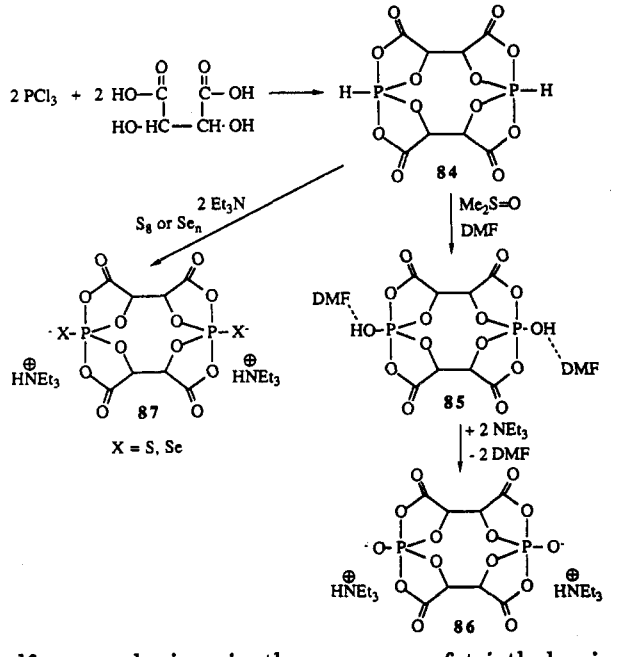
Scheme 41



Scheme 42



Scheme 43



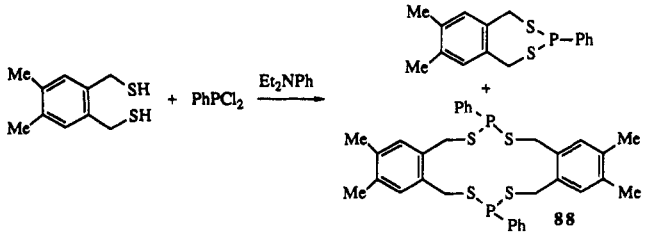
sulfur or selenium in the presence of triethylamine affords 87 (Scheme 43).[135,136]

Reactions of dichlorophosphines with dithiols instead of diols are also investigated, leading to a benzodithiaphosphepin and the corresponding dimer 88 (Scheme 44).[137,138]

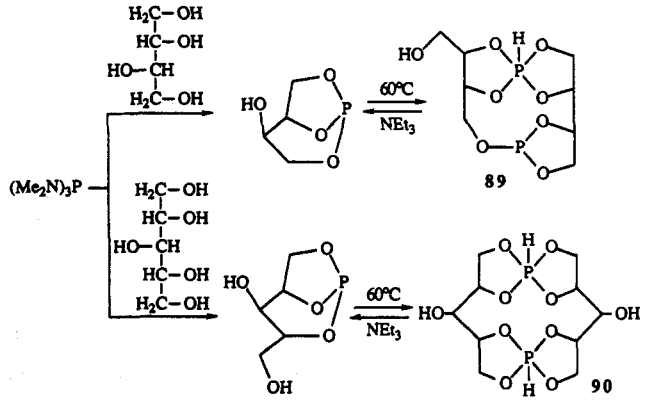
2. Reactions Involving Aminophosphines

Bicyclic phosphites obtained from the reaction of hexamethylphosphoric triamide with threitol or xylitol

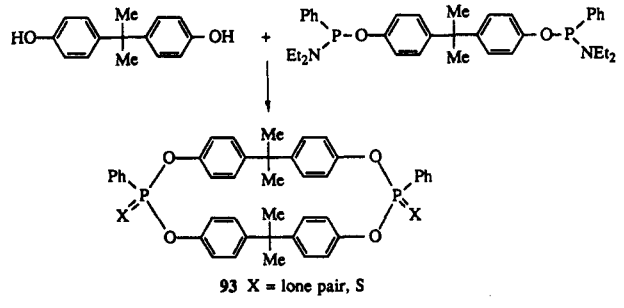
Scheme 44



Scheme 45

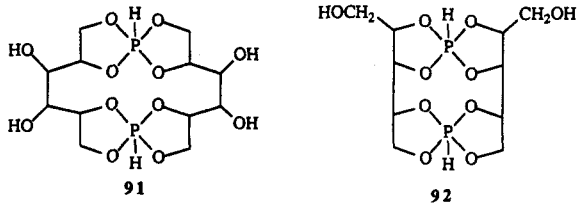


Scheme 46



undergo fast oligomerization at 60 °C leading to polycyclic phosphoranes 89 and 90 (Scheme 45).[139]

The bisspirophosphorane 91 is formed from $P(NMe_2)_3$ and D-(+)-mannitol or D-(+)-glucidol under mild experimental conditions (5 h, 40 °C). The same experiment with arabinitol affords 92.[140]

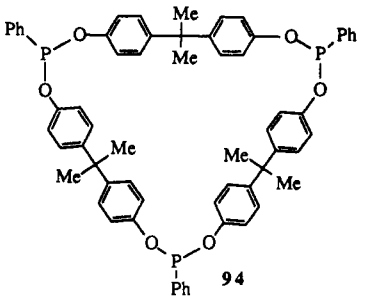


When heated with an equimolar amount of 2,2-bis(*p*-hydroxyphenyl)propane, the linear bisphosphinite $[C_6H_5(NEt_2)POC_6H_4]_2C(CH_3)_2$ undergoes cyclization with the formation of macrocycle 93 (Scheme 46).[141]

The triarylenecyclophosphonite 94 is prepared from the diarylenetriphosphinite $[C_6H_5(NEt_2)POC_6H_4C(CH_3)_2C_6H_4O]_2PC_6H_5$ according to the same procedure.[141]

3. Reactions Involving Silylated Derivatives

2-Chloro-2-oxo, -2-thio, or -2-imino-4,5-benzo-1,3,2-dioxaphospholane reacts with $Me_3SiO(CH_2CH_2O)_nSiMe_3$

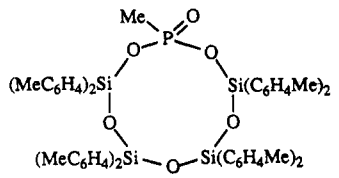


94

to give the corresponding polyethylene glycol. Intramolecular nucleophilic addition of the Me_3Si group to the P–X bond of these polyethylene glycols gives spirophosphoranes **95** with structure and properties of crown ethers (Scheme 47).[142,143]

On standing at room temperature, a mixture of bis(silyl ether), mono(silyl ether)–mono(alkyloxytrifluorophosphorane), and bis(alkyloxytrifluorophosphorane) evolves into a new mixture which contains the 16-membered ring **96** (Scheme 48).[144]

Condensation of α-ethoxy-ω-ethyloctakis(phenylmethyl)tetrasiloxane $C_2H_5O[Si(C_6H_4CH_3)_2\text{-}O]_4C_2H_5$ with methylphosphonic acid $MeP(O)(OH)_2$ leads to the corresponding macrocycle **97**.[145]

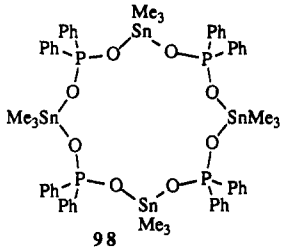


:0q; y = 77q

97

4. Miscellaneous Methods

A unique macrocyclic structure of tetrameric trimethyltin(IV) diphenylphosphinate $[Me_3SnO_2PPh_2]_4$ **98** containing a 16-membered $Sn_4O_8P_4$ inorganic ring is isolated from the reaction of Me_3SnCl and $NH_4O_2PPh_2$.[146]



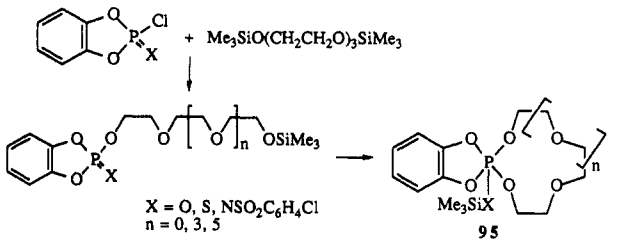
98

Triphenylphosphine and diisopropyl azodicarboxylate react with propane-1,3-diol, butane-1,3-diol, pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol, octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol in tetrahydrofurane at 0 °C to give large-ring cyclic dioxytriphenylphosphoranes **99** that appear to be oligomeric (Scheme 49).[147,148]

Nine-membered rings **100** incorporating sulfur, oxygen, and phosphorus are prepared in accordance with Scheme 50.[149,150]

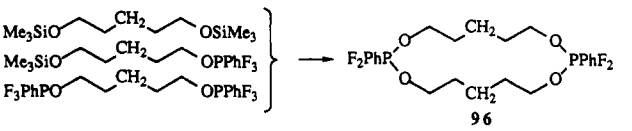
Methanolysis of a carboalkoxy enol phosphite leads to a minor product which appears to come from migration of ring oxygen to give the nine-membered ring **101** isolated as a thiophosphate (Scheme 51).[151]

Scheme 47



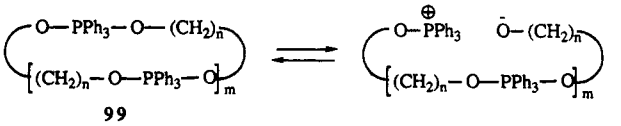
95

Scheme 48



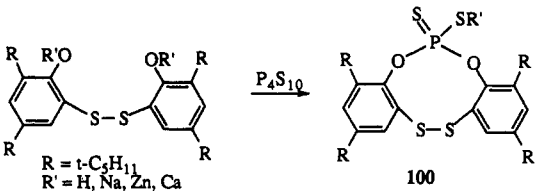
96

Scheme 49



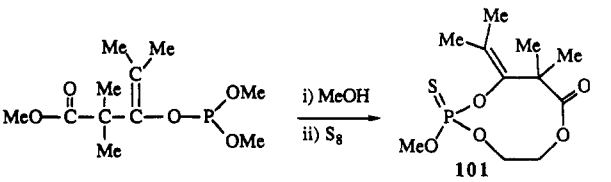
99

Scheme 50



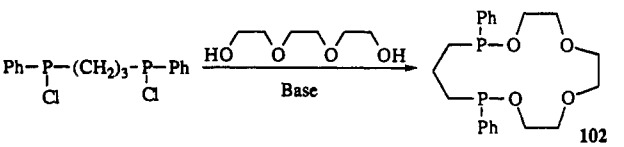
100

Scheme 51



101

Scheme 52



102

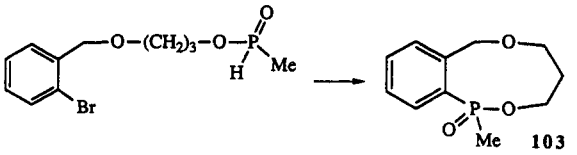
E. Intracyclic X–P–Y Linkage

1,3-Bis(chlorophenylphosphino)propane is reacted with a stoichiometric amount of triethylene glycol in dry THF in the presence of a base using high dilution conditions to favor the formation of the crown ether type compound **102** which is isolated from the resulting mixture by complexation with $Mo(CO)_4$ (norbornadiene) (Scheme 52).[152]

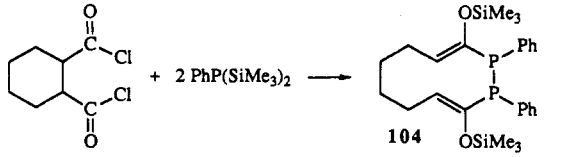
The benzooxaphosphacycloalkane **103** is prepared by palladium-catalyzed intramolecular cyclization of the corresponding mono(ω-*o*-bromophenylalkyl) ester (Scheme 53).[153]

Reaction of phenylbis(trimethylsilyl)phosphane with *trans*-1,2-cyclohexanedicarboxylic acid dichloride af-

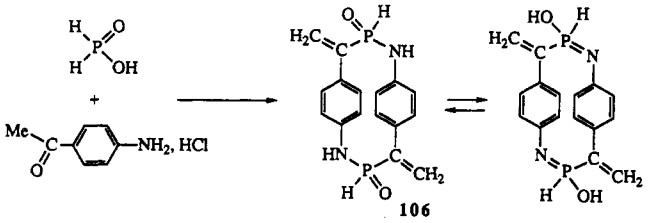
Scheme 53



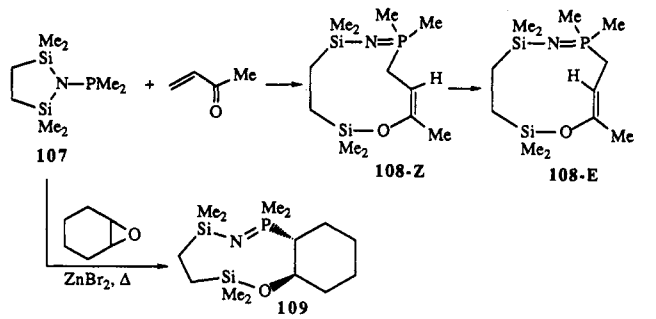
Scheme 54



Scheme 55

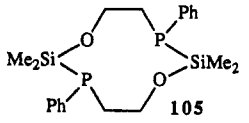


Scheme 56



fords the 1,2-diphospha-3,9-cyclodecadiene **104** in 75% yield (Scheme 54).[154,155]

Addition of dimethyldichlorosilane to the dilithium salt $PhP(Li)(CH_2)_2OLi$ at 0 °C gives exclusively the stable dimer **105**.[156]

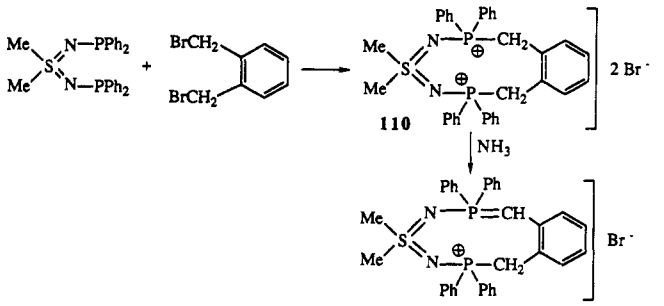


Treatment of 4′-aminoacetophenone hydrochloride with H_3PO_2 is claimed to lead in part to the cyclic phosphonamidate **106** (Scheme 55).[157]

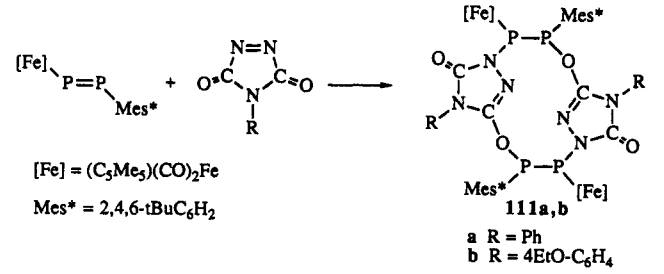
A ring expansion to a 10-membered cyclic phosphine imide is observed when the bis(silylamino)phosphine **107** reacts with methyl vinyl ketone.[158] The initial product **108-Z**, with *Z* configuration, apparently results from nucleophilic attack by phosphorus on the carbonyl carbon, followed by a silyl migration from nitrogen to oxygen. The Z isomer slowly converts to the *E* isomer **108-E**. An intramolecular silicon transfer also occurs when the phosphine **107** reacts with cyclohexene oxide. This zinc-catalyzed epoxide ring opening yields the phosphine imide **109** (Scheme 56).[159]

The reaction of 1,2-bis(bromomethyl)benzene with a *N,N′*-phosphino-substituted *S,S*-dimethylsulfodiimide leads to the nine-membered ring salt **110** (Scheme 57).[160]

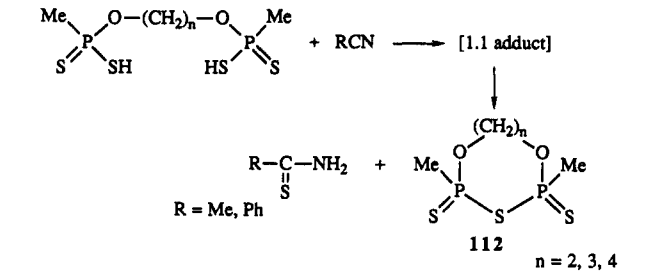
Scheme 57



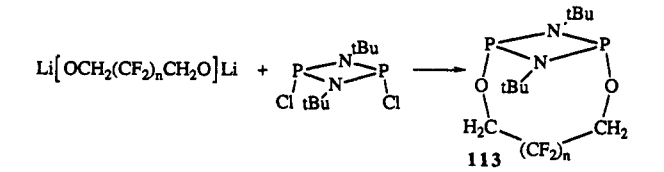
Scheme 58



Scheme 59



Scheme 60



The *(E,E)*-1,7-dioxa-4,5,10,11-tetraaza-3,4,8,9-tetraphosphadodeca-5,11-diene **111** is obtained from the reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P{=}P\text{–}Mes^*]$ with Δ^1-1,2,4-triazoline-3,5-diones in diethyl ether (Scheme 58).[161-164]

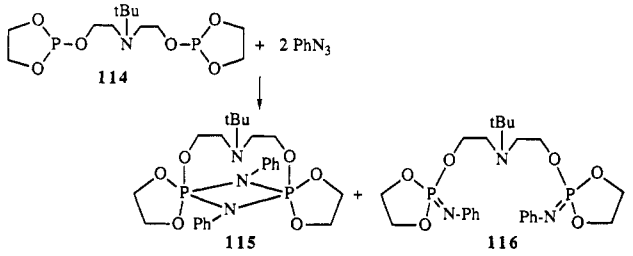
The reaction of bis(dithiophosphonic acids) with RCN gives a 1:1 adduct which decomposes to $RC(S)NH_2$ and cyclic trithiopyrophosphonates **112**. The stability of **112** decreases as *n* increases (Scheme 59).[165]

Lithium salts of polyfluorinated alcohols treated with *cis*-1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine give rise to the corresponding polyfluoro bis(alkoxy-bridged) diazadiphosphetidine species **113** (Scheme 60).[166]

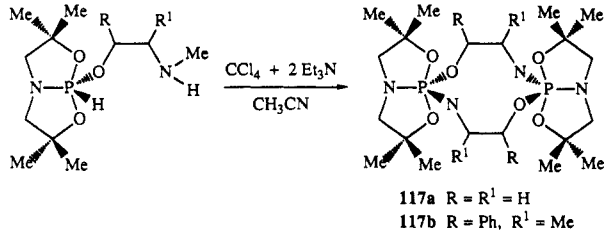
The bisphosphite **114** reacts exothermically with 2 equiv of phenyl azide to give a mixture consisting of macrocycle **115** and compound **116** (Scheme 61).[167,168]

Extension of the Atherton–Todd reaction to the 1-(organooxy)-1-hydridobicyclophosphoranes allows the preparation of the bis(bicyclophosphoranes) **117a,b** bearing a 10-membered ring (Scheme 62).[169,170]

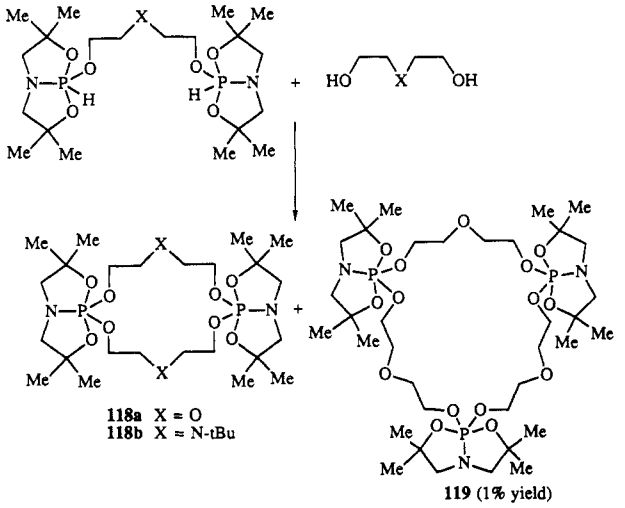
Scheme 61



Scheme 62



Scheme 63



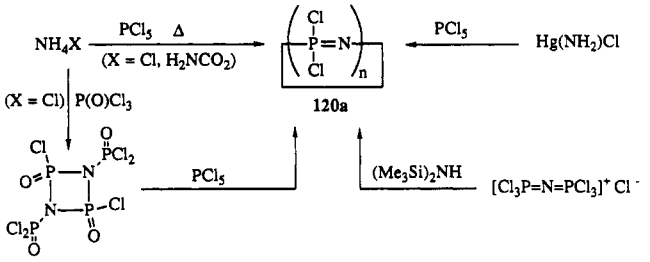
Such a reaction performed with bis(hydridobicyclophosphoranes) and α,ω-diols affords bicyclophosphoranes containing macrocycles **118a,b** and **119** (Scheme 63).[171]

