Preparation, Characterization, and Synthetic Potential of Unstable Compounds Containing Phosphorus–Carbon Multiple Bonds

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Received December 6, 1993 (Revised Manuscript Received June 6, 1994)

Contents

I. Introduction

One of the most important results in the field of phosphorus chemistry from the 1970s is probably the development of the chemistry of trivalent phosphorus derivatives bearing p_π–p_π bonds. Several major reviews detailing preparation, characterization, reactivity, and structural properties have given evidence of this expansion.[1-12] A comprehensive treatise has been provided by Regitz and Scherer.[13] The emergence of doubly and triply bonded trivalent phosphorus derivatives represents however a recent enrichment in the field of organic, inorganic and organometallic chemistry. Progress in this research was influenced by the so-called "double-bond rule" which states that compounds containing multiple bonds should be restricted to elements of the second row of the periodic table. This rule laid in the mind of chemists until 1961, when Gier reported the synthesis of the unstable methylidynephosphine HC≡P by passing PH_3 through an electric arc between graphite electrodes.[14] The ability of phosphorus to form p_π–p_π bonds with carbon atoms was for the first time demonstrated. However, this fundamental and exciting result remained a chemical curiosity for many years. The fact that HC≡P is spontaneously inflamable in air and that it polymerizes at a temperature as low as −120 °C has probably discouraged, for a long time, the development of this research. Interest returned in the 1980s, more precisely in 1976, when Becker noticed the formation of stable P–C double bond acyclic compounds and with the pioneering experiments on the gas-phase generation and spectroscopic characterization of short-lived species developed by Nixon and Kroto.[15] In the last 10 years, an impressive number of papers dealing with P=C and P≡C derivatives have been published. The nature of the double bond has been investigated by many theoretical studies. The strength of the P=C bond, evaluated by different ways, can be considered as 60–70% that of the C=C bond.[16-18] The weakness of the double bond between carbon and phosphorus, as for many other elements of the third row, has been

0009-2665/94/0794-1413$14.00/0

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attributed to a poor overlap of the bulky orbitals involved in the new bonds.[19,20] To stabilize the free p_π-hybridized phosphorus derivatives, two methodologies have been developed. The first one which achieves stabilization by including the p_π bond into which achieves stabilization by including the p_π bond into a delocalized system is of thermodynamic origin. Recent calculations and chemical reactivity have shown the importance of this effect; the conjugative ability of the P=C bond was found to be similar to the one of the C=C bond.[18,12] Aromaticity of various rings such as phosphabenzenes and azaphospholes has been largely demonstrated.[13,21-23] The stabilization by $n_N-\pi_{P=C}$ conjugation is observed in the acyclic systems; the C-hetero-substituted phosphaalkenes, which constitute an important class of compounds, show in general a remarkable stability.[24] The second one which consists in shielding the p_π bond by introduction of bulky substituents is of kinetic nature. The stabilization induced by this effect is particularly attractive for the synthesis of p_π bonds bearing only carbon substituents.[24]

The present report attempts to describe the preparation, characterization, and chemical properties of unstabilized phosphaalkenes, phosphaallenes, and phosphaalkynes. The special techniques used for the preparation and characterization of such species in the gas phase or in solution will be presented. Special attention will be drawn to the development of new procedures. The chronology of this research is nearly followed in the contents. History of this chemistry is going from detection and characterization of elusive species in the gas phase by pioneering experiments to the construction of a real and important organophosphorus chemistry mainly developed up to now with stabilized species. The last challenge now consists of introducing unstabilized species in this scheme in order to finally consider phosphaalkenes and phosphaalkynes as two classes of ordinary compounds. Recent developments in this area prove that chemistry of these derivatives is going in this way.

We need precise criteria to classify and evaluate literature reports in this area. First of all, those which have only been characterized by direct spectroscopic measurements in the gas phase (IRS, PES, MWS) or by chemical trapping will be considered as unstabilized species. Among the species which were isolated and fully spectroscopically characterized (NMR, IR, MS, etc.), only those which were found to oligomerize in the concentrated phase at a temperature near or lower than 20 °C will be retained. As a consequence, most of the species directly bonded to bulky substituents such as *tert*-butyl, trimethylsilyl, or those bearing an electron donating group on the carbon or on the phosphorus atom will not be considered. The main classical approaches described in the literature for the preparation of the p_π-bond systems will be examinated and limitations concerning the preparation of unstabilized species will be defined and analyzed when it is possible. Since reactivity of the P–C multiple bonds has been developed in detail in former reviews,[1,3-6,8,11-13] no special chapter will be devoted to this study. Chemical properties of unstabilized species will be presented with synthesis and spectroscopic characterization since for the transient species, chemical trapping is often given as a proof of structure. Special reactivity will be defined by mentioning, in each case, experimental conditions.