F. Cyclophosphazenes

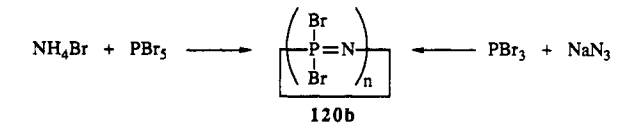
1. Cyclopolyphosphazenes

Cyclophosphazenes $(X_2P=N)_n$ ($n \geq 5$) are the oldest type of phosphorus macrocycles reported in the literature. The penta-, hexa-, and heptamers of phosphonitrile dichloride ($Cl_2P{\equiv}N$) were isolated and correctly identified by Stokes at the end of the nineteenth century.[1] A huge amount of publications and patents deals with phosphazenes. However, most of this work concerns cyclotri- or cyclotetraphosphazenes (n = 3, 4) and their polymerization, even if some of the earlier reviews in this topic also evoked macrocyclic phosphazenes.[172,173] Indeed, chlorocyclotri- and -tetraphosphazenes are the main products of the cyclocondensation of ammonium chloride with phosphorus pentachloride. Macrocyclic compounds ($n \geq 5$) are isolated from the crude mixture by fractional distillation, crystallization, or chromatography up to n = 15.[174,175] The earliest syntheses were carried out in

Scheme 64



Scheme 65



sealed tubes, heated at 150–200 °C, and in the absence of a solvent. This technique gave rise to serious explosion hazards due to the high pressure of hydrogen chloride within the tubes. Now the reaction is performed in the presence of a solvent, often *sym*-tetrachloroethane.[176]

Several other methods allow the obtention of oligochlorocyclophosphazenes, for instance the use of ammonium carbamate[177] or $Hg(NH_2)Cl$[178] instead of ammonium chloride, a two-step reaction of ammonium chloride with $P(O)Cl_3$ and then with PCl_5,[179] and the reaction of hexamethyldisilazane with $[Cl_3P{=}N{=}PCl_3]^+Cl^-$ (Scheme 64).[180]

The corresponding bromo derivatives **120b** ($n \geq 5$) are obtained in the reaction of phosphorus pentabromide with ammonium bromide[181] and separated until n = 16.[182] The pentamer is also obtained in low yield in the reaction of sodium azide with phosphorus tribromide (Scheme 65).[183]

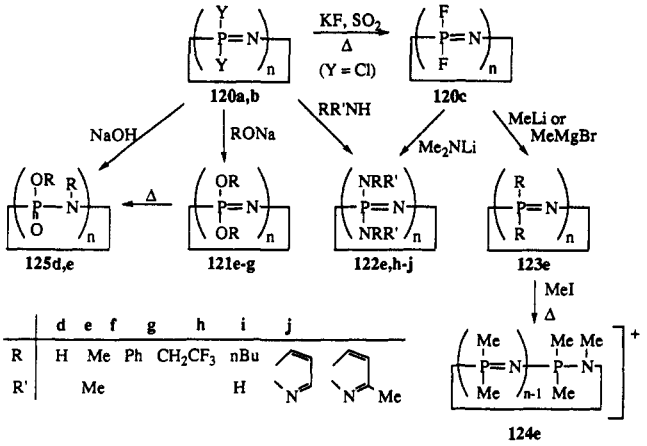
An analogous reaction, carried out with trimethylsilyl azide and RPI_2 allows the preparation of $[RIP{=}N]_n$ derivatives in good yields (R = Et, n = 22; R = Ph, p-ClC_6H_4, n = 5).[184]

The fluoro derivatives **120c** are prepared by fluorination of chloro oligomers **120a** with potassium fluorosulfite.[185,186] Partial fluorination is observed with a mixture of SbF_3–$SbCl_5$.[187] The vibrational data,[188,189] fragmentation patterns,[190,191] ^{35}Cl,[192] ^{19}F,[193] and ^{31}P NMR[194] of several oligophosphazene halides are known, as well as the X-ray structure determinations of the fluoro,[195] chloro,[196,197] and bromo[198] pentamers.

Chloro and fluoro derivatives are starting reagents for a series of substituted macrocyclic phosphazenes. The mechanism of the nucleophilic substitution of chlorine was suggested to be SN_2 by studying chlorine exchange between radioactive tetraethylammonium chloride and $(PCl_2N)_n$.[199] Reaction of **120a** with sodium derivatives of alcohols allows the isolation of the alkoxyphosphazenes **121e–g** (Scheme 66).[200,201] An interconversion of the phosphazene ring, increasing the proportion of lower homologues, was observed during the reaction of PhONa with a mixture of oligomers **120a**.[202,203] The X-ray structure determination of the hexadeca- and dodecamethoxy derivatives have been reported.[204,205]

The amino-substituted cyclophosphazenes **122** are obtained by reaction of amines[201,206–208] or lithio derivatives[209] with chloro- or fluorophosphazenes. The reac-

Scheme 66



tion of *n*-butylamine with a mixture of chlorophosphazenes ($3 \leq n \leq 7$) increases the proportion of higher homologues.[202,203] The X-ray structure determination of **122e** when $n = 6$, performed in 1964, is certainly the oldest phosphorus macrocyclic structure ever determined.[210,211] The structure when $n = 8$ is also known.[212]

The dimethylphosphazene **123e** was first obtained in low yield by reaction of methyllithium with fluorophosphazenes.[213-215] The yield was improved by the use of methylmagnesium bromide instead of methyllithium.[216,217] Dimethylphosphazenes form the longest series of cyclic molecules with known structures. Indeed, crystal structure determinations of $(PMe_2N)_n$ were undertaken for $n = 5$,[218] $n = 6$,[219] $n = 7$,[216] $n = 8$,[220] and $n = 9$–12.[217]

Partially substituted oligocyclophosphazenes are often obtained by starting from fluoro derivatives **120c**. The formation of C-substituted compounds occurs with (*p*-fluorophenyl)lithium[221] and (lithiomethyl)pyrrole,[222] whereas compounds with P–N bonds are formed with (dimethylamino)trimethylsilane or -stannane[223] or tris(trimethylstannyl)amine.[224] Partial reaction of ethane- or benzenethiolate with $N_5P_5Cl_{10}$ has also been reported.[223]

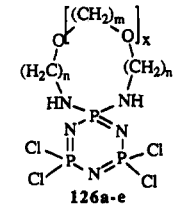
A few reactions concerning the phosphorus–nitrogen bond of organo-substituted phosphazenes are known. For instance, compound **123e** forms the monoquaternary salt **124e** when heated in methyl iodide,[215] whereas neat **121e** undergoes a thermal rearrangement when heated at 150 °C under reduced pressure.[226] Several isomers of oxocyclophosphazanes **125e** ($n = 5, 6$) are thus obtained. The first rearrangement phosphazene → phosphazane in the cyclic series was reported for **120a** ($n = 6$) which reacts with sodium hydroxide to yield the acid **125d** (R = H).[227,228]

2. Reactions Involving Cyclotri- or Cyclotetraphosphazenes

The reaction of hexachlorocyclotriphosphazene $N_3P_3Cl_6$ with polyamines, polyoxadiamines, or dithiadiamines gives products whose structures depend drastically on the nature of the polyamine and on the experimental conditions. Spiro **126a–e** and **127a–d**, dispiro **128a–d**, cis **129a–e** or trans **130**, ansa, dibino **131a–e** and **132a–c**, and tribino **133**[248] derivatives (Chart 2) were thus prepared.

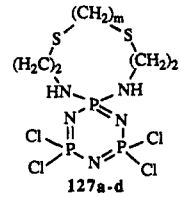
The reaction of octachlorocyclotetraphosphazatetraene $N_4P_4Cl_8$ with the polyamine $H_2N(CH_2)_3NH(CH_2)_4NH_2$ gives a polycyclic species **134**.[249]

Chart 2



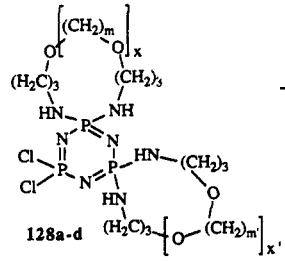
126a-e

126	n	m	x	Refs.
a	2	2	1	229,230
b	3	2	1	229-232
c	3	4	1	229,230,233,234
d	3	6	1	229,232
e	3	2	2	229,234-237



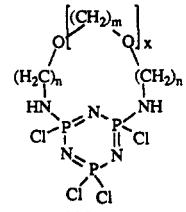
127a-d

127	a	b	c	d
m	3	4	5	6
Refs.	238	239	239	240



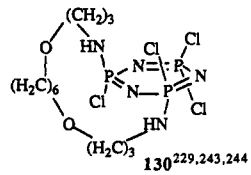
128a-d

128	m	m'	x	x'	Refs.
a	4	4	1	1	229,234,241
b	2	2	2	2	229,234,241
c	2	4	1	1	229,241
d	2	2	1	2	229,241

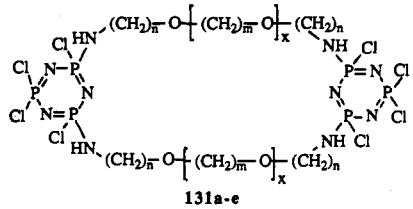


129a-e

129	n	m	x	Refs.
a	2	0	0	229,242
b	2	2	1	229,230
c	3	2	1	229-231
d	3	4	1	229,230,233
e	3	2	2	229,237

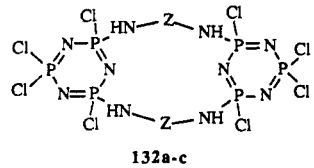


130[229,243,244]



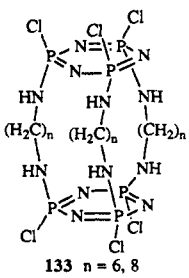
131a-e

131	n	m	x	Refs.
a	2	2	1	229,245
b	3	2	1	229,245,246
c	3	4	1	229,245
d	3	6	1	229
e	3	2	2	229,245

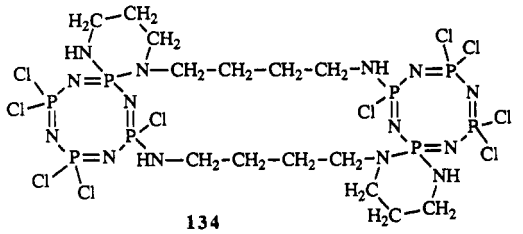


132a-c

132	a	b	c
Z		$(CH_2)_6$	$(CH_2)_8$
Refs.	247	248	248



133 n = 6, 8



134

Several macrocycles were prepared by reacting $N_3P_3Cl_6$ or $N_4P_4Cl_8$ with diols, bis(2-hydroxyethyl) ether, or bis(hydroxymethyl)-*O*-carborane. Ansa **135a**[250] and **135b**,[251] diansa **136**,[250] spiroansa **137**,[252] and dibino **138a**,[250,253,254] **138b**[252] derivatives (Chart 3) were thus isolated. Cyclic triphosphazene with four trifluoroethoxy side groups and two nongeminal chlorine atoms (1,3), $[N_3P_3(OCH_2CF_3)_4Cl_2]$ reacts with a diphenol to give the transannular derivative **135c**.[255]

Under controlled reaction conditions and without using a phase-transfer catalysis the polycondensation of $N_3P_3Cl_6$ and hydroquinone leads to a mixture of oligomers with formula $N_3P_3Cl_5$-[(*p*-OC_6H_4O)-($N_3P_3Cl_4$)]$_n$-(*p*-OC_6H_4O)-$N_3P_3Cl_5$. The first compound (n = 0) in this series could be isolated in a pure state. In addition, very small quantities of a double-bridged species $N_3P_3Cl_4$-(*p*-$OC_6H_4O)_2$-$N_3P_3Cl_4$ **138c** have been detected.[256,257]

III. Ring Opening

A. Intracyclic C–P–C Linkage

Almost all the macrocycles containing C–P–C linkages and obtained by ring opening are nine-membered rings. They are synthesized by opening of phosphorus five-membered rings according to three main pathways: thermal cleavage of P–C bonds, addition of unsaturated compounds, or oxidation of C=C bonds.

First attempts consisted of heating neat spirophosphoranes up to their melting point.[258–260] This induces the opening of two five-membered rings, followed by the formation of a C–C bond, leading to the tricoordinated phosphorus macrocycles **139a–j** (Table 7, Scheme 67). Addition reactions on the lone pair of phosphorus are observed with hydrogen chloride and methyl iodide. The ionic macrocycles **141a,c** are also obtained by heating a mixture of methyl iodide and spirophosphoranes, whereas the intermediate **140f** is isolated starting from a dimethylanilino-substituted spirophosphorane. Reaction of the ionic species **140** and **141** with tetraphenylborate leads to the corresponding borate salt of the phosphoniums.[258]

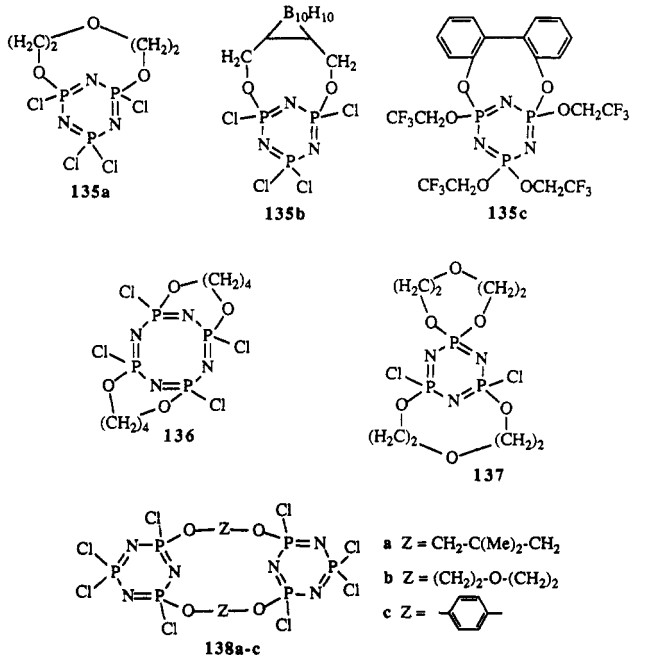
The tricyclophosphoranes **142a,b** obtained by addition of dimethyl acetylenedicarboxylate onto phospholes undergo a ring–chain tautomerism induced by heating.[261,262] Only one isomer is obtained for compounds **143a,b** as shown by ^{31}P and ^{1}H NMR spectra, i.e., the *cis,cis,trans,cis*-phosphonin (Scheme 68).

An analogous reaction carried out with 3-butyl-1,2-diphenylphosphindole affords the benzodihydrophosphonine **144** in low yield (10%). This compound presumably arises from hydrolysis of a polycyclic intermediate similar to the ylide **142** (Scheme 69).[263]

The phosphorus–germanium bond of germaphospholanes is easily cleaved with α-unsaturated carbonyl derivatives such as cinnamaldehyde and methyl vinyl ketone. The nine-membered germaphospha heterocycles **145a–b** are thus obtained as a mixture of diastereoisomers (Scheme 70).[264]

The phospholane ylide **146** slowly dimerizes with spontaneous ring opening, but the resulting double

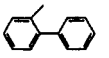
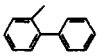
Chart 3



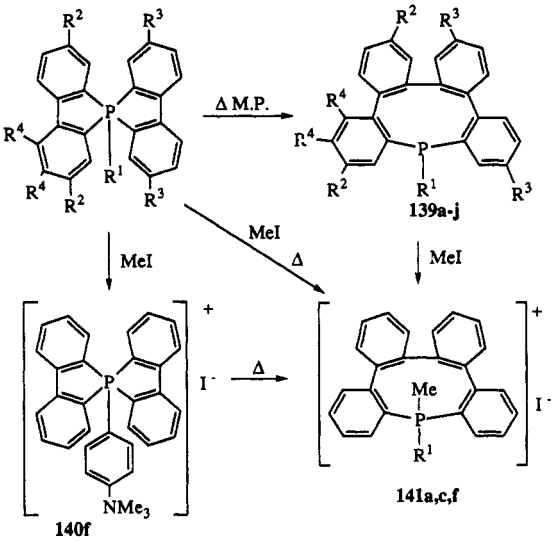
135a 135b 135c 136 137 138a-c

a Z = CH_2-$C(Me)_2$-CH_2
b Z = $(CH_2)_2$-O-$(CH_2)_2$
c Z =

Table 7. Compounds 139a–j

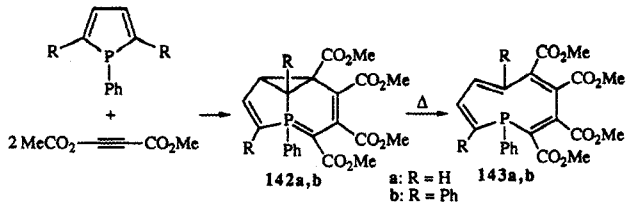
139	R^1	R^2	R^3	R^4	ref
a	Me	H	H	H	259
b	Me	Me	Me	H	260
c	Ph	H	H	H	258
d	Ph	Me	Me	H	260
e	Ph	H	NMe_2	H	258
f	*p*-$Me_2N(C_6H_4)$	H	H	H	258
g	*p*-$Me_2N(C_6H_4)$	H	H	$(CH)_4$	258
h	*m*-iPr(C_6H_4)	Me	Me	H	260
i		H	H	H	259
j		Me	Me	H	260

Scheme 67

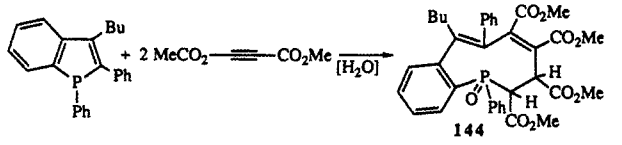


139a-j 140f 141a,c,f

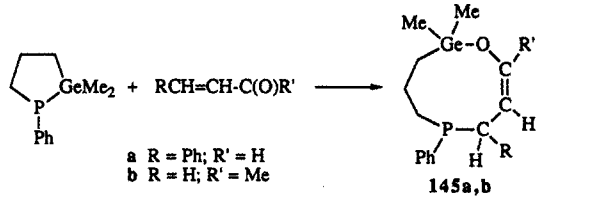
Scheme 68



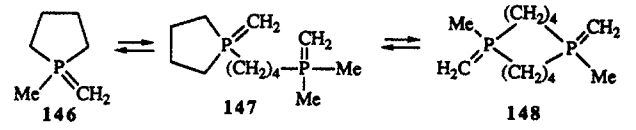
Scheme 69



Scheme 70



Scheme 71



ylides **147** and **148** are not isolated, due to the reversibility of the dimerization (Scheme 71).[265]

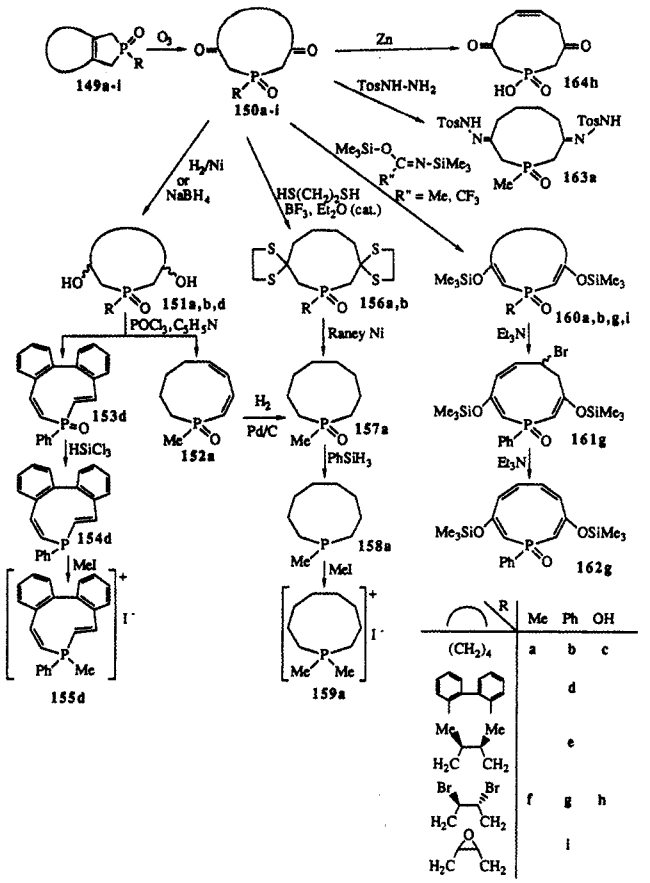
Diketo derivatives **150** are useful functional precursors of the series of phosphorus nine-membered macrocycles **151–164**. These precursors **150a–i** are obtained in good yields by ring-opening ozonolysis of phospholenes **149a–i** followed by reductive work up either by trimethyl phosphite or by a mixture of potassium iodide and acetic acid.[266–269] The diketo functionality of compounds **150a–i** gives rise to a versatile reactivity (Scheme 72).