This report covers the literature prior to the middle of 1993. Structure and bonding of the $p_\pi-p_\pi$ bonds, which are treated in detail in a chapter of this special issue will not be discussed but only used, if needed, for argumentation. Metallaphosphaalkenes, metallaphosphaalkynes and their ligating properties, recently reviewed, are consequently excluded from this article.[5,6]

II. Experimental Techniques

A. Gas-Phase Generation and Detection of Volatile Low-Coordinated Phosphorus Derivatives

The simplest phosphorus–carbon multiple bond derivatives are usually unstable at room temperature but are fairly stable in the gas phase even at high temperature. They have been generated under vacuum using mainly two techniques, the flash-vacuum thermolysis (FVT) and the vacuum gas–solid reactions (VGSR), and directly analyzed without condensation by microwave spectroscopy (MWS), photoelectron

spectroscopy (PES), and mass spectrometry (MS). The former is by far the most popular; technical descriptions of the device and synthetic applications can be found in several reviews and in a comprehensive treatise.[25] The development of the later technique appears less important although its contribution in the formation of many short-lived species, especially highly strained molecules, has often been the only conclusive one.[26-31] To our knowledge, Chapman was the first to use this technique in 1976 for the preparation of a transient benzabutadiene by a gas-phase dehalogenation of a diiodide precursor over zinc powder heated to 230 °C.[32] Extension to other chemical reactions has been successfully realized. Thus, Kroto and Nixon showed for the first time in 1979 that dehydrohalogenation of halophosphines on solid KOH[33,34] was a powerful method to generate unstabilized low-coordinated phosphorus derivatives (see below). Independently, this technique was used for the synthesis of highly strained molecules,[26] reactive imines,[26-29] and more recently for the construction of P–C multiple-bond derivatives (section III.C). We have called this technique "vacuum gas–solid reactions" (VGSR). This abbreviation will be used in this review to designate this procedure.

Experiments for the detection of elusive species in the gas phase are usually carried out as follows. The suitable apparatus (FVT or VGSR) is connected to a spectrometer and a real-time analysis of the gaseous flow is realized.[15,26-32,33] The temperature of the reactor is gradually increased until the starting material vanishes. Thus, the continuous change of band intensities allows the optimization of the device's architecture and the reaction conditions (temperature of the oven, nature of the solid reagent, etc.) in order to minimize the formation of byproducts.

These different experiments bring deep insight into the structure of reactive intermediates. The analysis of microwave spectra gives the most positive molecule identification, with the possibility of determining the dipole moment and the height of internal rotational barrier.[15] Photoelectron spectroscopy provides the values and the corresponding assignment of ionization potentials and thus information about the electronic structure.[15,31] The molecular ion of reactive species is given by high-resolution mass spectrometry (HRMS). Furthermore, the use of special techniques like MS/MS spectrometric experiments provides information allowing the precise definition of the structure of this ion. Identification of the P–C multiple bonds by IR spectroscopy has also been used. Interesting results have been obtained by real-time analysis of the gaseous flow (FT/IR techniques) or by condensation of the reactive species on a KBr window cooled to liquid nitrogen temperature.

B. Liquid-Phase Characterization of Short-Lived Species

In most cases, the full spectroscopic NMR data can be obtained by transferring the reactive species previously formed in the gas phase into an NMR tube. The procedure is simple: the gaseous flow is first condensed with a cosolvent on a liquid nitrogen cold trap; the solution is then transferred into a precooled tube and analyzed at low temperature under an inert gas pressure.

When reactive species are formed in solution, the presence of solvent and impurities dramatically limits direct spectroscopic analysis. In these cases, low-temperature ^{31}P NMR provides the most powerful tool for their detection since P=C and P≡C bonds have characteristic chemical shifts. However, unambiguous proof of the existence of these intermediates is only deduced from the analysis of the trapping or self-trapping products.

III. Gas-Phase Elimination Reactions

A. Flash-Vacuum Thermolysis (FVT) (Method A)

Flash-vacuum thermolysis of phosphines bearing substituents (X at phosphorus and Y at the α-carbon) has played a determining role in the formation of unstabilized P–C multiple-bond derivatives. Numerous combinations have been efficiently achieved up to now (for example X = Cl, F, H; Y = H, $SiMe_3$, $SnMe_3$, Cl, etc.). In most cases, the simplest species were not isolated in the pure state, but directly detected and characterized in the gas phase by microwave, photoelectron, IR, or mass spectroscopy.

1. Elimination of YX (Y = H, $SiMe_3$, $SnMe_3$; X = Cl, F)

a. HCl and Me_3SiCl Elimination. Pioneering experiments dealing with the gas-phase generation of short-lived species and their subsequent spectroscopic characterization have been developed by Kroto and Nixon.[15] Thus, the first detection of CH_2=PCl was performed by microwave spectroscopy. The dichlorophosphine precursor was heated under FVT conditions in a thermolysis oven directly connected to a microwave spectrometer. Various amounts of HC≡P were also detected during these experiments[33] (Scheme 1).