Reduction of carbonyl groups of phosphanone dioxides **150a,b,d** is achieved with sodium borohydride or by hydrogenation over a Raney nickel catalyst. A mixture of the three possible diastereomeric forms (one *dl* and two *meso*) is obtained for diols **151a,b**,[270] whereas a single diol is formed for **151d**.[271] Dehydration of compounds **151a,d** with $POCl_3$–pyridine supplies different dienes in each case, which are assigned, from ^1H NMR data, the *cis,cis-* or *cis,trans* structure **152a** and the *cis,trans* structure **153d**, respectively. Deoxygenation of oxide **153d** with $HSiCl_3$–pyridine gives the phosphonine **154d** which readily forms the methiodide **155d**. Spectral data reveals the *cis,trans* structure in both compounds.[271]

The bis-dithio ketals **156a,b** are formed from ethanedithiol and diketo derivatives **150a,b** with BF_3–etherate as catalyst. The reductive desulfurization of **156a** with Raney nickel affords the phosphonane **157a** which is also obtained by hydrogenation with Pd/C of the diene **152a**. Reduction of the phosphoryl function with phenylsilane gives the phosphine **158a** which is readily quaternized with methyl iodide to **159a**.[270]

Enolic character is noticeable in the phosphane diones **150**, as evidenced by the ease of silylation with bis-

Scheme 72



(trimethylsilyl)acetamides. Compounds **160a,b,g,i** thus obtained are extremely sensitive to moisture.[270,272] Compound **160g** is interesting as it loses 1 equiv of HBr when reacted with 1 equiv of triethylamine. Two isomers relative to the 1,5 substituents (Br and Ph) are detected on the ^{31}P NMR spectrum of the resulting bromophosphonine **161g**. Addition of a second equivalent of triethylamine induces a full dehydrohalogenation. The phosphonine oxide **162** is obtained together with a bicyclo derivative.[272]

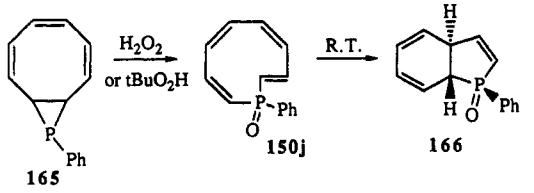
Finally, another type of reaction on the ketone functions concerns the formation of the dihydrazone derivative **163a** from **150a** and *p*-toluenesulfonyl hydrazine. In fact, only one example of reaction in which the diketo function is preserved has been described, i.e. the debromination of the dibromophosphane dione **150h** with zinc, leading to **164h**.[270]

In connection to the preceding series of compounds **150a–i**, the *trans,cis,cis,cis*-phosphonine oxide **150j** has been obtained by oxidation of the phosphirane **165** with H_2O_2[273] or *tert*-butyl hydrogen peroxide.[274] However, compound **150j** is only observable at low temperature, since it undergoes an intramolecular cycloaddition leading to the dihydrophosphaindole derivative **166** (Scheme 73).[273,274]

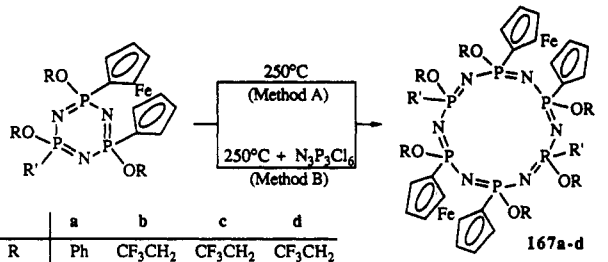
B. Intracyclic N–P–N Linkage

Most of the macrocycles synthesized by ring opening are either issued from cyclophosphazenes or from tetraaminophosphorane derivatives. The oldest reports concern ring opening of halogenocyclophosphazenes. Thus, any $(NPCl_2)_n$ can be converted into a mixture of $(NPCl_2)_n$ derivatives by heat.[1,202,275,276] This reaction is

Scheme 73

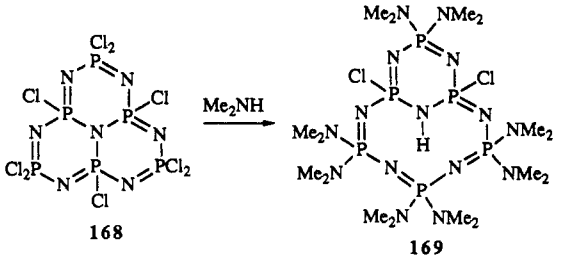


Scheme 74

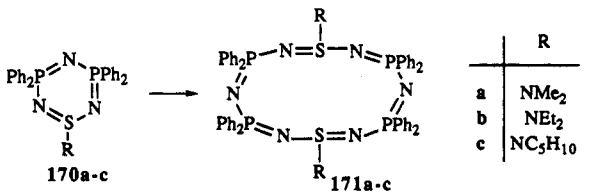


	a	b	c	d
R	Ph	CF_3CH_2	CF_3CH_2	CF_3CH_2
R'	OPh	CF_3CH_2O	Ph	PhO
Method	A, B	A	A	A

Scheme 75



Scheme 76



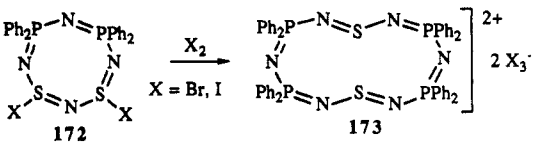
	R
a	NMe_2
b	NEt_2
c	NC_5H_{10}

also observed with phosphazenes which possess both organic and halogen side groups.[277] The reaction is far more difficult with fully substituted cyclotriphosphazenes. However, the ring strain imparted by transannular metallocenyl units to organo-substituted cyclotriphosphazenes induces an easier ring opening and yields cyclic oligomers when heated at 250 °C. In some cases, the presence of a catalytic amount of $N_3P_3Cl_6$ is needed as an initiator of the oligomerization (Scheme 74). The main product of the reaction is often the cyclic hexamer **167** which is generally obtained in low yield, except for **167a** (33% yield).[278,279]

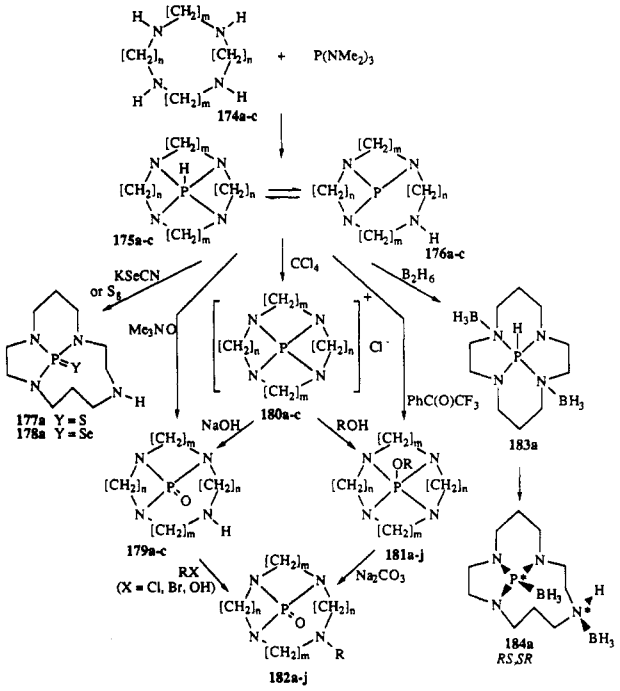
Ring strain in the condensed ring structure of nitrilohexaphosphonitrilic chloride **168** induces the cleavage of the central bond when reacted with dimethylamine. Two of the bridgehead chlorine atoms of the twelve-membered ring **169** remain unsubstituted (Scheme 75).[280,281]

The ring-opening of mixed phosphazenethiazyl rings is easier than for phosphazenes. Thus, the spontaneous conversion of **170** into the dimer **171** has been reported[282,283] and confirmed by an X-ray structure determination of **171a** (Scheme 76).[282]

Scheme 77



Scheme 78



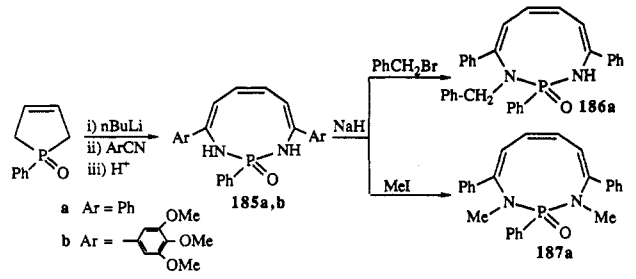
	a	b	c	d	e	f	g	h	i	j
m	3	3	4	3	3	3	3	3	3	3
n	2	3	3	2	2	2	2	2	2	2
R	Ph	Ph	Ph	$H_2C{=}CH$	$HC{\equiv}C$	Cp_2Fe	$C_6H_5CH_2$	$C_6H_5(CH_2)_2$	$nC_{11}H_{23}$	$CH(Ph)CF_3$

Reaction of the related eight-membered ring **172** with bromine or iodine gives the unexpected dicationic species **173** (Scheme 77).[284]

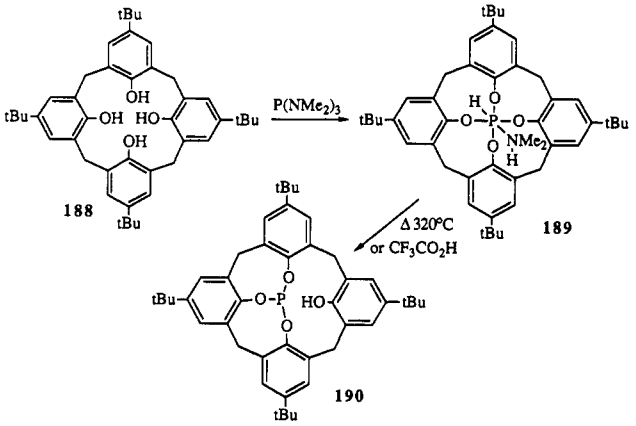
The second type of macrocycles with N–P–N linkages, synthesized by ring opening, are tetraaminophosphorane derivatives which are obtained as a mixture of P^V–P^{III} tautomers by transamination reactions of tetraaminomacrocycles **174a–c** with hexamethylphosphoric triamide.[285,286] Examination of the effect of ring size on the P^{III}–P^V tautomerism shows that compound **a** gives a mixture in which the "closed" tetracyclic phosphorane tautomer **175** predominates, whereas compound **b** only gives the isomeric "open" tricyclic P^{III} tautomer **176**. Less symmetrical azamacrocycles, for instance, isocyclam "3322", leads to a mixture of P^V and regioisomers of P^{III} (Scheme 78).[285]

Various attempts have been made to displace the tautomeric equilibrium toward the open tricyclic structure **176**, mainly by complexation.[287–289] Such behavior is also observed in the case of oxidation of phosphorus by molecular sulfur, potassium selenocyanate,[290] or trimethylamine oxide[291] leading to the corresponding sulfide **177a**, selenide **178a**, and oxide **179a**. Compounds **179**[292] are also obtained by a two-step process. After oxidation of the mixture P^{III}–P^V with CCl_4, the resulting phosphoniums **180a–c** are hydrolyzed with sodium hydroxide to yield the oxides **179a–c**. Reaction of electrophiles with the N–H

Scheme 79



Scheme 80



functions of **176a–c** gives mono-N-substituted macrocycles **182a–i**, which are also obtained by base-induced isomerization of the pentacoordinated alkoxyphosphoranes **181a–i**. Removal of the phosphoryl protection by acid hydrolysis of the oxides **182a–i** yields mono-N-functionalized tetraazamacrocycles.[286] The phosphorane alkoxide **181j**, obtained by reaction of cyclamphosphorane with trifluoroacetophenone, is spontaneously converted to its structural isomer **182j**.[293]

Addition of 1 mol equiv of diborane to the cyclamphosphorane **175a**, in equilibrium with the open form **176a**, leads to a complex mixture from which the bis(borane)cyclamphosphorane **183a** and the open form **184a** are isolated. Compound **183a** is also slowly but totally converted to **184a** in a few weeks when left in solution.[294] An X-ray structure determination of the open phosphane **184a** shows that the diastereoisomer formed is (*R*,*S*;*S*,*R*), the one in which the P–B and N–B bonds are oriented *trans* to each other.[295]

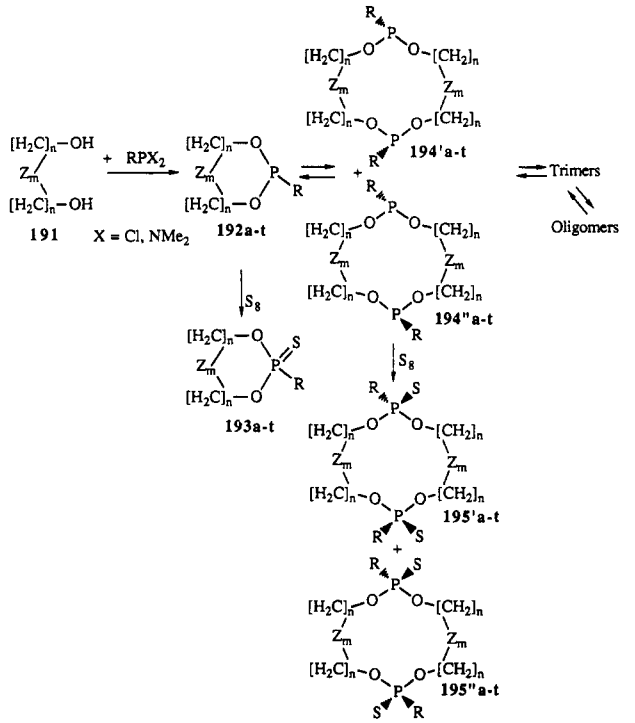
Reaction of 1-phenylphospholene oxide with excess butyllithium and aromatic nitriles induces a ring opening and gives the diazaphosphacyclononatrienes **185a,b** in very low yield (3–5%) after hydrolysis with aqueous ammonium chloride.[296] A monoalkylation on nitrogen is obtained with a mixture of NaH and benzyl bromide, whereas a dialkylation reaction is observed with NaH and methyl iodide (Scheme 79).[296]

C. Intracyclic O–P–O Linkage

In contrast to the reaction of phosphorus triamide with polyaminomacrocycles **174** (see above), the reaction with polyoxy macrocycles **188** does not lead to a P^{V}–P^{III} equilibrium, but gives a single compound, **189**, a hexacoordinate phosphorus in *p-tert*-butylcalix[4]arene (Scheme 80).[297]

The pentacoordinate analogue of **189** has never been isolated. Indeed, all attempts to remove dimethylamine

Scheme 81



by heat or reaction with trifluoroacetic acid only lead to the tricoordinate phosphorus macrocycle **190**.[297]

However, this type of macrocycle is not representative of most phosphorus macrocycles with O–P–O linkage obtained by ring opening. Indeed, the principal method of synthesis concerns the ring-opening polymerization of cyclic phosphonites. First reports did not elucidate the structure of the polymers, long chains, or macrocycles (see for instance[298–300]), but detailed investigations revealed the formation of dimeric and trimeric molecules along with higher polymeric species.[301] Oligomers are sometimes observed during the synthesis of monomers **192** from diols **191** and dichloro- or diaminophosphines. However, ^{31}P NMR studies of crude dioxaphosphepanes **192n** reveal that dimers and oligomers come from this monomer rather than from an initial [2 + 2] or [1 + 1] cyclocondensation reaction (Scheme 81, Table 8).[302]

Several factors influence the oligomerization. First of all, high-grade purity monomers dimerize very slowly,[301] while impurities, particularly traces of water seem to be a determinant factor of oligomerization.[303] The rate of reaction also depends on the type of phosphonite. An extra cyclic P–C bond is needed to observe a ring opening.[304] The oligomerization is accelerated according to the following series of R substituents Ph ≪ Me < Et < iPr < tBu.[302,305] Phosphonites with R = F, Cl, OMe, OPh, or NMe_2 are stable and do not show any tendency to oligomerization.[305] The last criterion which influences the oligomerization is the size of the ring. Five-membered rings (phospholanes **192a–e**) oligomerize faster than six-membered rings (phosphorinanes **192f–m**) and much more faster than seven-membered rings (phosphepanes **192n**).[302] Furthermore, the yield of dimers is very low (<1%) starting from phosphocanes **192o–t** (eight-membered rings).[306,307]

In one case, a measure of the mean degree of oligomerization gives a value around 8,[302] but only the

Table 8. Compounds 192–198

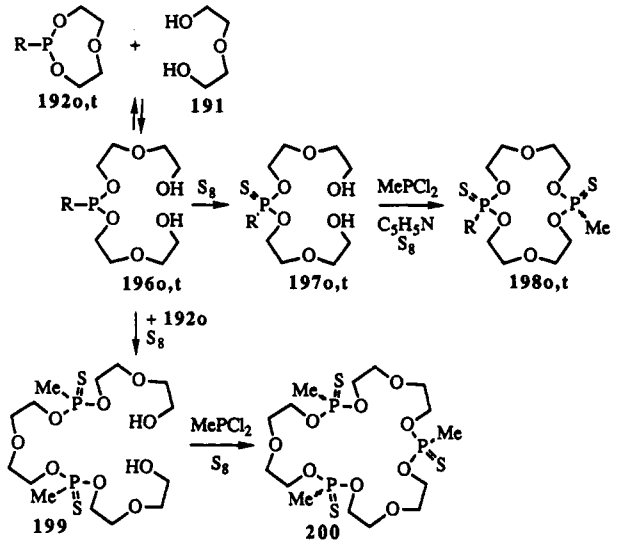
	Z_m	R	ref(s)
		$n = 1$	
a		Me	304,305
b		Et	305
c		tBu	304,305
d		Ph	303–305
e		c-C_6H_{11}	304,305
f	CH_2	Me	302,306
g	CH_2	Et	302
h	CH_2	iPr	302
i	CH_2	tBu	302
j	CH_2	Ph	302
k	CMe_2	Me	301,305,309
l	CMe_2	Et	305
m	CMe_2	iPr	305
		$n = 2$	
n		tBu	302,305
o	O	Me	305–307
p	S	Me	305,307
q	CMe_2	Me	305,307
r	NMe	Me	305,307
s	PMe	Me	308
t	O	Ph	307

dimers have been characterized, although not fully isolated. In almost all cases two diastereoisomers (*cis* and *trans*) are observed. The only exception comes from macrocycle **194s** in which two additional phosphorus atoms give rise to the expected five diastereoisomers.[308] The tricoordinated phosphorus macrocycles **194** are in equilibrium with oligomers and monomers. Heat or dilution allows the recovery of the starting monomers **192**.[301,305] Furthermore, the oxidizability of these compounds prevents the isolation of P^{III} forms. On the other hand, reaction of a mixture of monomers, dimers, and oligomers with elemental sulfur gives rise to stable compounds. Among them, monomers **193** and dimers **195** are isolated.[301–307] Contrary to the P^{III} forms, no equilibrium is observed between neither monomers P^{IV} and dimers P^{IV}, nor between the two diastereoisomeric P^{IV} dimers, *cis* **194′** and *trans* **194″**, which differ by the relative orientation of the R groups with respect to the mean plane of the molecule. The relative amount of the diastereoisomers is generally different from the statistical 1/1 ratio and depends on the size of the R substituent. For instance, only one isomer is isolated for compound **195c** (R = tBu), the *trans* isomer **195″c**.[304] In most cases, characterization of *cis* and *trans* isomers is achieved by ^{31}P and ^{1}H NMR, and these assignments have been confirmed by X-ray structure determinations for the *trans* ten-membered ring **195″d**[304] and the *cis* twelve-membered ring **195′k**.[309]

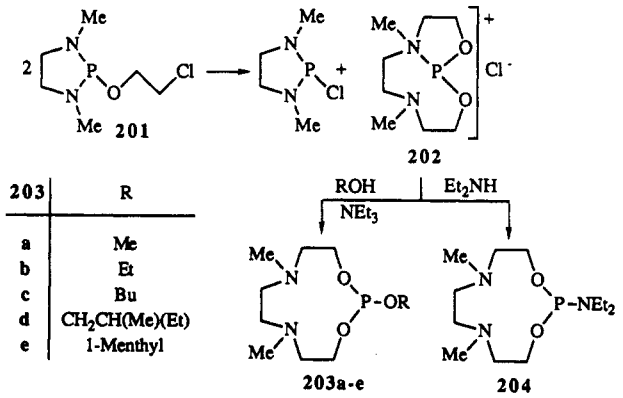
The spontaneous ring-opening process of phosphonites is often very slow, and the yield of isolated macrocycles is very low, so the method needs to be improved. This has been achieved by developing a stepwise controlled synthesis, starting from the ring-opening reaction of phosphonites **192** by glycol (Scheme 82).[305,306]

Phosphadiols **196** are in equilibrium with the starting products and a mixture of oligomeric species. Addition of sulfur allows to isolate the P^{IV} derivatives of the monomer **193**, the diol **197**, and a small amount of **199**. Treatment of phosphadiols **197** and **199** with methyldichlorophosphine induces a ring closure and yields 16- and 24-membered rings, compounds **198** and **200**, respectively. Both compounds exist in two diastereoisomeric forms *cis* and *trans* for **198**, *cis,cis* and *cis,trans* for the trimer **200**, which is obtained only when R = Me.[307]

Scheme 82

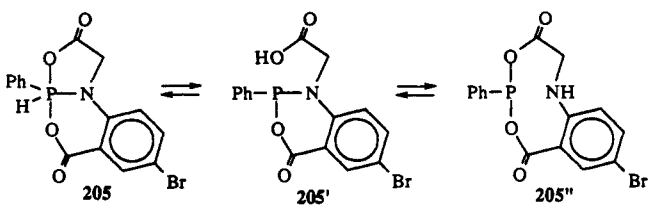


Scheme 83



In contrast to dioxaphospholanes, diazaphospholanes do not oligomerize spontaneously on standing in solution.[305] However, the β-chloroethoxy substituent on phosphorus in compound **201** induces a quantitative and spontaneous ring-opening reaction leading to the ammonium salt **202**. Then, 11-membered macrocycles **203** and **204** are obtained by reaction with alcohols[310,311] or amines,[312] respectively (Scheme 83).

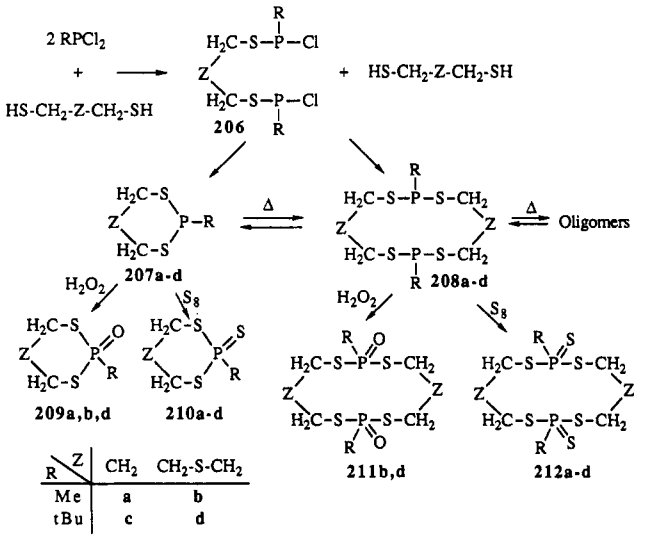
Compound **205** prepared from the reaction of phenyldichlorophosphine on 5-bromo-*N*-(carboxymethyl)-anthranilic acid, in the presence of triethylamine, exhibits an equilibrium connecting a bicyclophosphorane and its isomers.[313]



D. Intracyclic S–P–S or P–P–P Linkage

The chemical behavior of dithiaphosphonites is rather different from that of dioxaphosphonites. For instance, dithia five-membered rings do not show any tendency

Scheme 84



to oligomerize, whereas the corresponding dioxa compounds are difficult to isolate as monomers.[314] However, dimers **208a–d** and oligomers are formed in the synthesis of thia six- and eight-membered rings, the dithiaphosphorinanes **207a,c**[314] and trithiaphosphocanes **207b,d**[315] respectively (Scheme 84).

The thia P^{III} derivatives are much more stable than the corresponding oxo P^{III} derivatives. Indeed, compounds **207** and the *cis* and *trans* isomers of compounds **208** are isolated by column chromatography.[305,314,315] However, an equilibrium exists between monomers, dimers, and oligomers. For instance, a solution of pure *trans*-**208c** dimer heated at 80 °C gives a mixture of *cis*- and *trans*-**208c**. If this mixture is heated at 160 °C, the monomeric species **207c** appears.[314] A similar behavior is observed for **208b** upon heating or diluting; the equilibrium is displaced toward the monomer **207b**.[315] This may explain the formation of a certain amount of monomer in the course of the synthesis of the dimer, even when the diphosphorus derivative **206** is the only compound detected by ^{31}P NMR after the first step of the reaction.[315]

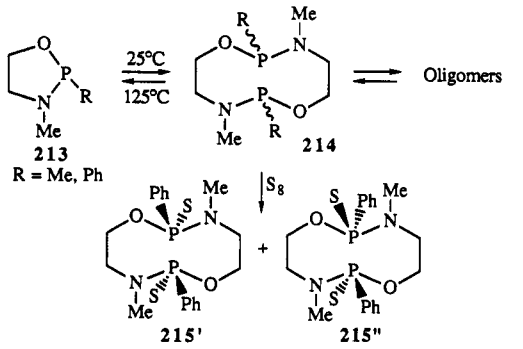
P^{IV} derivatives are obtained by reaction with sulfur (**210** and **212**) or hydrogen peroxide (**209** and **211**).[315] The dependence of NMR parameters on ring size of these compounds has been studied,[316] and the structure of macrocycle *cis*-**212d** has been determined by X-ray diffraction.[317]

Only one example of macrocycle containing a P–P–P linkage is known. Thus, heating pentamethylcyclopentaphosphine $(PMe)_5$ with chromium, molybdenum, or tungsten hexacarbonyls for long reaction times (16–30 h) results in the formation of the nine-membered ring complex $(PMe)_9M_2(CO)_6$.[318]

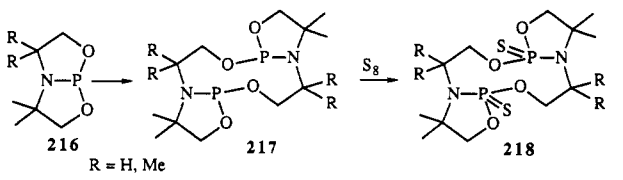
E. Intracyclic X–P–Y Linkage

In contrast to macrocycles containing symmetric C–P–C, N–P–N, O–P–O, or S–P–S linkages which constitute an abundant series of compounds, few macrocycles containing unsymmetrical phosphorus units are obtained by ring-opening reactions. Most of them arises from the cleavage of a P–O bond. For instance, oxazaphospholidines **213**, obtained by reaction of 2-(methylamino)ethanol with dichloro- or bis(dimethylamino)phosphines, slowly polymerize at room

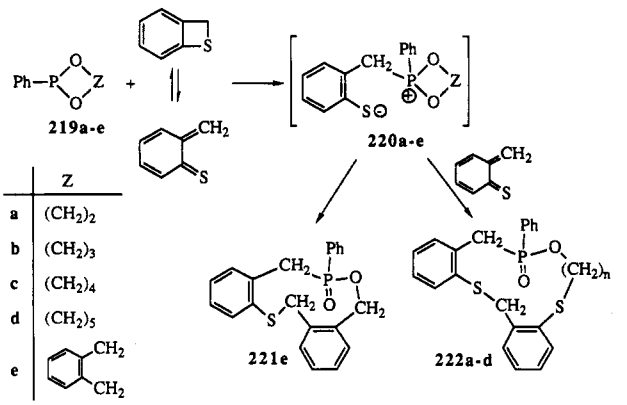
Scheme 85



Scheme 86



Scheme 87

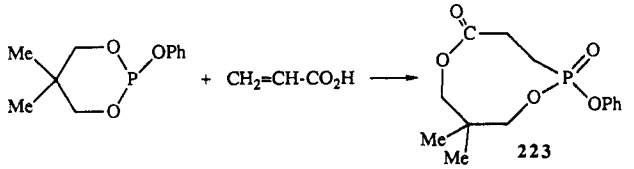


temperature.[319] The reaction is reversible since the monomer is regenerated by the action of heat. The first step of the oligomerization is the formation of dimers **214**[305,320] which exist in two diastereoisomeric forms.[320] Reaction with sulfur allows to isolate diastereoisomers **215′** and **215″** (Scheme 85).

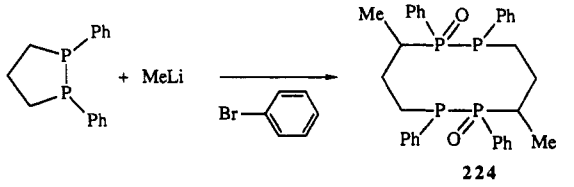
The bicyclic derivative **216** also undergoes a dimerization at room temperature.[321] However, in contrast to the above reports, only one isomer is obtained. A crystal structure of compound **217** establishes that this compound is formed by rupture and reformation of two P–O bonds.[322] The orientation of the phosphorus lone pairs is *trans* relative to the mean plane of the 10-membered ring. The same orientation is also observed in the P^{IV} derivative **218**[323] (Scheme 86).

Ring opening does not always occur by spontaneous reaction but may also be induced by addition of an external reagent. Cyclic phosphonites **219** add at the exocyclic carbon center of the *O*-quinoïdal form of benzothiete, leading to the zwitterionic intermediates **220a–e**.[324,325] The type of rearrangement of these intermediates depends on the phosphonite used. The *o*-xylylene derivative **219e** induces an intramolecular rearrangement of **220e** leading to **221e**, whereas the rearrangement of intermediates **220a–d** requires a second molecule of benzothiete, leading to the macrocycles **222a–d** (Scheme 87).[324,325]

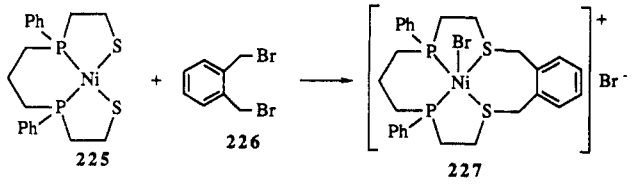
Scheme 88



Scheme 89



Scheme 90



A similar mechanism is proposed to explain the formation of the nine-membered ring phosphonate **223** obtained in better than 50% yield in the reaction of phenyl neopentane-diyl phosphite with acrylic acid (Scheme 88).[326]

Ring opening of 1,2-diphenyl-1,2-diphospholane with methyl lithium and subsequent reaction with bromobenzene surprisingly affords the 10-membered heterocycle **224** in 76% yield (Scheme 89).[327]

IV. Template Reactions

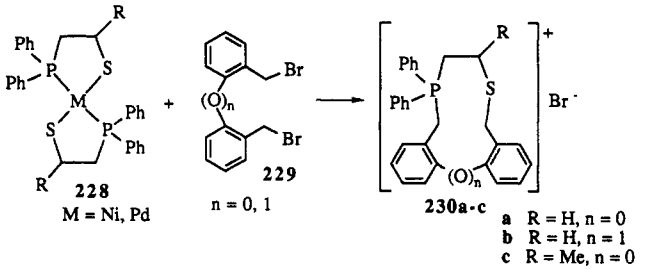
A. Cyclization at a Substituent of Phosphorus

The multistep synthetic routes used for the synthesis of macrocycles incorporating a C–P–C linkage are often successfully replaced by template syntheses. The cyclization may occur either at phosphorus or at a substituent of phosphorus. This is the case for the first phosphorus macrocyclic complex synthesized by exploiting the template effect, **227**, which was prepared by alkylation of the nickel complex of the tetradentate mercaptophosphine **225** with dibromoxylene **226** (Scheme 90).[328]

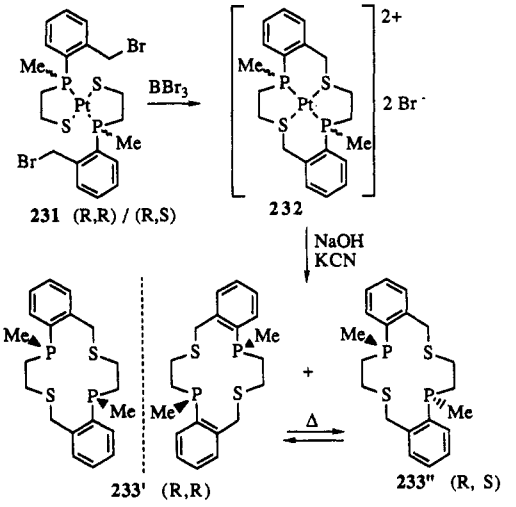
An analogous reaction carried out with the nickel or palladium complex **228** and **226** results in the formation of a free eight-membered cyclic phosphonium, whereas the dibromo derivatives **229** leads to the 10- and 11-membered macrocyclic salts **230a–c** in good yield (54–78%) (Scheme 91).[328]

Treatment of an equimolar mixture of the (*R*,*R*) and (*R*,*S*) diastereoisomers of **231** with boron tribromide induces an intramolecular cyclization at sulfur. Decomplexation of the resulting macrocyclic complex **232** is achieved with sodium hydroxide and potassium cyanide. The racemic (*R*,*R*) diastereoisomers **233′** and the meso (*R*,*S*) diastereoisomer **233″** of the resulting free diphosphorus macrocycle are obtained in very low yield, 1% and 0.5% respectively. Heating a pure sample of **233′** results in the formation of a mixture of **233′** and

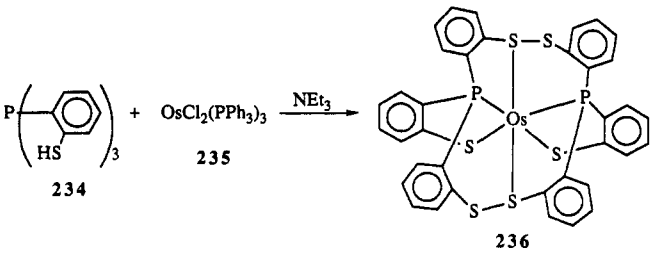
Scheme 91



Scheme 92



Scheme 93



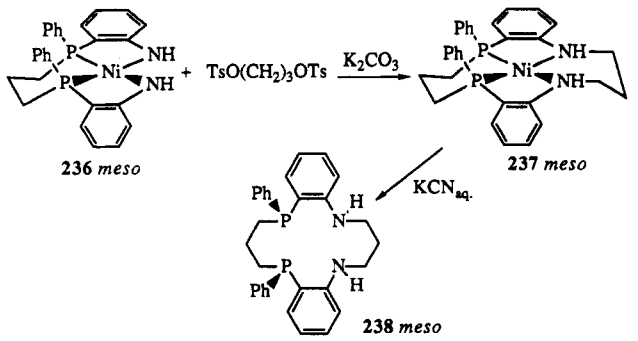
233″, as a consequence of the epimerization at phosphorus (Scheme 92).[329]

Another example of cyclization at sulfur is observed for the hexadentate macrocyclic complex **236**. This complex is formed by the oxidative coupling of S–H group via disulfide bonds obtained by reaction of tris(mercapto phenyl)phosphine (**234**) with the osmium complex **235**. An X-ray structure determination of **236** confirms the formation of a 14-membered macrocycle with thiolate arms (Scheme 93).[330]

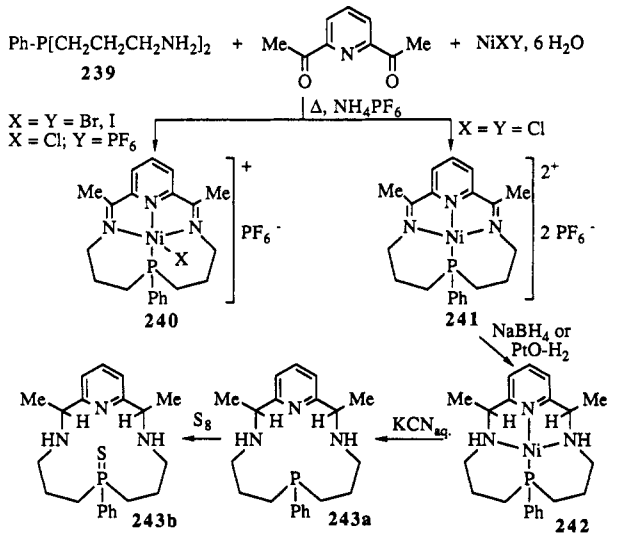
Cyclizations at nitrogen using template reactions are rarely used for the synthesis of phosphorus macrocycles. However, this method has been applied in the reaction of the neutral amidonickel complex **236** with propane-1,3-diyl ditoluene-*p*-sulfonate. This *meso* complex undergoes a facile cyclization reaction. The retention of the *meso* configuration in the complex **237** and in the free macrocycle **238**, obtained with aqueous potassium cyanide, is confirmed by X-ray structure determinations of both compounds (Scheme 94).[331]

In situ cyclocondensations of diamines with dialdehydes or diketones in the presence of metal ions is an important way of synthesizing of macrocycles, which has been applied to phosphorus macrocycles. For