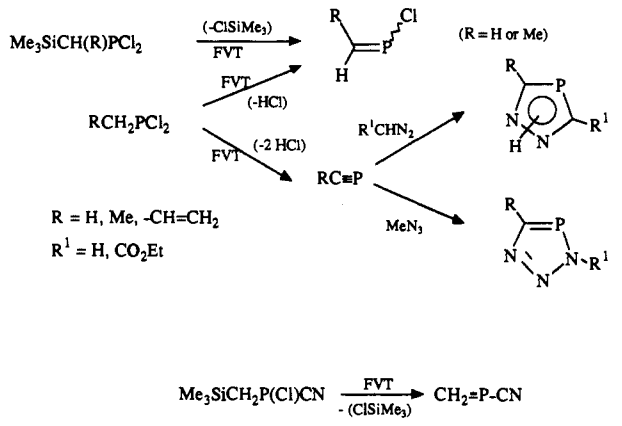
Scheme 1

$$CH_3PCl_2 \underset{HCl}{\overset{FVT\ (-HCl)}{\rightleftharpoons}} CH_2{=}P{-}Cl \underset{HCl}{\overset{FVT\ (-HCl)}{\rightleftharpoons}} HC{\equiv}P$$

To avoid the undesired back-reaction (formation of the dichlorophosphine precursor by HCl addition), various bases like KOH at −78 °C,[34] tricyclohexylhexahydro-*s*-triazine at 20 °C,[35] or KOH/K_2CO_3 at −78 °C[36] were used to remove HCl from the gas phase. Thus, pure CH_2=PCl and HC≡P were obtained in 30 and 35% yield, respectively, using a FVT/HCl elimination sequence and identified by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.[35] The stability of these two species is higher than expected or previously reported: HC≡P which was described to polymerize at a temperature up to −120 °C when it was formed by passing PH_3 through an electric arc between graphite electrodes,[14] has a half-life of 5 min at −10 °C in solution. This difference is probably due to the presence of some impurities in the first experiment, which catalyze the self-condensation. As it will be further mentioned, this behavior is general: the stability of these species is strongly dependent upon their purity.

By an analogous approach, CH_3CH=PCl, CH_3C≡P, and CH_2=CHC≡P were obtained (Scheme 2). HC≡P was also characterized by photoelectron,[37] microwave,[38] and raman spectroscopy;[39] MeC≡P by microwave,[40] photoelectron,[41] ^{31}P, ^1H, and ^{13}C NMR spectroscopy,[35] and IR spectroscopy;[42,43] identification of CH_2=CHC≡P was based solely on microwave spectroscopy.[44] Phosphaalkynes were also characterized by chemical trap-

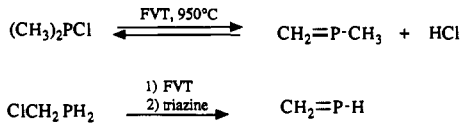
Scheme 2



ping in 1,3-dipolar cycloadditions with diazo compounds and azides[36,45] leading to the corresponding diaza- and triazaphospholes (Scheme 2). Generally, all the 1,3-dipolar cycloadditions between phosphaalkynes and diazo derivatives are reported to be regiospecific but with diazo ester and methylidynephosphine, a mixture of regioisomer adducts is obtained.[46]

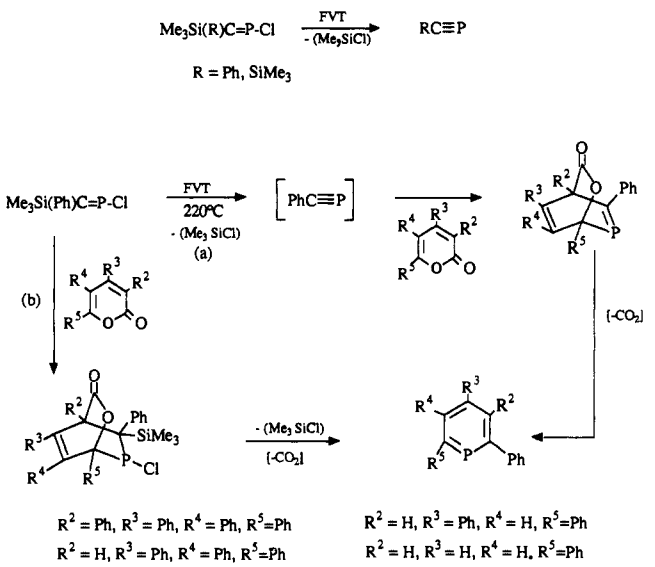
2-Phosphapropene was also prepared by gas-phase pyrolysis of chlorodimethylphosphine and identified by photoelectron and mass spectra.[47] Methylidenephosphine, the phosphaalkene parent compound, was prepared by dehydrochlorination of the corresponding α-chlorophosphine under FVT conditions and characterized by mass spectroscopy[35] (Scheme 3).

Scheme 3



Whereas the thermal HCl elimination is inefficient from a preparative point of view, the corresponding halosilane elimination is synthetically more useful. Pyrolysis of (trimethylsilyl)dichlorophosphines was found to improve the yield of the simplest *P*-chlorophosphaalkenes [RC(H)=PCl];[35,48,49] however, the presence of $ClSiMe_3$ was reported to decrease the stability of these low-coordinated phosphorus derivatives.[35] Detection by microwave spectroscopy of CH_2=PCN in the thermolysis products of $Me_3SiCH_2P(Cl)CN$ clearly demonstrates the preferred Me_3SiCl over the Me_3SiCN elimination.[50] (Phenylmethylidyne)phosphine and [(trimethylsilyl)methylidyne]phosphine were obtained in good yields by heating, respectively, chloro[phenyl(trimethylsilyl)methylene]phosphine[51] or chloro[bis(trimethylsilyl)methylene]phosphine[52] and were then fully characterized in solution by ^{31}P, ^{1}H, and ^{13}C NMR.[51,52] (Phenylmethylidyne)phosphine was also characterized by MWS[53] and PES[54,55] and [(trimethylsilyl)methylidyne]phosphine by PES.[55] Slow decomposition of PhC≡P is observed above −50 °C (half-life: 7 min/0 °C). Decomposition of Me_3SiC≡P occurs at room temperature (half-life: 50 min/20 °C). Phosphaalkynes generated by this approach were also trapped by means of cycloaddition reactions with α-pyrones. Thus, the formation of phenylphosphorin (R = Ph) upon heating the corresponding *P*-chlorophosphaalkenes at 220 °C with α-pyrone in the presence

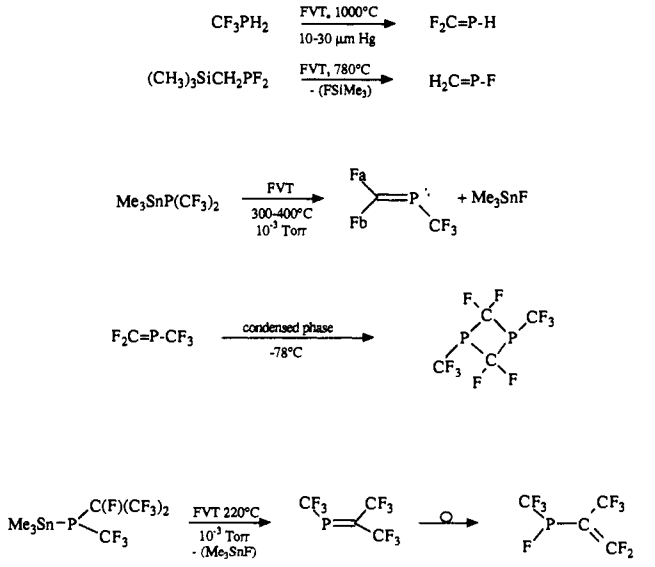
Scheme 4



of KF/[18]-crown-6 has been explained by a [4 + 2] cycloaddition of α-pyrones to the PhC≡P intermediate followed by decarboxylation of the bicyclic lactone intermediate[56] (pathway a). However, a second pathway (b) which involves decarboxylation of the intermediate adduct, issued from a [4 + 2] cycloaddition of $Me_3Si(Ph)C$=PCl with α-pyrones cannot be discarded[57] (Scheme 4).

b. HF and Me_3SiF Elimination. Another interesting leaving group is the fluoro substituent. CF_2=PH was produced by pyrolysis of CF_3PH_2 (Scheme 5) and

Scheme 5



directly identified by microwave spectroscopy as early as 1976.[33] Half-life of CF_2=PH (1.3 min at 20 °C) was determined by stopping the flow through the cell and measuring the rate of disappearance of the absorptions in a static system.

Fluorophosphaethene CH_2=PF was obtained by gas-phase thermal elimination of $FSiMe_3$ from $(CH_3)_3SiCH_2PF_2$[58] (Scheme 5). The resulting thermolysis products were transferred directly into the cell of a microwave spectrometer. A detailed rotational analysis of this compound was made. Bond lengths were determined [r(C=P) = 1.644 Å, r(P—F) = 1.598 Å] and the dipole

components of $H_2C{=}PF$ measured (μ_A = 1.355 D and μ_B = 0.156 D) indicating a low polarization of the system.