Scheme 94



Scheme 95

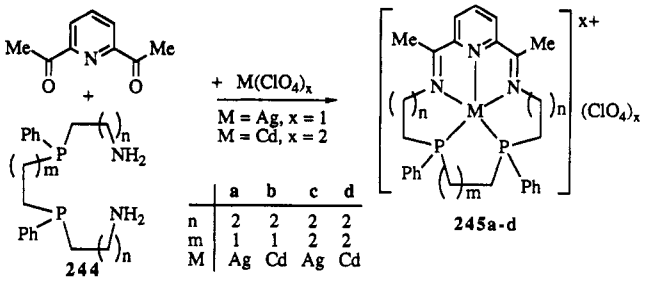


instance, heating the diaminophosphine **239**, diacetyl pyridine, and NiXY and then adding NH_4PF_6 generally produces the pentacoordinate nickel complexes **240**, whereas reaction with $NiCl_2$ results in the formation of the tetracoordinate macrocyclic complex **241**. Reduction of **241** is accomplished with both $NaBH_4$ and PtO–H_2. The free reduced ligand **243a** is prepared after displacement from the coordination sphere of nickel in **242** by cyanide ions in water. The generation of the free ligand is confirmed by the formation of the phosphine sulfide **243b** after reaction with sulfur (Scheme 95).[332]

The synthesis of a macrocyclic complex strongly depends on the length of the phosphinodiamine and the metal used. Reactions of diphosphinodiamines of type **244** ($n = 1, 2$; $m = 1, 2$) with diacetylpyridine were carried out with perchlorates of Mn^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Ag^{+}. However, macrocyclic complexes **245** have been formed and isolated only in the presence of Ag^{+} or Cd^{2+} and for the two longest chain diphosphinodiamines (Scheme 96). The corresponding tetraphenylborate derivatives of complexes **245** are obtained by metathesis.[333]

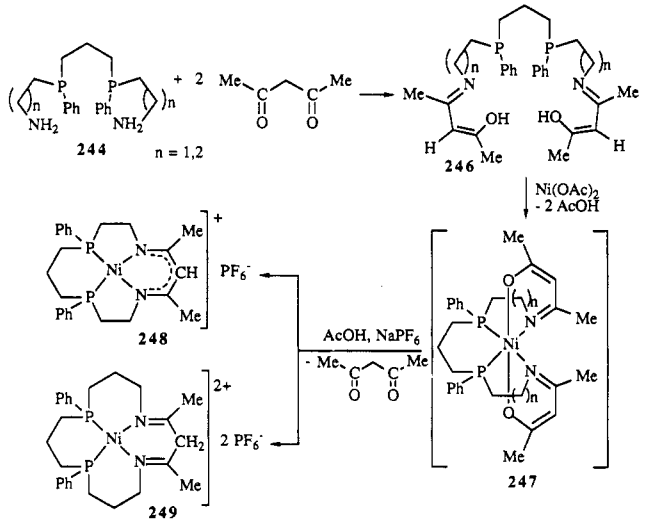
The type of diketone used also influences the *in situ* condensation reaction. Attempted syntheses of macrocyclic complexes by reaction of the diphosphinodiamines **244** with acetylacetone and nickel acetate proved unsuccessful. However, complexes **248** and **249** are obtained by a two-step process, which requires first the synthesis of the Schiff base ligand **246**. Addition of nickel acetate presumably leads to the hexacoordinate

Scheme 96



	a	b	c	d
n	2	2	2	2
m	1	1	2	2
M	Ag	Cd	Ag	Cd

Scheme 97



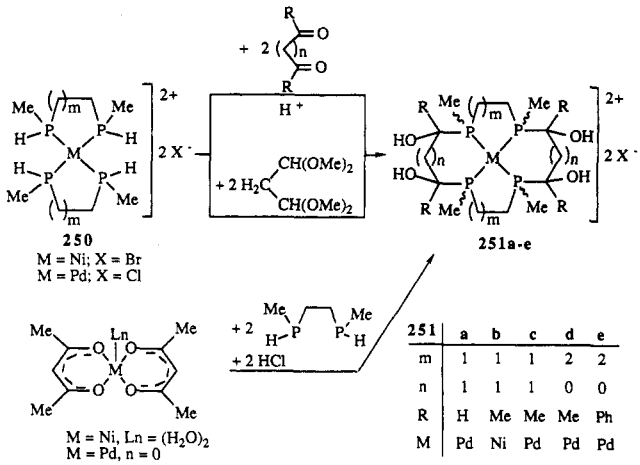
Schiff base Ni complex **247**, although this species has never been isolated. Acetic acid and $NaPF_6$ induce an intramolecular rearrangement of **247** and yield two different complexes, **248** and **249**, depending on the chain length. The 14-membered macrocyclic complex is isolated in the dienato form **248**, while the 16-membered ring is obtained in the diene form **249**. X-ray structure analysis of **249** shows the formation of the *meso* isomer (Scheme 97).[334,335]

B. Cyclization at Phosphorus

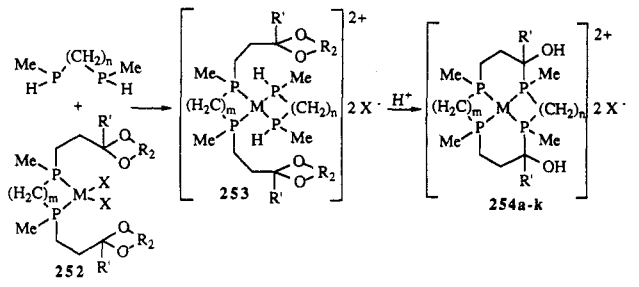
Carbonyl compounds may undergo the addition of secondary phosphine complexes to yield compounds which contain OH groups in the α position relative to phosphorus. Thus, the 2-fold-substituted nickel or palladium complexes of disecondary phosphines **250** are converted into the macrocyclic complexes **251** by reaction with α- or β-dicarbonyl derivatives (Scheme 98).[336,337]

The conversion **250** + diketone → **251** only operates when a 14-membered ring is produced. When $m = 1$, the reaction of complex **250** with biacetyl ($n = 0$) only gives ill-defined products, and no reaction occurs between complex **250** ($m = 2$) and acetylacetone ($n = 1$). However, macrocyclic complexes **251b–e** are isolated by reaction of complexes **250** with diketones. In all cases, **251** is formed principally as a mixture of only two isomers although eight chiral centers, four C and four P, exist in these molecules. Both isomers are isolated in pure form for compound **251c** and characterized by X-ray diffraction. In both isomers, the OH groups occupy the axial position, and for one isomer, all the methyl groups on phosphorus are in the *cis*

Scheme 98



Scheme 99



position, in contrast to the situation for the other isomer.[336,337]

Compounds **251b,c** may also be prepared by reaction of palladium or nickel acetylacetonate with a disecondary phosphine and HCl. In this reaction, only one isomer is obtained for **251c**, but two isomers are obtained for **251b**. A related macrocyclic complex **251a** is formed in the reaction of **250** with malonaldehyde tetramethyl acetal and traces of HCl to convert the acetal used into aldehyde accessible for the addition of the P–H bonds. Several configurational isomers of complex **251a** are formed in this reaction.[337]

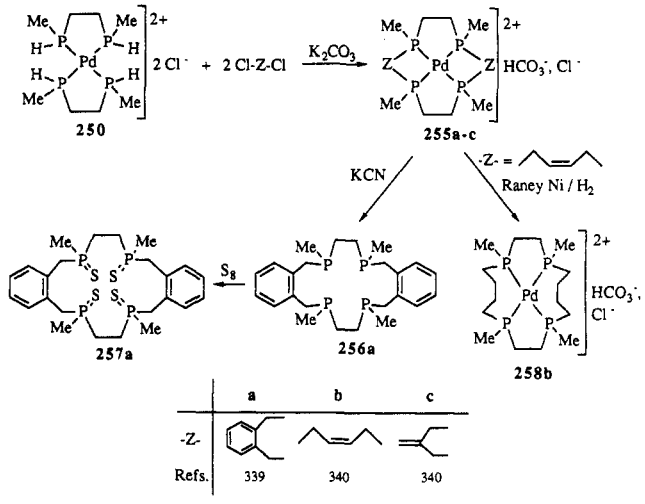
An analogous reaction is observed in the stepwise ring closure of the intermediate acetal or ketal complexes **253**, obtained by replacement of the halogens X of complexes **252** by bis(secondary phosphines).[338] The influence of metal ions in ring closure reactions is again exemplified in this reaction. Indeed, zinc complexes react very slowly and lead to ill-defined compounds, whereas nickel, palladium, and platinum complexes give macrocyclic complexes **254a–k**, obtained in good yields as a mixture of diastereoisomers. A total of 20 diastereoisomers may result from the six centers of chirality; however, in most cases, the number of diastereoisomers obtained, deduced from ^{31}P NMR spectra, is lower. The best result, observed with the palladium complex **254f** (3 diastereoisomers) may be due to the close fit of the 14-membered ring to Pd(II) (Scheme 99, Table 9): Complexes **254a–k** are extraordinarily stable. They are not replaced by cyanide ions, even on heating in concentrated solutions of aqueous KCN.[338]

The 2-fold-substituted palladium complex of disecondary phosphine **250** may also serves as precursor in cyclocondensation reactions with dichlorides in the presence of K_2CO_3. A mixture of three diastereoisomers

Table 9. Compounds 254a–k

254	(O–R$_2$–O)	R′	M	X	*m*	*n*	no. of isomers obtained
a	$(EtO)_2$	H	Ni	Cl	2	2	undefined
b	$(EtO)_2$	H	Ni	Cl	2	3	undefined
c	$(EtO)_2$	H	Pd	Cl	2	2	undefined
d	$(EtO)_2$	H	Pd	Cl	2	3	6
e	$O(CH_2)_2O$	Me	Ni	Br	2	3	4
f	$O(CH_2)_2O$	Me	Pd	Cl	2	2	3
g	$O(CH_2)_2O$	Me	Pd	Cl	2	3	6
h	$O(CH_2)_2O$	Me	Pt	Cl	2	2	4
i	$O(CH_2)_2O$	Me	Pt	Cl	2	3	6
j	$O(CH_2)_2O$	Me	Pd	Cl	3	2	5
k	$O(CH_2)_2O$	Me	Pd	Cl	3	3	undefined

Scheme 100



is obtained for **255a**, among which the pure *syn* (*R,S,R,S*) is isolated and characterized by X-ray diffraction. Treatment of **255a** with KCN induces the release of the free macrocyclic ligand **256a** which may be transferred to another metal or sulfurized (Scheme 100).[339]

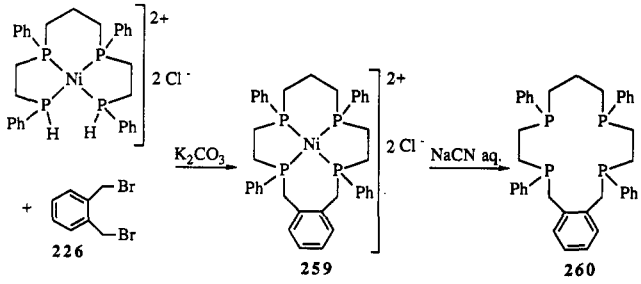
An exchange reaction of anions in complex **255a** proceeds with HCl or NH_4PF_6, and the metallic center may be oxidized to Pd(IV) with H_2O_2 and then reduced again to Pd(II) with KCN.[339] Compounds **255** are obtained in good yields (up to 99%) when the Z group is an unsaturated chain, but no reaction is observed with saturated links such as $Cl(CH_2)_nCl$ (n = 3, 4).[340] However, a saturated complex **258b** may be synthesized, but not isolated, by reaction of complex **255b** with Raney nickel.[340]

Dibromides such as **226** also undergo cyclocondensation reactions with disecondary phosphine complexes. In fact, complex **259** represented the first example of a template reaction involving a phosphine ligand at the reaction center.[341] The chlorine anions may be exchanged with BF_4^- or SCN^- by metathetical reactions, and the uncomplexed macrocycle **260** is obtained by reaction with aqueous NaCN (Scheme 101).[341,342]

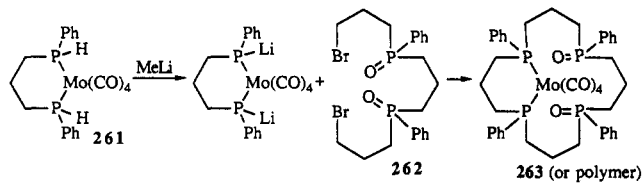
Methyllithium may be used as a base instead of potassium carbonate. Thus, the macrocyclic complex **263** is presumably obtained by reaction of complex **261** first with methyl lithium and then with the phosphorus dibromo derivative **262**. However, complex **263** is not fully characterized and might be a polymer (Scheme 102).[343]

Elimination of lithium halide also occurs in the reaction of complex **264** (X = Li) with chlorophosphines.

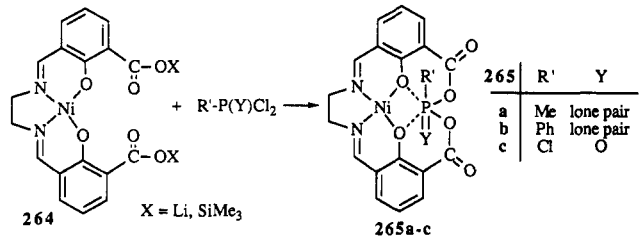
Scheme 101



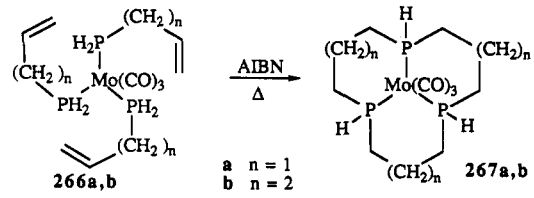
Scheme 102



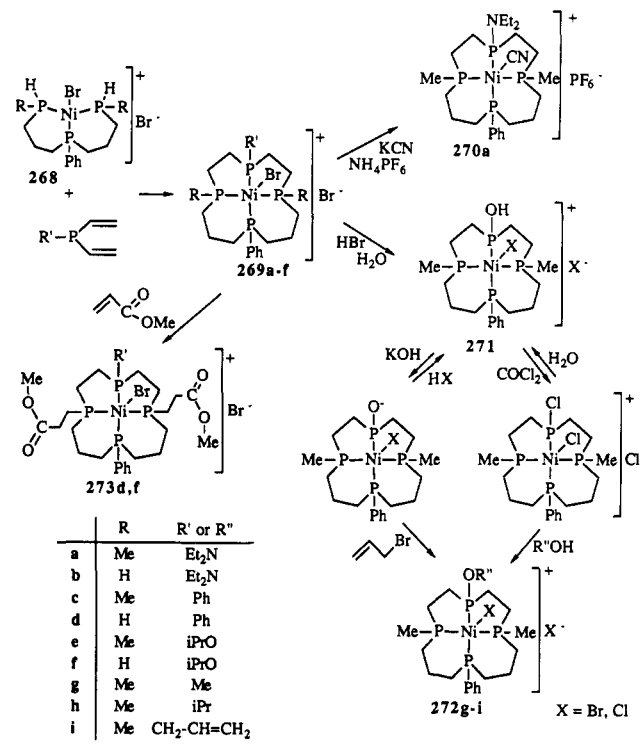
Scheme 103



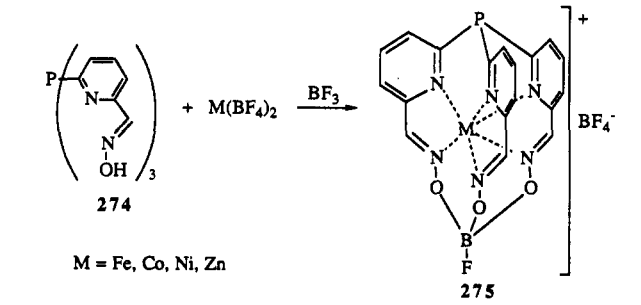
Scheme 104



Scheme 105



Scheme 106



The resulting macrocyclic complexes **265a–c** are also obtained in better yield starting from the silyl derivative **264** (X = $SiMe_3$) (Scheme 103).[344]

The last type of synthesis taking advantage of template effect concerns the P–H bond addition across carbon–carbon double bonds. This reaction may be promoted under photolytic conditions but it is best induced by azobis(isobutyronitrile) (AIBN) as free radical initiator. The triphosphino macrocyclic complexes **267a,b** are thus obtained in good yield. An X-ray structure determination of **267a** shows that the formation of this complex involves anti-Markovnikov P–H bond addition across C=C bonds of allyl groups (Scheme 104).[345,346]

If the reaction is carried out with the disecondary phosphine complex **268** and a divinylphosphine, the first step is the coordination of the later compound to nickel, followed by a rapid addition of the P–H moieties to the vinyl group.[347] No activation is needed in this case to obtain 14-membered macrocyclic complexes **269a–f**, generally as a mixture of four diastereoisomers.[348] A metathetical reaction with KCN and NH_4PF_6 affords four isomers from which one is isolated and characterized by X-ray crystallography.[348]

The presence of functional groups such as NEt_2 or H on phosphorus allows a variety of modifications. Thus, complex **269a** reacts with water and HBr to yield complex **271** which is the starting reagent for the synthesis of other functional complexes **272g–i**. These complexes are obtained by two methods, either deprotonation of the P–OH function followed by addition of allyl bromide, or transformation of the P–OH function into P–Cl followed by reaction with alcohols. Macrocyclic diesters **273d,f** are formed by addition of the P–H functions of complexes **269d,f** to the double bond of methyl acrylate (Scheme 105).[348]

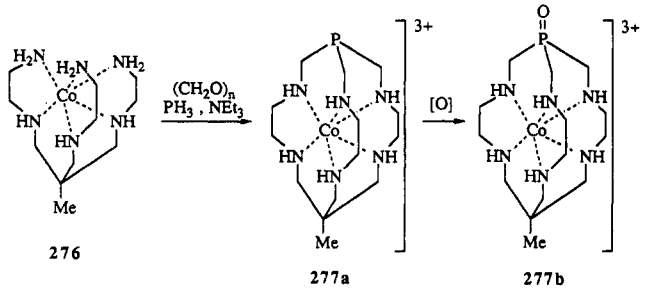
V. Cryptands and Polymacrocyclic Compounds

In contrast to carbon and nitrogen cryptands and macrobicycles which constitute the now well-known classes of compounds (see for instance ref 7), phosphorus cryptands are still rare, despite the fact that the first one was obtained in 1970.[349]

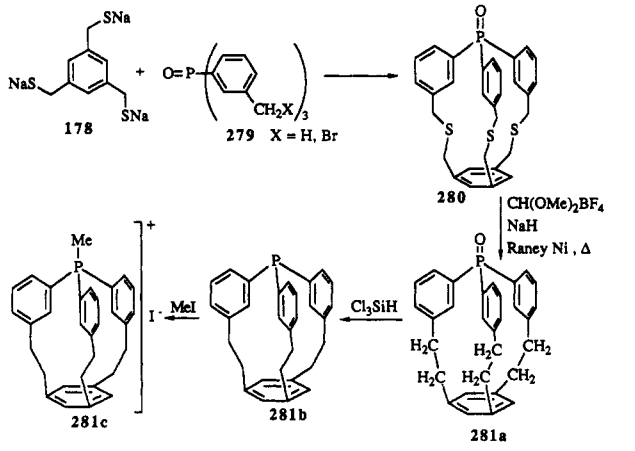
Indeed, the template reaction of the tris(pyridyl)phosphine **274**, first with $M(BF_4)_2$ and then with boron trifluoride, led to a series of monophosphorus cryptates **275** of iron, cobalt, nickel, and zinc whose magnetic properties were described (Scheme 106).[349] The structure of the nickel complex has been confirmed by X-ray diffraction.[350]

After this pioneering work, only about 10 publications have appeared, almost all of them being published over

Scheme 107



Scheme 108



the last five years. Several patents also report the preparation of phosphorus cryptands. Nevertheless, reading them carefully, it appears difficult to know exactly the type of compound really obtained, so they will not be mentioned here.