c. Me_3SnF Elimination. In order to minimize separation problems, Me_3SnF which is known to form easily eliminated solid polyadducts is another interesting alternative. This method, principally used by Grobe *et al.*, was found to be an efficient way to prepare perfluorophosphaalkenes. For example, $CF_3P{=}CF_2$ was obtained in almost quantitative yield by gas-phase thermal Me_3SnF elimination[59-61] starting from $Me_3SnP(CF_3)_2$ and characterized by mass spectroscopy[59] (Scheme 5). The structure of this perfluorophosphaalkene and the presence of a double bond were confirmed by electron diffraction[61] (P–C bond length = 1.686 Å). Stereochemistry of this derivative was precised by ^{19}F and ^{31}P NMR[59,60] data [$\delta\,^{31}P$ = 20 ppm; δ F = 2.9 ppm ($^2J_{PF_a}$ = 192 Hz), F trans to CF_3; and δ F = −29.9 ppm ($^2J_{PF}$ = 103 Hz), F cis to CF_3, δ_{CF_3} = −44 ppm]. It is interesting to note the substituent effect with fluorine: a comparatively high stability of the P=C system together with a pronounced dienophilicity of this derivative was observed. The kinetic stability of $F_2C{=}PCF_3$ in the gas or liquid phase was surprising. Thus in *ca.* 10% toluene or pentane solution, the phosphaalkene dimer is first detectable after about 10 h at 25 °C. Therefore reactivity studies in organic solvents were possible under ordinary conditions. A dimerization (mainly head to tail dimer) is observed when condensing the gaseous flow of perfluorophosphaalkene at −78 °C together with small amounts of the head to head dimer (Scheme 5). However, self-condensation products $(F_3CPCF_2)_x$ are the only observed derivatives when warming up the condensed phase at room temperature.[60]

Addition of HX leads either to P–X- or to C–X-bonded saturated systems.[62,63a] The direction of addition is mainly determined by the properties of the HX partner pointing out a fairly low polarity of the P=C bond (Scheme 6). Reaction with secondary amines (R_2NH) in the molar ratio 1:2 at temperatures between −120 and −40 °C leads to the formation of (trifluoromethyl)phosphaalkenes of the type $F_3CP{=}C(F)NR_2$ which are stable at room temperature.[63b] Dienophilic properties of $CF_3P{=}CF_2$ were established by reaction with various dienes. In all cases, the [4 + 2] cycloadditions of the fluorophosphaalkenes proceed under mild conditions at temperatures from −20 to +15 °C with good yields (75–100%)[64-66] (Scheme 6).

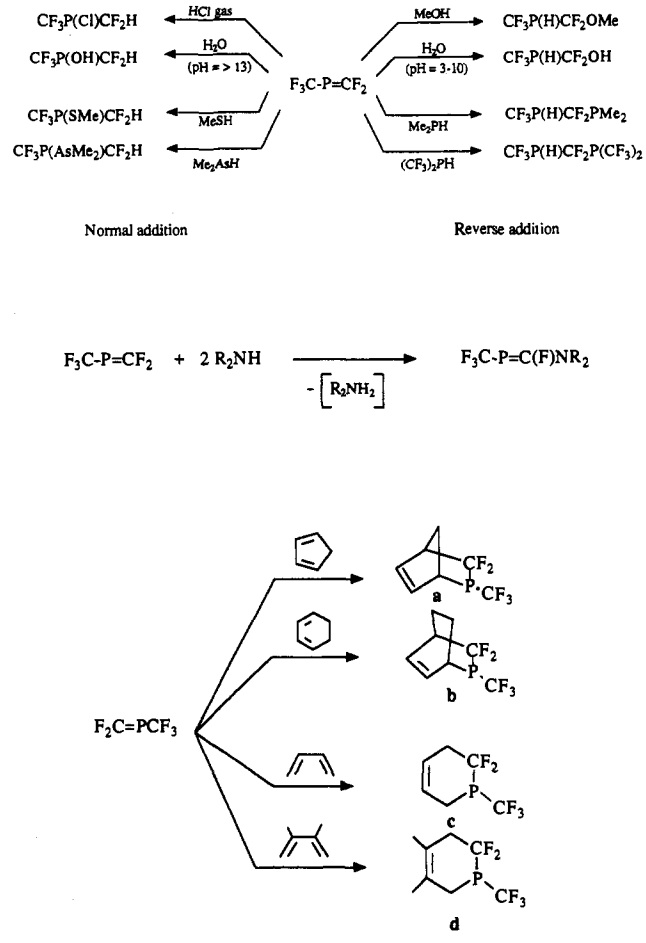
Thermal elimination of Me_3SnF from the corresponding stannylphosphines proved to be a quite general access to fluorinated phosphaalkenes as demonstrated by the following examples: $C_2F_5P{=}C(F)CF_3$,[67] $Me_3SnP{=}CF_2$,[59] $F_3CP{=}C(F)CF_3$,[68] $C_2F_5P{=}CF_2$,[68] $F_3CP{=}C(H)F$,[69,70] $Me{-}P{=}CF_2$,[71] and $EtP{=}CF_2$.[71]

Surprisingly, elimination of Me_3SnF from the stannylphosphine $Me_3Sn(CF_3)PC(F)(CF_3)_2$ by gas-phase pyrolysis at 220 °C yields the perfluoroisopropenylphosphine $F_3CP(F)C(CF_3){=}CF_2$ instead of the expected isopropylidene derivative $F_3CP{=}C(CF_3)_2$. This result can be explained by a spontaneous isomerization of the labile intermediate $F_3CP{=}C(CF_3)_2$[72] (Scheme 5).

2. Miscellaneous Reactions

a. Retro-Ene and Retro-Diels–Alder Reactions. The retro-ene and retro-Diels–Alder reactions are important synthetic methods for the preparation of unsaturated and often reactive molecules. Heteroatoms can be present and doubly as well as triply bonded molecules can be prepared. Synthetic applications of these two methods have been recently reviewed.[73,74] While a number of unsaturated nitrogen-, sulfur-, and silicon-[75] containing species have been synthesized, it is striking that only a few phosphaalkenes have been prepared by such approaches.

Scheme 6

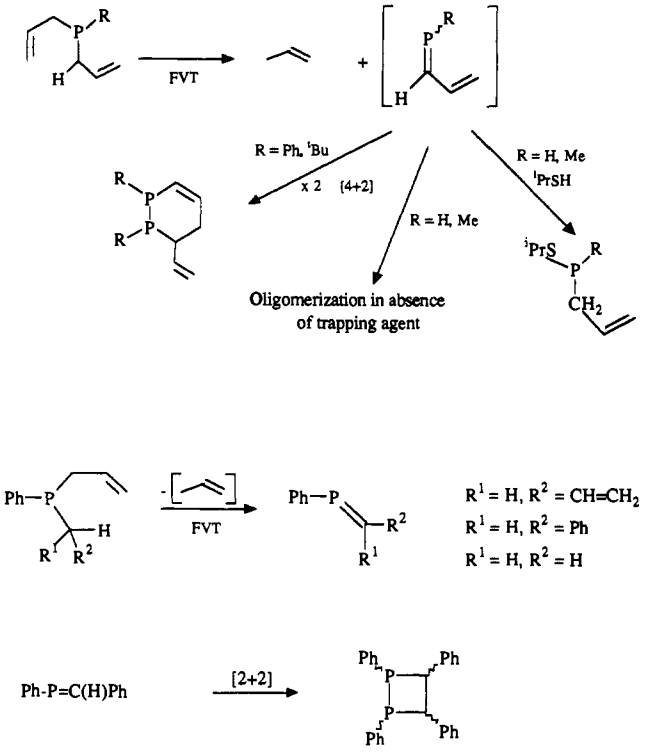


i. Retro-Ene Reactions. 1-Phosphabutadienes (R = Ph, ^{t}Bu) were generated by thermolysis of the corresponding diallylphosphines. Low-temperature ^{31}P NMR data of the two isomers (δ = 205.7, 191.5, and 205.7, 204.4, respectively) are in good agreement with the proposed structures. These intermediates dimerize on warming in a [4 + 2] cycloaddition. The diphosphacyclohexadiene isomers were characterized by NMR and mass spectrometry[76] (Scheme 7).

Independently, the unsubstituted phosphadienes and the *P*-methylphosphadienes were prepared by a similar approach. They were characterized by MS, PES, and IR spectroscopy and chemical trapping. Oligomerization was observed upon warming in absence of trapping agent[77] (Scheme 7).

By using kinetic studies, a six-center cyclic transition state unimolecular reaction mechanism was proposed in the propene elimination starting from allyl phosphines.[76,78] This result extends the analogy between P–C and C–C double bonds.[12] The phosphaalkene bearing a phenyl substituent was not isolated but only characterized by its dimeric structure formed in a head to head [2 + 2] cycloaddition reaction and the transient

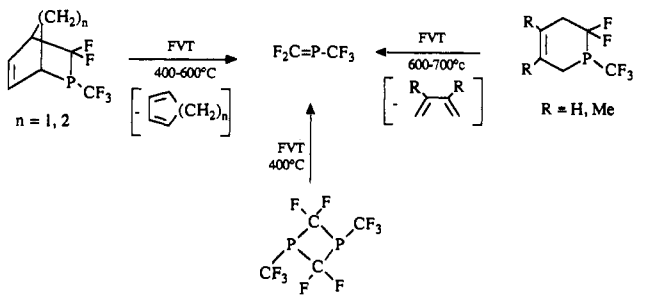
Scheme 7



P-(phenylmethylidene)phosphine only leads to oligomers (Scheme 7).

ii. Retro-Diels–Alder Reactions. Only a few phosphaalkenes have been prepared by retro-Diels–Alder reactions upon flash-vacuum thermolysis. Perfluorophosphapropene was formed upon heating the corresponding norbornene, cyclohexene, cyclopentadiene, or other various cycloadducts (Scheme 8). For most of