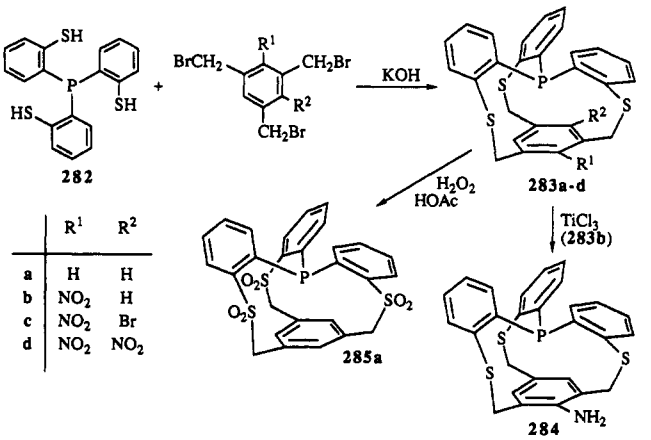
An encapsulation process was used to synthesize the cage complexes **277a,b** starting from the cobalt complex **276**, paraformaldehyde, phosphine, and triethylamine.[351] The phosphine oxide derivative **277b**, whose structure was established by X-ray studies, arises from the oxidation of **277a** during work up (Scheme 107).[351]

High dilution coupling of the trismercapto sodium salt **278** and the phosphine oxide **279** affords the cyclophane **280** in 17% yield after purification.[352] Desulfurization then reduction of the phosphine oxide **281a** gave the phosphacyclophane **281b** which underwent a fast enantiomerization, as shown by the sharp singlet for the methylene protons in ^{1}H NMR spectrum (Scheme 108).[352]

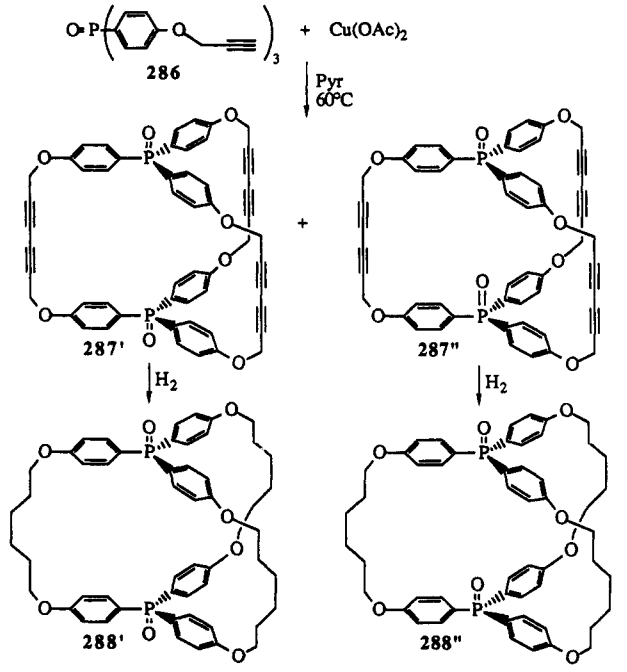
The easy reaction of the phosphacyclophane **281b** with methyl iodine, giving **281c**, and the complexation with $PdCl_2(PhCN)_2$ indicate that the phosphorus lone pair is readily available, presumably due to an *out* geometry of the cyclophane (pyramidalization of the phosphine out from the cyclophane).[352]

In contrast, the phosphacyclophanes **283a–d** have *in* geometries proved by X-ray crystallographic analysis for compounds **283a**,[353,354] the dinitro derivative **283d**, and the amino-substituted cryptand **284**.[355] Phosphacyclophanes **283a–d** are prepared in low yield by addition of KOH to a refluxing solution of the trismercapto phosphine **282** and α,α',α''-tribromomesitylene derivatives under conditions of high dilution. Treatment of **283b** with $TiCl_3$ allows the reduction of the nitro group and gives the aminophosphacyclophane **284** (Scheme 109).[355]

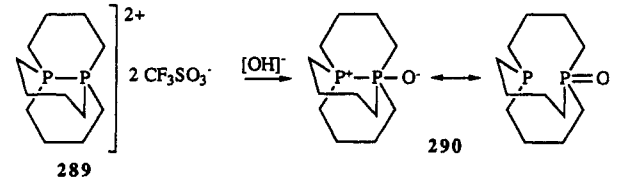
Scheme 109



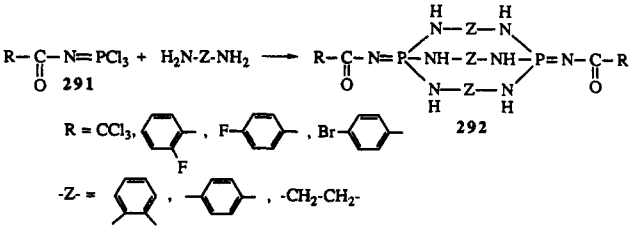
Scheme 110



Scheme 111

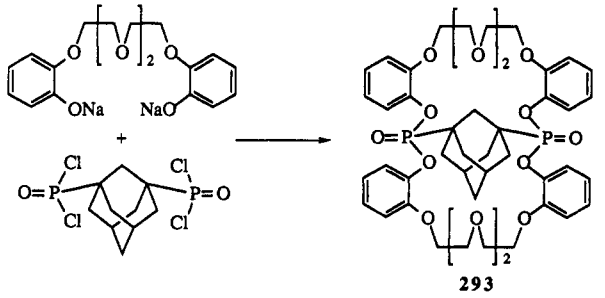


Scheme 112

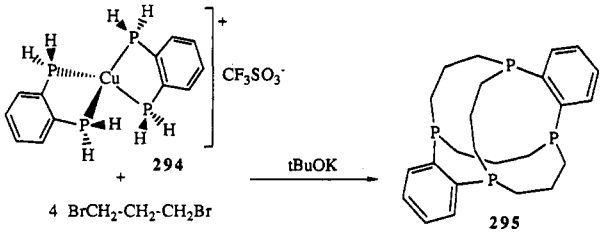


The phosphorus of **283a** is remarkably unreactive, presumably due to steric encumbrance induced by the *in* geometry. Heating compound **283a** in refluxing acetic acid and hydrogen peroxide yields only the corresponding trisulfone **285a**. Moreover, the phos-

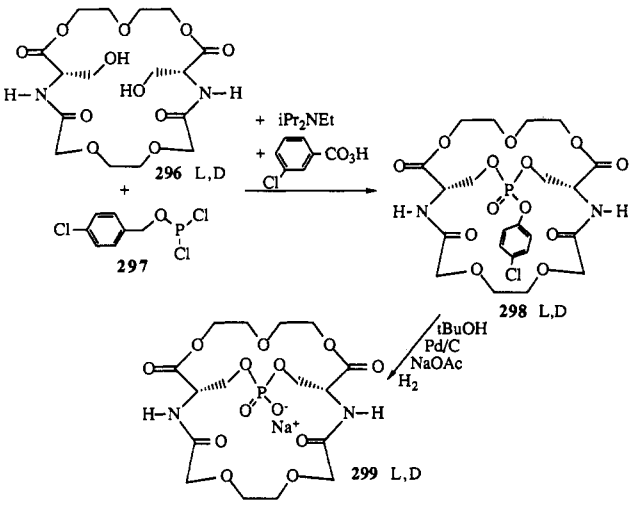
Scheme 113



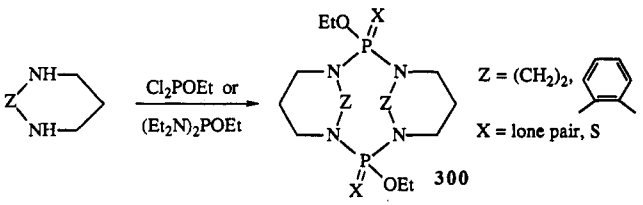
Scheme 114



Scheme 115



Scheme 116



Scheme 117

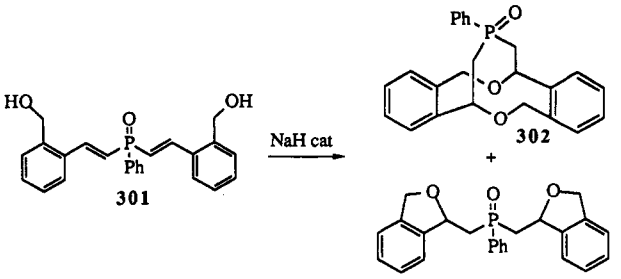


Table 10. Macrocycles Characterized by X-ray Structural Studies

macrocycles	ref(s)	macrocycles or cryptands	ref(s)
1a	11	**122e** (n = 6)	209–211
1d	11	**122e** (n = 8)	212
1e	11	**123e** (n = 5)	218
1n	11	**123e** (n = 6)	219
2a (2 isomers)	9,13	**123e** (n = 7)	216
2b	13,17	**123e** (n = 8)	220
2c	13	**123e** (n = 9)	217
2d	13	**123e** (n = 10)	217
16a (2 isomers)	41	**123e** (n = 11)	217
16b	41	**123e** (n = 12)	217
17d	43	**126b**	229,231
21	46	**126c**	229,233
22	46	**126e**	229,235,236
24a	47	**127a**	238
24d	47	**127d**	240
26d	47	**128a**	229,241
28b (P=O)	50	**128b**	229,241
48	70	**129a**	242
52a	73	**129c**	229,231
53 (*cis* and *trans*)	74	**129d**	229,233
59bf	78	**130**	229,243
60p	89	**131b**	229,246
60r	82	**135c**	255
67c	113	**138c**	256
67g	106	**150a**	269
67l	103	**150g**	269
67n	104	**171a**	282
67o	102	**173**	284
67p	105	**195″d**	304
69	108	**195′k**	309
81	130	**212d**	317
85	132,134	**217**	322,323
98	146	**218**	323
104	154	**238**	331
111b	161,162	**283a**	353,354
120a (n = 5)	196,197	**283d**	355
120b (n = 5)	198	**284**	355
120c (n = 5)	195	**287′**	356,357
121e (n = 6)	205	**287″**	356
121e (n = 8)	204	**288″**	356,357

phine remains essentially unprotonated after bubbling HBr into a solution of **283a**.[354]

Phosphine oxide bifunctional cryptands have been obtained by dimeric coupling of the tris propargylphosphine oxide **286** induced by copper(II) acetate. *exo,exo*-**287′** and *exo,endo*-**287″** cryptands are isolated in 14 and 7%, respectively.[356,357] Hydrogenation of cryptands **287′** and **287″** specifically provides the reduced cryptands **288′** and **288″** (Scheme 110).

Surprisingly, studies of the complexation properties of these diphosphine oxide cryptands toward various neutral organic guests show that initial *exo* complexation of the phosphoryl group is the preferred mechanism for **288″** while initial *endo* complexation is preferred for **287″**. This different behavior may be due to changes in the host cavity, but is not directly related to the phosphorus–phosphorus distance which is similar in both compounds: 5.68 and 6.15 Å for **287″** and **288″**, respectively.[357]

These values preclude any phosphorus–phosphorus interaction in **287″** and **288″** in contrast to compound **290** which has some P···P bonding, according to ^{31}P NMR (Scheme 111).[358]

Another type of diphosphorus cryptand, **292**, is prepared in 68–73% yield by reaction of the trichloro derivative **291** with various diamines (Scheme 112).[76]

The cryptand **293** is obtained in 31% yield, together with the macrobicyclic derivative **77**, in the reaction of a diphenoxy sodium salt with adamantanediphosphonic dichloride (Scheme 113).[116,128]

Finally, two special types of phosphorus cryptands are to be noticed. The first one is the tetrahedral cage **295** which is isolated in 50% yield after alkylation of the complex **294** with 1,3-dibromo propane (Scheme 114).[359]

The last type of cryptand to be mentioned are compounds in which the phosphorus atom is not the "node" of the cryptand. Reaction of the L,D macrocycle **296** with the phosphorodichloridite **297** gives the L,D cryptand **298** in 31% yield, whereas the L,L cryptand is impossible to obtain by the same way starting from the L,L macrocyclic precursor (Scheme 115).[360] Hydrogenolysis of the chlorobenzyl group affords the sodium salt **299**.

Reaction of benzodiazacycloheptene with Cl_2POEt or $(Et_2N)_2POEt$ gives the dimer **300** which is treated with sulfur to give the corresponding disulfide (Scheme 116). Similar reactions are also carried out with 1,4-diazacycloheptane.[361]

Both "crisscross" and "normal" intramolecular addition reactions, induced by catalytic amounts of NaH, are observed with the bis(hydroxymethyl) derivative **301**, resulting in the formation of the polycyclic compound **302** in 55% yield (Scheme 117).[362]

VI. References

(1) Stokes, H. N. *Am. Chem. J.* **1897**, *19*, 782.
(2) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(3) Markovskii, L. N.; Kal'chenko, V. I. *Zh. Vses. Khim. O-va. im. D.I. Mendeleeva* **1985**, *30*, 528.
(4) Tsvetkov, E. N.; Bovin, A. N.; Syundyukova, V. K. *Usp. Khim.* **1988**, *57*, 1353; *Russ. Chem. Rev.* **1988**, 776.
(5) Sinyavskaya, E. I. *Koord. Khim.* **1986**, *12*, 1155.
(6) Kabachnik, M. I.; Polikarpov, Y. M. *Zh. Obsch. Khim.* **1988**, *58*, 1937; *J. Gen. Chem. SSSR* **1988**, *58*, 1729.
(7) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721.
(8) Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053.
(9) Davis, R. E.; Hudson, C. W.; Kyba, E. P. *J. Am. Chem. Soc.* **1978**, *100*, 3642.
(10) Kyba, E. P.; Chou, S. S. P. *J. Chem. Soc., Chem. Commun.* **1980**, 449.
(11) Kyba, E. P.; John, A. M.; Brown, B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139.
(12) Kyba, E. P.; Chou, S. S. P. *J. Am. Chem. Soc.* **1980**, *102*, 7012.
(13) Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, S. T.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *103*, 3868.
(14) Fox, M. A.; Campbell, K. A.; Kyba, E. P. *Inorg. Chem.* **1981**, *20*, 4163.
(15) Kyba, E. P.; Chou, S. S. P. *J. Org. Chem.* **1981**, *46*, 860.
(16) Kyba, E. P.; Liu, S. T. *Inorg. Chem.* **1985**, *24*, 1613.
(17) Kyba, E. P.; Clubb, C. N.; Larson, S. B.; Schueler, V. J.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 2141.
(18) Märkl, G.; Hoferer, M. *Tetrahedron Lett.* **1992**, *33*, 3621.
(19) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1980**, 177.
(20) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *Inorg. Chim. Acta* **1980**, *45*, L239.
(21) Ciampolini, M.; Dapporto, P.; Dei, A.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1982**, *21*, 489.
(22) Dapporto, P.; Ciampolini, M.; Nardi, N.; Zanobini, F. *Inorg. Chim. Acta* **1983**, *76*, L153.
(23) Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1983**, *22*, 13.
(24) Ciampolini, M.; Nardi, N.; Zanobini, F.; Cini, R.; Orioli, P. L. *Inorg. Chim. Acta* **1983**, *76*, L17.
(25) Mangani, S.; Orioli, P. L.; Ciampolini, M.; Nardi, N.; Zanobini, F. *Inorg. Chim. Acta* **1984**, *85*, 65.
(26) Ciampolini, M.; Nardi, N.; Dapporto, P.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* **1984**, 995.
(27) Ciampolini, M.; Nardi, N.; Dapporto, P.; Innocenti, P.; Zanobini, F. *J. Chem. Soc. Dalton Trans.* **1984**, 575.
(28) Ciampolini, M.; Nardi, N.; Orioli, P. L.; Mangani, S.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* **1984**, 2265.
(29) Mealli, C.; Sabat, M.; Zanobini, F.; Ciampolini, M.; Nardi, N. *J. Chem. Soc., Dalton Trans.* **1985**, 479.
(30) Ciampolini, M.; Nardi, N.; Orioli, P. L.; Mangani, S.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* **1985**, 1179.
(31) Ciampolini, M.; Nardi, N.; Orioli, P. L.; Mangani, S.; Zanobini, F. *J. Chem. Soc., Dalton Trans.* **1985**, 1425.
(32) Ciampolini, M. *Pure Appl. Chem.* **1986**, *58*, 1429.
(33) Wei, L.; Bell, A.; Warner, S.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 8302.
(34) Wei, L.; Bell, A.; Ahn, K. H.; Holl, M. M.; Warner, S.; Williams, I. D.; Lippard, S. J. *Inorg. Chem.* **1990**, *29*, 825.
(35) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567.
(36) Bodrin, G. V.; Polikarpov, Y. M.; Medved, T. Y.; Kabachnik, M. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1978**, 1930; *Bull. Acad. Sci. SSSR* **1979**, 1700.
(37) Kaplan, L. J.; Weisman, G. R.; Cram, D. J. *J. Org. Chem.* **1979**, *44*, 2226.
(38) Tsvetkov, E. N.; Kron, T. E.; Sinyavskaya, E. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1986**, 2456.
(39) Van Zon, A.; Torny, G. J.; Frijns, J. H. G. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 326.
(40) Widhalm, M. *Monatsch. Chem.* **1990**, *121*, 1053.
(41) Widhalm, M.; Kratky, C. *Chem. Ber.* **1992**, *125*, 679.
(42) Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1974**, *39*, 1748.
(43) Dräger, M. *Chem. Ber.* **1974**, *107*, 3246.
(44) (a) Vincens, M.; Gong-Cheng, F.; Grimaldo-Möron, J. T.; Vidal, M. *Tetrahedron Lett.* **1988**, *29*, 6247. (b) Toulhoat, C.; Vincens, M.; Vidal, M. *Bull. Soc. Chim. Fr.* **1993**, *130*, 647.
(45) Toulhoat, C.; Vidal, M.; Vincens, M. *Phosphorus, Sulfur Silicon* **1993**, *78*, 119.
(46) Savage, P. B.; Desper, J. M.; Gellman, S. H. *Tetrahedron Lett.* **1992**, *33*, 2107.
(47) Savage, P. B.; Holmgren, S. K.; Gellman, S. H. *J. Am. Chem. Soc.* **1993**, *115*, 7900.
(48) Savage, P. B.; Holmgren, S. K.; Desper, J. M.; Gellman, S. H. *Pure Appl. Chem.* **1993**, *65*, 461.
(49) Smith, R. J.; Powell, A. K.; Barnard, N.; Dilworth, J. R.; Blower, P. J. *J. Chem. Soc., Chem. Commun.* **1993**, 54.
(50) Jurkschat, K.; Uhlig, W.; Mügge, C.; Tzschach, A.; Schmidt, B.; Dräger, M. *Z. Anorg. Allg. Chem.* **1988**, *556*, 161.
(51) Schwabacher, A. W.; Zhang, S.; Davy, W. *J. Am. Chem. Soc.* **1993**, *115*, 6995.
(52) Van Reijendam, J. W.; Baardam, F. *Tetrahedron Lett.* **1972**, 5181.
(53) Benhamou, M.; Kraemer, R.; Germa, H.; Majoral, J. P.; Navech, J. *Phosphorus Sulfur* **1982**, *14*, 105.
(54) Navech, J.; Kraemer, R.; Majoral, J. P. *Tetrahedron Lett.* **1980**, *21*, 1449.
(55) Scott, L. T.; Unno, M. *J. Am. Chem. Soc.* **1990**, *112*, 7823.
(56) Ellermann, J.; Poersch, F.; Kunstmann, R.; Kramolowsky, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 203.
(57) Allen, D. W.; Mann, F. G.; Millar, I. T. *Chem. Ind.* **1966**, 196.
(58) Allen, D. W.; Millar, I. T.; Mann, F. G. *J. Chem. Soc. C* **1967**, 1869.
(59) Horner, L.; Kunz, H.; Walach, P. *Phosphorus* **1975**, *6*, 63.
(60) Venkataramu, S. D.; El-Deek, M.; Berlin, K. D. *Tetrahedron Lett.* **1976**, 3365.
(61) Horner, L.; Walach, P.; Kunz, H. *Phosphorus Sulfur* **1978**, *5*, 171.
(62) Christol, H.; Cristau, H. J.; Fallouh, F.; Hullot, P. *Tetrahedron Lett.* **1979**, 2591.
(63) Cristau, H. J.; Chiche, L.; Fallouh, F.; Hullot, P.; Renard, G.; Christol, H. *Nouv. J. Chim.* **1984**, *8*, 191.
(64) Vincens, M.; Grimaldo-Möron, J. T.; Pasqualini, R.; Vidal, M. *Tetrahedron Lett.* **1987**, *28*, 1259.
(65) Vincens, M.; Grimaldo-Möron, J. T.; Vidal, M. *Tetrahedron* **1991**, *47*, 403.
(66) Toulhoat, C.; Vincens, M.; Vidal, M. *C. R. Acad. Sci. Paris, Ser. 2* **1991**, *313*, 1399.
(67) Gomelya, N. D.; Feshchenko, N. G. *Zh. Obshch. Khim.* **1988**, *58*, 2652.
(68) Pilgram, K.; Korte, F. *Tetrahedron* **1963**, *19*, 137.
(69) Naidu, M. S. R.; Bull, E. O. J.; Prasad, M. V. S. R. *J. Indian Chem. Soc.* **1992**, *69*, 409.
(70) Hope, H.; Viggiano, M.; Moezzi, B.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 2550.
(71) Dutasta, J. P.; Simon, P. *Tetrahedron Lett.* **1987**, 3577.
(72) Dutasta, J. P.; Simon, P. *Phosphorus, Sulfur Silicon* **1990**, *51*, 363.
(73) Dutasta, J. P.; Van Oostenrick, L.; Tinant, B.; Declercq, J. P. *Phosphorus, Sulfur Silicon* **1993**, *75*, 63.
(74) Dutasta, J. P.; Declercq, J. P.; Esteban-Calderon, C.; Tinant, B. *J. Am. Chem. Soc.* **1989**, *111*, 7136.
(75) Cristau, H. J.; Garcia, C. *Synthesis* **1990**, 315.
(76) Rudavskii, V. P.; Zagnibeda, D. M.; Kucherova, M. N. *Farm. Zh. (Kiev)* **1975**, *30*, 47.
(77) Nifant'ev, E. E.; Zavalishina, A. I.; Smirnova, E. I.; Kofanova, N. V. *Zh. Obshch. Khim.* **1984**, *54*, 1207.
(78) Gonce, F.; Caminade, A. M.; Jaud, J.; Vignaux, P.; Majoral, J. P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 237.
(79) Majoral, J. P.; Caminade, A. M. The chemistry of inorganic ring systems. *Studies in Inorganic Chemistry*; Steudel, R., Ed.; Elsevier Science Publ. B.V.: Amsterdam, 1992; Vol. 4, Chapter 12, p 209.
(80) Majoral, J. P.; Badri, M.; Caminade, A. M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1988**, *27*, 3873.