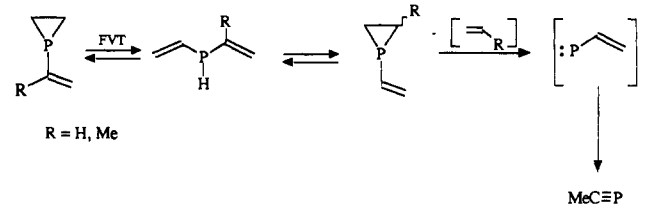
Scheme 8



these adducts, the thermal gas-phase retro [4 + 2] cleavage was found to be the best source for the formation of this perfluorophosphaalkene.[60,70,71-79] The enthalpy of the cycloreversion reaction of the cyclopentadiene adduct as well as the estimated bond energies for the P=C σ and π bonds have been determined from appearance potentials and thermochemical literature data. For $CF_3P{=}CF_2$ reasonable values of 330 and 157 kJ/mol have been estimated for the σ and π C–P bond, respectively.[79] The perfluorophosphaalkene dimer is also an excellent precursor; the retro [2 + 2] reaction under FVT conditions leads quantitatively to the expected phosphaalkene.[99] Reactivity of this structure has been developed previously (section III.A.1).

b. Vinylphosphirane Thermolysis. As a somewhat unexpected result, phosphapropyne was obtained

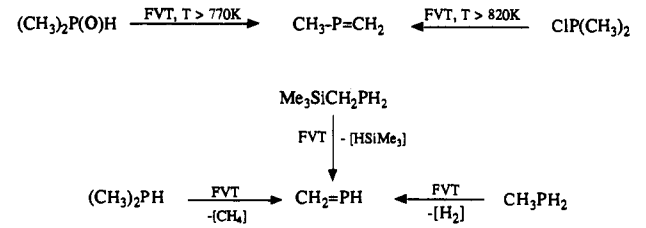
Scheme 9



by gas-phase thermolysis of vinylphosphirane or divinylphosphine (Scheme 9). The same product was also obtained upon heating the *P*-methyl derivatives under similar conditions. An equilibrium between divinylphosphines and vinylphosphiranes was postulated. The formation of phosphapropyne can be rationalized by the formation of a vinylphosphinidene intermediate[80] in a retro [2 + 1] reaction starting from the phosphirane derivatives. The thermolysis of the divinylphosphine parent compound proved to be a viable route to phosphapropyne. As it was described earlier,[81] MeC≡P is stable at room temperature for at least 1 week in solution as already reported.

c. Thermal Dehydration; CH_4, $HSiMe_3$, and Isobutene Eliminations. The thermal dehydration of dimethylphosphine oxide and observation by PES of the corresponding phosphapropene is a rather surprising reaction (Scheme 10). From MNDO cal-

Scheme 10

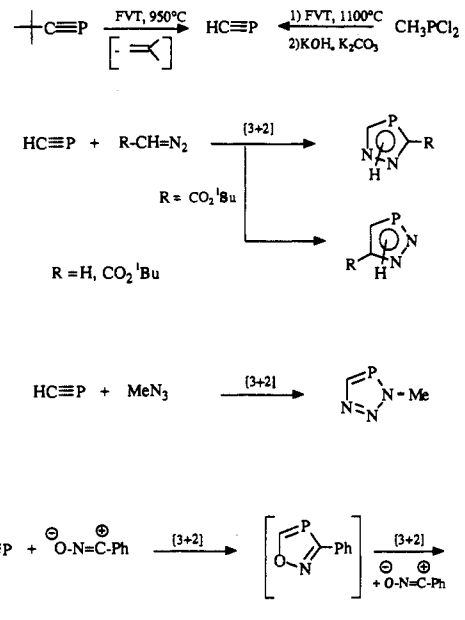


culations, a "chemically activated" $(CH_3)_2P$–OH tautomer was suggested as an intermediate. After optimization of the reaction conditions, better results were obtained with the HCl elimination starting from chlorodimethylphosphine (section III.A.1).[82,83,47]

The phosphaalkene parent compound was originally detected by Hopkinson in the pyrolysis products of dimethylphosphine (CH_4 elimination) and was characterized by microwave spectrometry.[33] Later, the same compound was prepared by hydrogen elimination starting from methylphosphine[84] and by silane elimination starting from the corresponding silylphosphine[85] (Scheme 10). Characterization by microwave studies has allowed the determination of the ground-state rotational constants,[84] dipole moments,[85] molecular structure,[86] and hyperfine structure.[87] The dipole moment components have also been determined (μ_a = 0.723 D and μ_b = 0.466 D).