(81) Majoral, J. P.; Badri, M.; Caminade, A. M.; Gorgues, A.; Delmas, M.; Gaset, A. *Phosphorus, Sulfur Silicon* **1990**, *49*, 413.
(82) Badri, M.; Majoral, J. P.; Caminade, A. M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* **1990**, *112*, 5618.
(83) Badri, M.; Majoral, J. P.; Gonce, F.; Caminade, A. M.; Sallé, M.; Gorgues, A. *Tetrahedron Lett.* **1990**, *31*, 6343.
(84) Gonce, F.; Caminade, A. M.; Majoral, J. P. *Tetrahedron Lett.* **1991**, *32*, 203.
(85) Majoral, J. P.; Badri, M.; Caminade, A. M. *Heteroatom Chem.* **1991**, *2*, 45.
(86) Colombo, D.; Caminade, A. M.; Majoral, J. P. *Inorg. Chem.* **1991**, *30*, 3365.
(87) Oussaid, B.; Garrigues, B.; Caminade, A. M.; Majoral, J. P. *Phosphorus, Sulfur Silicon* **1992**, *73*, 41.
(88) Gonce, F.; Caminade, A. M.; Boutonnet, F.; Majoral, J. P. *J. Org. Chem.* **1992**, *57*, 970.
(89) Oussaid, B.; Garrigues, B.; Jaud, J.; Caminade, A. M.; Majoral, J. P. *J. Org. Chem.* **1993**, *58*, 4500.
(90) Oussaid, B.; Garrigues, B.; Caminade, A. M. *Phosphorus, Sulfur Silicon* **1993**, *77*, 322.
(91) Colombo-Khater, D.; Caminade, A. M.; Delavaux-Nicot, B.; Majoral, J. P. *Organometallics* **1993**, *12*, 2861.
(92) Caminade, A. M.; Colombo-Khater, D.; Mitjaville, J.; Galliot, C.; Mas, P.; Majoral, J. P. *Phosphorus, Sulfur Silicon* **1993**, *75*, 67.
(93) Majoral, J. P.; Badri, M.; Caminade, A. M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1991**, *30*, 344.
(94) Benhamou, M.; Majoral, J. P.; Navech, J. *Phosphorus Sulfur* **1981**, *11*, 211.
(95) Engelhardt, U.; Bünger, T. *Z. Anorg. Allg. Chem.* **1984**, *517*, 177.
(96) Kudrya, T. N.; Shtepanek, A. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1978**, *48*, 927; *J. Gen. Chem. SSSR* **1978**, 844.
(97) Kirsanov, A. V.; Zasorina, V. A.; Shtepanek, A. S.; Pinchuk, A. M. *Dokl. Akad. Nauk SSSR* **1981**, *259*, 1112; *Dokl. Chem.* **1982**, 373.
(98) Zasorina, V. A.; Shtepanek, A. S.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1982**, *52*, 1081.
(99) Kudrya, T. N.; Chaikovskaya, A. A.; Rozhkova, Z. Z.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1982**, *52*, 1092.
(100) Pinchuk, A. M.; Zasorina, V. A.; Shtepanek, A. S.; Rozhkova, Z. Z.; Solotonov, A. F.; Raevskii, O. A. *Zh. Obshch. Khim.* **1983**, *53*, 2012.
(101) Chaikovskaya, A. A.; Kudrya, T. N.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1987**, *57*, 671.
(102) Kudrya, T. N.; Tkachev, V. V.; Atovmyan, L. O.; Gubnitskaya, E. S.; Chaikovskaya, A. A.; Pinchuk, A. M. *Zh. Strukt. Khim.* **1991**, *32*, 175.
(103) Tkachev, V. V.; Chaikovskaya, A. A.; Atovmyan, L. O.; Sazonova, G. V.; Kudrya, T. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1987**, 2745.
(104) Raevskii, O. A.; Tkachev, V. V.; Atovmyan, L. O.; Umarova, I. O.; Solotnov, A. F.; Kudrya, T. N.; Chaikovskaya, A. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, 2028.
(105) Malinovskii, S. T.; Kudrya, T. N.; Chaikovskaya, A. A.; Pinchuk, A. M.; Malinovskii, T. I. *Zh. Strukt. Khim.* **1986**, *27*, 163.
(106) Malinovskii, S. T.; Simonov, Y. A.; Kudrya, T. N.; Chaikovskaya, A. A.; Malinovskii, T. I. *Zh. Strukt. Khim.* **1984**, *25*, 130.
(107) Kirsanov, A. V.; Kudrya, T. N.; Shtepanek, A. S. *Zh. Obshch. Khim.* **1980**, *50*, 2452; *J. Gen. Chem. SSSR* **1981**, 1980.
(108) Tkachev, V. V.; Atovmyan, L. O.; Umarova, I. O.; Raevskii, O. A.; Kudrya, T. N.; Pinchuk, A. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1985**, 1775.
(109) Kirsanov, A. V.; Kudrya, T. N.; Balina, L. V.; Shtepanek, A. S. *Dokl. Akad. Nauk SSSR* **1979**, *247*, 613; *Dokl. Chem.* **1980**, 358.
(110) Yatsimirskii, K. B.; Budarin, L. I.; Shtepanek, A. S.; Telyatnik, A. I.; Smirnov, V. A. *Teor. Eksp. Khim.* **1976**, *12*, 421.
(111) Yatsimirskii, K. B.; Bidzilya, V. A.; Golovkova, L. P.; Shtepanek, A. S. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1142; *Dokl. Chem.* **1979**, 78.
(112) Yatsimirskii, K. B.; Korol, E. N.; Golovatyi, V. G.; Kudria, T. N.; Talanova, G. G. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1359; *Dokl. Chem.* **1979**, 89.
(113) Raevskii, O. A.; Umarova, I. O.; Tkachev, V. V.; Atovmyan, L. O.; Shtepanek, A. S.; Kudrya, T. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1986**, 2003.
(114) Yurchenko, R. I.; Klepa, T. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1990**, *60*, 2226.
(115) Yurchenko, R. I.; Yurchenko, V. G.; Klepa, T. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1991**, *61*, 380.
(116) Koodrja, T. N.; Stepanek, A. S.; Yurchenko, R. I.; Tchaikovskaja, A. A.; Lavrova, S. E. *Phosphorus, Sulfur Silicon* **1990**, *51*, 384.
(117) Podgornyi, A. V.; Tolmachev, A. A.; Shtepanek, A. S.; Kudryavtsev, A. A.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1990**, *60*, 2440.
(118) Tolmachev, A. A.; Podgornyi, A. V.; Kostyuk, A. N.; Tsymbal, I. F.; Kozlov, E. S.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1992**, *62*, 1422.
(119) Bradshaw, J. S.; Huszthy, P.; Izatt, R. M. *J. Heterocycl. Chem.* **1986**, *23*, 1673.
(120) Talanova, G. G.; Podgornyi, A. V.; Zasorina, V. A.; Yatsimirskii, K. B. *Dokl. Akad. Nauk SSSR* **1991**, *318*, 347; *Dokl. Chem.* **1991**, 125.
(121) Razumova, N. A.; Evtikhov, Z. H.; Petrov, A. A. *Zh. Obshch. Khim.* **1968**, *38*, 1117; *J. Gen. Chem. SSSR* **1968**, 1072.
(122) Penney, C. L.; Belleau, B. *Can. J. Chem.* **1978**, *56*, 2396.
(123) Bhatia, M. S.; Kaur, B.; Devi, S.; Xavierkutty, M. C. *Indian J. Chem.* **1984**, *23B*, 776.
(124) Bhatia, M. S.; Devi, S.; Jindal, R.; Kaur, B. *J. Indian Chem. Soc.* **1988**, *65*, 275.
(125) Sikder, N.; Vaidyanathaswamy, R. *Indian J. Chem.* **1992**, *31B*, 513.
(126) Pinchuk, A. M.; Podgornyi, A. V.; Zasorina, V. A.; Talnova, G. G.; Shtepanek, A. S. *Dokl. Akad. Nauk Ukr. SSR, Ser. B: Geol. Khim. Biol. Nauki* **1987**, 53.
(127) Yurchenko, R. I.; Yurchenko, V. G.; Podgornyi, A. V. *Zh. Obshch. Khim.* **1991**, *61*, 772.
(128) Chaikovskaya, A. A.; Kudrya, T. N.; Yurchenko, R. I.; Voitsekhovskaya, O. M.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1988**, *58*, 1925.
(129) Moran, J. K.; Roundhill, D. M. *Phosphorus, Sulfur Silicon* **1992**, *71*, 7.
(130) Grynszpan, F.; Aleksiuk, O.; Biali, S. E. *J. Chem. Soc., Chem. Commun.* **1993**, 13.
(131) Munoz, A.; Lamandé, L.; Koenig, M.; Wolf, R.; Brossas, J. *Phosphorus Sulfur* **1981**, *11*, 71.
(132) Dubourg, A.; Roques, R.; Declercq, J. P.; Boyer, D.; Lamande, L.; Munoz, A.; Wolf, R. *Phosphorus Sulfur* **1983**, *17*, 97.
(133) Dubourg, A.; Roques, R.; Garrigues, B.; Boyer, D.; Munoz, A.; Klaébé, A. *C. R. Acad. Sci. Paris, Ser. 2* **1981**, *293*, 757.
(134) Lamandé, L.; Munoz, A.; Boyer, D.; Garrigues, B.; Wolf, R. *Phosphorus Sulfur* **1983**, *18*, 85.
(135) Lamandé, L.; Munoz, A.; Garrigues, B. *Phosphorus Sulfur* **1987**, *30*, 181.
(136) Lamandé, L.; Munoz, A. *Phosphorus Sulfur* **1987**, *32*, 1.
(137) Arbuzov, B. A.; Kadyrov, R. A.; Gnevashev, S. G.; Arshinova, R. P. *Dokl. Akad. Nauk SSSR* **1987**, *295*, 867; *Dokl. Chem.* **1988**, 329.
(138) Arshinova, R. P.; Gnevashev, S. G.; Kadyrov, R. A.; Klochkov, V. V.; Arbuzov, B. A. *Zh. Obshch. Khim.* **1988**, *58*, 2417.
(139) Munoz, A.; Lamandé, L. *Phosphorus, Sulfur Silicon* **1990**, *51*, 380.
(140) Lamandé, L.; Munoz, A. *Phosphorus Sulfur* **1987**, *30*, 459.
(141) Nifant'ev, E. E.; Blokhin, Y. I.; Ergashev, M. Y. *Dokl. Akad. Nauk* **1992**, *325*, 73; *Dokl. Chem.* **1992**, 133.
(142) Markovskii, L. N.; Kal'chenko, V. I.; Sinitsa, A. D.; Serguchev, Y. A.; Negrebetskii, V. V.; Bogel'fer, L. Y. *Dopov. Akad. Nauk Ukr. SSR, Ser. B: Geol. Khim. Biol. Nauki* **1981**, 56.
(143) Kal'chenko, V. I.; Atamas, L. I.; Serguchev, Y. A.; Markovskii, L. N. *Zh. Obshch. Khim.* **1984**, *54*, 1754.
(144) Robert, D.; Gawad, H. A.; Riess, J. G. *Bull. Soc. Chim. Fr.* **1987**, 511.
(145) Andrianov, K. A.; Vasil'eva, T. V.; Kozlova, L. V. *Izv. Akad. Nauk SSSR* **1965**, 381; *Bull. Acad. Sci. SSSR* **1965**, 366.
(146) Newton, M. G.; Haiduc, I.; King, R. B.; Silvestru, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1229.
(147) Von Itzstein, M.; Jenkins, I. D. *J. Chem. Soc. Perkin Trans. 1* **1986**, 437.
(148) Von Itzstein, M.; Jenkins, I. D. *J. Chem. Soc. Perkin Trans. 1* **1987**, 2057.
(149) Imaev, M. G.; Sokolova, S. V.; Felkyaeva, S. D. *Zh. Obshch. Khim.* **1965**, *35*, 742; *J. Gen. Chem. SSSR* **1965**, 741.
(150) Imaev, M. G. *Zh. Obshch. Khim.* **1965**, *35*, 1864; *J. Gen. Chem. SSSR* **1965**, 1857.
(151) Bentrude, W. G.; Johnson, W. D.; Khan, W. A.; Witt, E. R. *J. Org. Chem.* **1972**, *37*, 631.
(152) Powell, J.; Lough, A.; Wang, F. *Organometallics* **1992**, *11*, 2289.
(153) Xu, Y.; Zhang, J. *Tetrahedron Lett.* **1985**, *26*, 4771.
(154) Appel, R.; Hünerbein, J.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 61.
(155) Appel, R.; Hünerbein, J.; Knoch, F.; Korte, S.; Kündgen, U.; Paulen, W.; Zimmermann, R. *Phosphorus Sulfur* **1983**, *18*, 19.
(156) Andriamizaka, J. D.; Escudié, J.; Couret, C.; Satgé, J. *Phosphorus Sulfur* **1982**, *12*, 279.
(157) Yudelevich, V. I.; Fetter, A. P.; Sokolov, L. B.; Ionin, B. I.; Lifshits, M. I. *Zh. Obshch. Khim.* **1980**, *50*, 2650; *J. Gen. Chem. USSR* **1980**, 2137.
(158) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289.
(159) Buynak, J. D.; McKenzie Graff, N.; Jadhav, K. P. *J. Org. Chem.* **1984**, *49*, 1828.
(160) Appel, R.; Eichenhofer, K. W. *Chem. Ber.* **1971**, *104*, 3859.
(161) Weber, L.; Bastian, H.; Boese, R.; Stammler, H. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1778.
(162) Weber, L.; Bastian, H.; Boese, R.; Stammler, H. G.; Neumann, B. *Chem. Ber.* **1992**, *125*, 1821.
(163) Weber, L.; Lücke, E.; Frebel, M.; Bastian, H. *Phosphorus, Sulfur Silicon* **1992**, *64*, 71.
(164) Weber, L. *Phosphorus, Sulfur Silicon* **1993**, *77*, 21.
(165) Kutyrev, G. A.; Korolev, O. S.; Yarkova, E. G.; Cherkasov, R. A.; Pudovik, A. N. *Zh. Obshch. Khim.* **1986**, *56*, 1233.
(166) Kamil, W. A.; Bond, M. R.; Willett, R. D.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2829.
(167) Osman, F. H.; El-Hamouly, W. S.; Abdel-Gawad, M. M.; Abassi, M. M. *Phosphorus Sulfur* **1982**, *14*, 1.
(168) Osman, F. H.; Kamel, M. M.; El-Khateb, A. A.; Shabana, R. *Chem. Ind. (London)* **1984**, 302.
(169) Houalla, D.; Bounja, Z.; Skouta, S.; Riesel, L.; Lindemann, D. *Tetrahedron Lett.* **1992**, *33*, 2817.

(170) Houalla, D.; Bounja, Z.; Skouta, S.; Riesel, L.; Lindemann, D. *Phosphorus, Sulfur Silicon* **1993**, *77*, 216.
(171) Houalla, D.; Bounja, Z.; Skouta, S.; Sanchez, M.; Wolf, R. *Phosphorus, Sulfur Silicon* **1993**, *75*, 71.
(172) Shaw, R. A.; Fitzsimmons, B. W.; Smith, B. C. *Chem. Rev.* **1962**, *62*, 247.
(173) Paddock, N. L. *Quart. Rev.* **1964**, *18*, 168.
(174) Novobilsky, V.; Kolsky, V.; Wanek, W. *Z. Anorg. Allg. Chem.* **1975**, *416*, 187.
(175) Novobilsky, V.; Kolsky, V.; Wanek, W. *Z. Anorg. Allg. Chem.* **1976**, *423*, 273.
(176) Lund, L. G.; Paddock, N. L.; Proctor, J. E.; Searle, H. T. *J. Chem. Soc.* **1960**, 2542.
(177) Retuert, J.; Martinez, F. *Chem. Ind. (London)* **1985**, 597.
(178) Horn, H. G.; Becke-Goehring, M. *Naturwissenschaften* **1969**, *56*, 137.
(179) Abouchaccra, T.; Helioui, M.; Puskaric, E.; De Jaeger, R.; Heubel, J. *J. Chem. Res. (S)* **1981**, 230.
(180) Hammoutou, Y.; Heubel, J.; De Jaeger, R. *Phosphorus, Sulfur Silicon* **1993**, *79*, 97.
(181) Coxon, G. E.; Sowerby, D. B.; Tranter, G. C. *J. Chem. Soc.* **1965**, 5697.
(182) Novobilsky, V. *Z. Anorg. Allg. Chem.* **1976**, *427*, 189.
(183) Seger, J.; Kouril, M.; Alberti, M.; Pronayova, N. *Z. Chem.* **1990**, *30*, 215.
(184) Kovaleva, T. V.; Mel'nichuk, E. A.; Feshchenko, N. G. *Zh. Obshch. Khim.* **1984**, *54*, 223.
(185) Chapman, A. C.; Paddock, N. L.; Paine, D. H.; Searle, H. T.; Smith, D. R. *J. Chem. Soc.* **1960**, 3608.
(186) Paddock, N. L.; Serreqi, J. *Can. J. Chem.* **1974**, *52*, 2546.
(187) Paddock, N. L.; Patmore, D. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1029.
(188) Steger, E.; Mildner, G. *Z. Naturforsch.* **1961**, *16b*, 836.
(189) Chapman, A. C.; Paddock, N. L. *J. Chem. Soc.* **1962**, 635.
(190) Brion, C. E.; Paddock, N. L. *J. Chem. Soc. (A)* **1968**, 388.
(191) Brion, C. E.; Paddock, N. L. *J. Chem. Soc. (A)* **1968**, 392.
(192) Keat, R.; Porte, A. L.; Tong, D. A.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1648.
(193) Chivers, T.; Paddock, N. L. *J. Chem. Soc., Chem. Commun.* **1968**, 704.
(194) Thomas, B.; Grossmann, G. *Z. Chem.* **1983**, *23*, 27.
(195) Hartsuiker, J. G.; Wagner, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1425.
(196) Schlueter, A. W.; Jacobson, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 2051.
(197) Schlueter, A. W.; Jacobson, R. A. *J. Chem. Soc. A* **1968**, 2317.
(198) Hartsuiker, J. G.; Wagner, A. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1069.
(199) Sowerby, D. B. *J. Chem. Soc.* **1965**, 1396.
(200) Rallo, F. *Ric. Sci., Rend. Sez. A* **1965**, *8*, 1134.
(201) Allen, G.; Oldfield, D. J.; Paddock, N. L.; Rallo, F.; Serregi, J.; Todd, S. M. *Chem. Ind.* **1965**, 1032.
(202) Kireev, V. V.; Korshak, V. V.; Sulkowski, W.; Mulyashova, I. P.; Zhuravleva, I. I.; Sadkova, T. P.; Maiorova, G. M. *Dokl. Akad. Nauk SSSR* **1978**, *239*, 853; *Dokl. Chem.* **1978**, 137.
(203) Mitropol'skaya, G. I.; Kireev, V. V.; Korshak, V. V.; Goryaev, A. A. *Zh. Obshch. Khim.* **1982**, *52*, 2486.
(204) Paddock, N. L.; Trotter, J.; Whitlow, S. H. *J. Chem. Soc. (A)* **1968**, 2227.
(205) Dougill, M. W.; Paddock, N. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1022.
(206) Nabi, S. N.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1618.
(207) Gallicano, K. D.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 417.
(208) Gallicano, K. D.; Paddock, N. L. *Can. J. Chem.* **1982**, *60*, 521.
(209) Calhoun, H. P.; Paddock, N. L.; Wingfield, J. N. *Can. J. Chem.* **1975**, *53*, 1765.
(210) Wagner, A. J.; Vos, A. *Rec. Trav. Chim. Pays-Bas* **1964**, *84*, 603.
(211) Wagner, A. J.; Vos, A. *Acta Crystallogr.* **1968**, *B24*, 1423.
(212) Calhoun, H. P.; Paddock, N. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1976**, 38.
(213) Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Can. J. Chem.* **1971**, *49*, 164.
(214) Paddock, N. L.; Ranganathan, T. N.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1972**, 1578.
(215) Searle, H. T.; Dyson, J.; Ranganathan, T. N.; Paddock, N. L. *J. Chem. Soc., Dalton Trans.* **1975**, 203.
(216) Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 304.
(217) Oakley, R. T.; Rettig, S. J.; Paddock, N. L.; Trotter, J. *J. Am. Chem. Soc.* **1985**, *107*, 6923.
(218) Dougill, M. W.; Sheldrick, B. *Acta Crystallogr.* **1977**, *B33*, 295.
(219) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 3118.
(220) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 2530.
(221) Chivers, T.; Paddock, N. L. *Inorg. Chem.* **1972**, *11*, 848.
(222) Sharma, R. D.; Rettig, S. J.; Paddock, N. L.; Trotter, J. *Can. J. Chem.* **1982**, *60*, 535.
(223) Chivers, T.; Oakley, R. T.; Paddock, N. L. *J. Chem. Soc. (A)* **1970**, 2324.
(224) Roesky, H. W.; Janssen, E. *Chem. Ber.* **1975**, *108*, 2531.
(225) Thomas, B.; Grossmann, G. *Z. Anorg. Allg. Chem.* **1985**, *523*, 112.
(226) Dhathathreyan, K. S.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Dalton Trans.* **1981**, 1928.
(227) Stokes, H. N. *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 437.
(228) Stokes, H. N. *Am. Chem. J.* **1898**, *20*, 740.
(229) Labarre, J. F.; Sournies, F. *Advances in Supramolecular Chemistry*; Gokel, G. W., Ed.; JAI Press: Greenwich, 1993; Vol. 4.
(230) El Bakili, A.; Castera, P.; Faucher, J. P.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1989**, *195*, 21.
(231) Enjalbert, R.; Galy, J.; El Bakili, A.; Castera, P.; Faucher, J. P.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1989**, *196*, 207.
(232) Scheidecker, S.; Semenzin, D.; Etemad-Moghadam, G.; Sournies, F.; Koenig, M.; Labarre, J. F. *Phosphorus, Sulfur Silicon* **1993**, *80*, 85.
(233) Cameron, T. S.; Linden, A.; El Bakili, A.; Castera, P.; Faucher, J. P.; Graffeuil, M.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1989**, *212*, 281.
(234) Sournies, F.; El Bakili, A.; Zanin, B.; Labarre, J. F.; Jaud, J. *J. Mol. Struct.* **1990**, *220*, 43.
(235) Cameron, T. S.; Linden, A.; Sournies, F.; El Bakili, A.; Labarre, J. F. *J. Mol. Struct.* **1989**, *197*, 41.
(236) Jaud, J.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1989**, *212*, 305.
(237) Sournies, F.; El Bakili, A.; Labarre, J. F.; Perly, B. *J. Mol. Struct.* **1989**, *196*, 201.
(238) Enjalbert, R.; Galy, J.; Galliot, C.; Scheidecker, S.; Bonnet, J. P.; Labarre, J. F. *J. Mol. Struct.* **1992**, *271*, 95.
(239) Scheidecker, S. Ph.D. Thesis, no. 1507, P. Sabatier University, Toulouse, July 2, 1993.
(240) Jaud, J.; Raynaud, B.; Scheidecker, S.; Labarre, J. F. *J. Mol. Struct.* **1992**, *271*, 289.
(241) Zanin, B.; Faucher, J. P.; Labarre, J. F. *Inorg. Chim. Acta* **1990**, *172*, 147.
(242) Enjalbert, R.; Galy, J.; Castera, P.; Labarre, J. F. *Acta Crystallogr.* **1988**, *C44*, 1813.
(243) Zanin, B.; Sournies, F.; Labarre, J. F.; Enjalbert, R.; Galy, J. *J. Mol. Struct.* **1990**, *240*, 77.
(244) Zanin, B.; Scheidecker, S.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1991**, *246*, 133.
(245) Sournies, F.; Castera, P.; El Bakili, A.; Faucher, J. P.; Graffeuil, M.; Labarre, J. F. *J. Mol. Struct.* **1990**, *221*, 245.
(246) Enjalbert, R.; Galy, J.; Sournies, F.; Labarre, J. F. *J. Mol. Struct.* **1990**, *221*, 253.
(247) Kuznetsova, S. S.; Smirnov, R. P. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1978**, *21*, 346.
(248) Castera, P.; Faucher, J. P.; Granier, M.; Labarre, J. F. *Phosphorus Sulfur* **1987**, *32*, 37.
(249) Kiliç, A.; Kiliç, Z.; Shaw, R. *Phosphorus, Sulfur Silicon* **1991**, *57*, 111.
(250) Shaw, R. A. *Phosphorus, Sulfur Silicon* **1989**, *45*, 103.
(251) Prigozhina, M. P.; Petrovskii, P. V.; Komarova, L. G.; Rusanov, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, 177.
(252) Shaw, R. A.; Ture, S. *Phosphorus, Sulfur Silicon* **1991**, *57*, 103.
(253) Al-Madfa, H. A.; Shaw, R.; Ture, S. *Phosphorus, Sulfur Silicon* **1990**, *53*, 333.
(254) Alkubaisi, A. H.; Shaw, R. A. *Phosphorus, Sulfur Silicon* **1991**, *55*, 49.
(255) Allcock, H. R.; Turner, M. L.; Visscher, K. B. *Inorg. Chem.* **1992**, *31*, 4354.
(256) Meetsma, A.; van de Grampel, J. C.; Brandt, K.; Jedlinski, Z. *Acta Crystallogr.* **1988**, *C44*, 1122.
(257) Brandt, K.; Jekel, A. P.; Meetsma, A.; van de Grampel, J. C. *Inorg. Chim. Acta* **1989**, *157*, 251.
(258) Wittig, G.; Maercker, A. *Chem. Ber.* **1964**, *97*, 747.
(259) Hellwinkel, D. *Chem. Ber.* **1965**, *98*, 576.
(260) Hellwinkel, D.; Lindner, W. *Chem. Ber.* **1976**, *109*, 1497.
(261) Waite, N. E.; Tebby, J. C. *J. Chem. Soc. C* **1970**, 386.
(262) Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1978**, *15*, 1319.
(263) Hughes, A. N.; Amornraksa, K.; Phisithkul, S.; Reutrakul, V. *J. Heterocycl. Chem.* **1976**, *13*, 65.
(264) Couret, C.; Escudié, J.; Satgé, J.; Redoulès, G. *Rec. Trav. Chim. Pays-Bas* **1976**, *95*, 240.
(265) Schmidbaur, H.; Scherm, H. P.; Schubert, U. *Chem. Ber.* **1978**, *111*, 764.
(266) Quin, L. D. *Phosphorus Sulfur* **1986**, *27*, 109.
(267) Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370.
(268) Quin, L. D.; Middlemas, E. D. *Pure Appl. Chem.* **1980**, *52*, 1013.
(269) Quin, L. D.; Middlemas, E. D.; Rao, N. S.; Miller, R. W.; McPhail, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 1893.
(270) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.
(271) Middlemas, E. D.; Quin, L. D. *J. Am. Chem. Soc.* **1980**, *102*, 4839.
(272) Rao, N. S.; Quin, L. D. *J. Org. Chem.* **1984**, *49*, 3157.
(273) Rao, N. S.; Quin, L. D. *J. Am. Chem. Soc.* **1983**, *105*, 5960.
(274) Quin, L. D.; Rao, N. S.; Topping, R. J.; McPhail, A. T. *J. Am. Chem. Soc.* **1986**, *108*, 4519.
(275) De Ficquelmont, A. M. *C. R. Hebd. Seances Acad. Sci.* **1937**, *204*, 689.

(276) De Ficquelmont, A. M. *C. R. Hebd. Seances Acad. Sci.* **1937**, *204*, 867.
(277) Allcock, H. R.; McDonnell, G. S.; Desorcie, J. L. *Inorg. Chem.* **1990**, *29*, 3839.
(278) Manners, I.; Riding, G. H.; Dodge, J. A.; Allcock, H. R. *J. Am. Chem. Soc.* **1989**, *111*, 3067.
(279) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596.
(280) Harrison, W.; Oakley, R. T.; Paddock, N. L.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1971**, 357.
(281) Oakley, R. T.; Paddock, N. L. *Can. J. Chem.* **1973**, *51*, 520.
(282) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.
(283) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1985**, *24*, 2237.
(284) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.
(285) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.
(286) Filali, A.; Yaouanc, J. J.; Handel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 560.
(287) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.
(288) Dupart, J. M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167.
(289) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677.
(290) Bouvier, F.; Dupart, J. M. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 301.
(291) Bouvier, F.; Dupart, J. M.; Grand, A.; Riess, J. G. *Inorg. Chem.* **1987**, *26*, 2090.
(292) Richman, J. E.; Flay, R. B.; Gupta, O. D. *ACS Symp. Ser.* **1981**, *171*, 271.
(293) Bouvier, F.; Vierlig, P.; Dupart, J. M. *Inorg. Chem.* **1988**, *27*, 1099.
(294) Dupart, J. M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051.
(295) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776.
(296) Lampin, J. P.; Laurent, H.; Mathey, F. *Compt. Rend. Acad. Sci. Paris Ser. C* **1975**, *280*, 1153.
(297) Khasnis, D. V.; Burton, J. M.; Lattman, M.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1991**, 562.
(298) Mukaiyama, T.; Fujisawa, T.; Tamura, Y.; Yokota, Y. *J. Org. Chem.* **1964**, *29*, 2572.
(299) Nifant'ev, E. E.; Nasonovskii, I. S.; Miklashevskii, A. V.; Zavalishina, A. I.; Smirnova, E. I. *Zh. Org. Khim.* **1975**, *11*, 2206.
(300) White, D. W. *Phosphorus* **1971**, *1*, 33.
(301) Albrand, J. P.; Dutasta, J. P.; Robert, J. B. *J. Am. Chem. Soc.* **1974**, *96*, 4584.
(302) Dutasta, J. P.; Guimaraes, A. C.; Robert, J. B. *Tetrahedron Lett.* **1977**, 801.
(303) Dutasta, J. P.; Guimaraes, A. C.; Martin, J.; Robert, J. B. *Tetrahedron Lett.* **1975**, 1519.
(304) Dutasta, J. P.; Grand, A.; Guimaraes, A. C.; Robert, J. B. *Tetrahedron* **1979**, *35*, 197.
(305) Dutasta, J. P.; Martin, J.; Robert, J. B. *Heterocycles* **1980**, *14*, 1631.
(306) Dutasta, J. P.; Robert, J. B. *J. Am. Chem. Soc.* **1978**, *100*, 1925.
(307) Dutasta, J. P. *J. Chem. Res. (S)* **1986**, 22.
(308) Dutasta, J. P.; Jurkschat, K.; Robert, J. B. *Tetrahedron Lett.* **1981**, 2549.
(309) Dutasta, J. P.; Grand, A.; Robert, J. B. *Acta Crystallogr.* **1978**, *B34*, 3820.
(310) Sliwa, H.; Picavet, J. P. *Tetrahedron Lett.* **1977**, 1583.
(311) Vaccher, C.; Mortreux, A.; Petit, F.; Picavet, J. P.; Sliwa, H.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1984**, *23*, 3613.
(312) Powell, J.; Ng, K. S.; Ng, W. W.; Nyburg, S. C. *J. Organomet. Chem.* **1983**, *243*, C1.
(313) Lamandé, L.; Munoz, A. *Phosphorus, Sulfur Silicon* **1993**, *75*, 241.
(314) Dutasta, J. P.; Martin, J.; Robert, J. B. *J. Org. Chem.* **1977**, *42*, 1662.
(315) Martin, J.; Robert, J. B. *Nouv. J. Chim.* **1980**, *4*, 515.
(316) Martin, J.; Robert, J. B. *Org. Magn. Reson.* **1981**, *15*, 87.
(317) Grand, A.; Martin, J. *Acta Crystallogr.* **1982**, *B38*, 3052.
(318) Elmes, P. S.; Gatehouse, B. M.; West, B. O. *J. Organomet. Chem.* **1974**, *82*, 235.
(319) Greenhalgh, R.; Newbery, J. E.; Woodcock, R.; Hudson, R. F. *J. Chem. Soc., Chem. Commun.* **1969**, 22.
(320) Robert, J. B.; Weichmann, H. *J. Org. Chem.* **1978**, *43*, 3031.
(321) Bonningue, C.; Houalla, D.; Sanchez, M.; Wolf, R.; Osman, F. H. *J. Chem. Soc., Perkin Trans. 2* **1981**, 19.
(322) Bonningue, C.; Houalla, D.; Wolf, R.; Jaud, J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 773.
(323) Duthu, B.; El Abed, K.; Houalla, D.; Wolf, R.; Jaud, J. *Can. J. Chem.* **1992**, *70*, 809.
(324) Niedermann, H. P.; Eckes, H. L.; Meier, H. *Tetrahedron Lett.* **1989**, *30*, 155.
(325) Eckes, H. L.; Niedermann, H. P.; Meier, H. *Chem. Ber.* **1991**, *124*, 377.
(326) Clovis, J. S.; Sullivan, F. R. *Tetrahedron Lett.* **1971**, 2263.
(327) Kauffmann, T.; Antfang, E.; Olbrich, J. *Chem. Ber.* **1985**, *118*, 1022.
(328) Marty, W.; Schwarzenbach, G. *Chimia* **1970**, *24*, 431.
(329) Jones, T. L.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1411.
(330) Dilworth, J. R.; Zheng, Y.; Miller, J. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1757.
(331) Ansell, C. W. G.; Cooper, M. K.; Dancey, K. P.; Duckworth, P. A.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 439.
(332) Riker-Nappier, J.; Meek, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 442.
(333) Cabral, J. de O.; Cabral, M. F.; Drew, M. G. B.; Nelson, S. M.; Rodgers, A. *Inorg. Chim. Acta* **1977**, *25*, L77.
(334) Scanlon, L. G.; Tsao, Y. Y.; Cummings, S. C.; Toman, K.; Meek, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6849.
(335) Scanlon, L. G.; Tsao, Y. Y.; Toman, K.; Cummings, S. C.; Meek, D. W. *Inorg. Chem.* **1982**, *21*, 1215.
(336) Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 375.
(337) Bartsch, R.; Hietkamp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3624.
(338) Bartsch, R.; Hietkamp, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1984**, *23*, 3304.
(339) Brauer, D. J.; Gol, F.; Hietkamp, S.; Peters, H.; Sommer, H.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* **1986**, *119*, 349.
(340) Toulhoat, C.; Vidal, M.; Vincens, M. *Phosphorus, Sulfur Silicon* **1992**, *71*, 127.
(341) DelDonno, T. A.; Rosen, W. *J. Am. Chem. Soc.* **1977**, *99*, 8051.
(342) DelDonno, T. A.; Rosen, W. *Inorg. Chem.* **1978**, *17*, 3714.
(343) Baacke, M.; Morton, S.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* **1980**, *113*, 1343.
(344) Dey, K.; Biswas, A. K.; Sinha Roy, A. K. *Ind. J. Chem.* **1981**, *20A*, 848.
(345) Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700.
(346) Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Hackney, M. L. J.; Norman, A. D. *Inorg. Chem.* **1989**, *28*, 2811.
(347) Brauer, D. J.; Lebbe, T.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 438.
(348) Brauer, D. J.; Dörrenbach, F.; Lebbe, T.; Stelzer, O. *Chem. Ber.* **1992**, *125*, 1785.
(349) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3500.
(350) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Chem. Commun.* **1970**, 879.
(351) Höhn, A.; Geue, R. J.; Sargeson, A. M.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1644.
(352) Bolm, C.; Sharpless, K. B. *Tetrahedron Lett.* **1988**, *29*, 5101.
(353) Pascal, R. A., Jr.; West, A. P., Jr.; Van Engen, D. *J. Am. Chem. Soc.* **1990**, *112*, 6406.
(354) L'Esperance, R. P.; West, A. P., Jr.; Van Engen, D.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2672.
(355) West, A. P.; Smyth, N.; Kraml, C. M.; Ho, D. M.; Pascal, R. A. *J. Org. Chem.* **1993**, *58*, 3502.
(356) Friedrichsen, B. P.; Powell, D. R.; Whitlock, H. W. *J. Am. Chem. Soc.* **1990**, *112*, 8931.
(357) Friedrichsen, B. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 9132.
(358) Alder, R. W.; Ganter, C.; Harris, C. J.; Orpen, A. G. *Phosphorus, Sulfur Silicon* **1993**, *77*, 234.
(359) Wild, S. B. *Pure Appl. Chem.* **1990**, *62*, 1139.
(360) Van Oijen, A. H.; De Bont, H. B. A.; Van Boom, J. H.; Liskamp, R. M. J. *Tetrahedron Lett.* **1991**, *32*, 7723.
(361) Nifant'ev, E. E.; Zavalishina, A. I.; Smirnova, E. I.; Filimonov, V. F. *Zh. Obshch. Khim.* **1985**, *55*, 2806.
(362) Pietrusiewicz, K. M.; Kuznikowski, M. *Phosphorus, Sulfur Silicon* **1993**, *77*, 57.