Since phosphaalkynes can be generated by flash-vacuum thermolysis, it is not surprising that (*tert*-butylmethylidyne)phosphine can be converted into methylidynephosphine by cleavage of isobutene. Even though this reaction is not complicated by the simultaneous evolution of HCl as in the case of (dichloromethyl)phosphine (section III.1), the low yield obtained (~10%) and the synthetic expenditure required for $^tBuC{\equiv}P$ negate any possible advantages in comparison to the generation of HC≡P from (dichloromethyl)-

Scheme 11

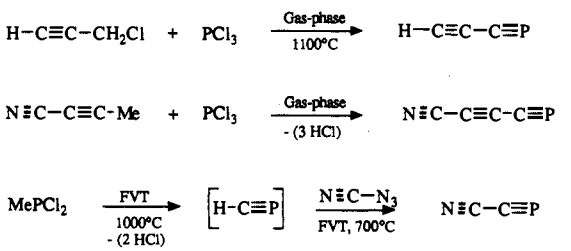


phosphine. HC≡P was characterized by ^{31}P NMR and by chemical trapping with stable dipoles like diazo compounds, methyl azide and benzonitriloxide, to give the corresponding azaphospholes.[36] From these various reactions, the synthetic potential of simple phosphaalkynes can easily be appreciated (Scheme 11).

B. Gas-Phase Condensation (Method B)

Phosphaalkynes are usually produced in the gas phase by pyrolytic elimination of HX (X = F, Cl) from suitable starting materials. In the case of HC≡CC≡P, attempts to synthesize a valuable precursor were unsuccessful. It was subsequently found that copyrolysis of a 2:1 mixture of $HC{\equiv}CCH_2Cl$ and PCl_3 led to the desired product, which was identified by microwave spectroscopy[88] (Scheme 12). Formation of the ethynyl(dichloromethyl)phosphine intermediate has been strongly suggested.

Scheme 12



By using this copyrolysis process, cyanophosphabutadiyne was produced by flowing 1-cyanoprop-1-yne and phosphorus trichloride (Scheme 12). The optimum yield was observed at a pyrolysis temperature lower than 1100 °C.[89]

Cyano phosphaethyne was detected in the products of the gas-phase reaction between cyanogen azide and HC≡P. The reaction involves a coupling between a possible •CN radical obtainable from NCN_3 with HC≡P, dichloromethylphosphine being used as a source of HC≡P[90,91] (Scheme 12).

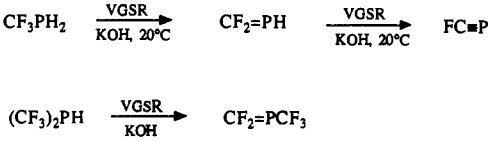
In these gas-phase condensations, these three heterophosphapolyynes are probably obtained in a very low yield, but the highly sensitive microwave technique still can detect them. No other approach to these interesting products has been described so far.

C. Vacuum Gas–Solid Reactions (VGSR)

1. Base-Induced Elimination of HX (X = F, Cl, Method C)

a. Fluorophosphaalkenes and Fluorophosphaalkynes. It has been discovered that HF could be efficiently eliminated by passing CF_3PH_2 at room temperature through a spiral glass tube filled with broken solid KOH pellets[92] (Scheme 13). *C*-Fluorophosphaalkene and *C*-fluorophosphaalkyne which were obtained by this approach show a higher stability and purity than those formed under FVT conditions.[33,93,92] They were characterized by microwave,[33,93,92] photoelectron,[93] IR,[94,95] and NMR[49] spectroscopy.

Scheme 13



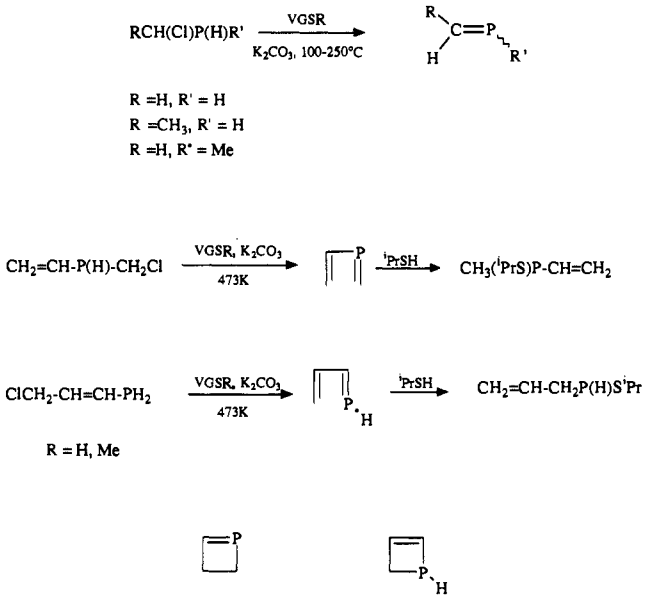
This reaction has been efficiently extended to the synthesis of $CF_3P{=}CF_2$.[96-99] This compound was found to be stable at −78 °C but rapidly polymerizes at room temperature[96] (see section III.A.1).

Interestingly, dehydrofluorination of α-fluorophosphines occurs at room temperature. Facility of HF elimination can be attributed to the relatively high P–H acidity induced by the fluorine atom (structure **A**, X = F). The following examples clearly demonstrate that HX elimination is strongly favored when the leaving group (X = F, Cl) is bonded to the carbon in α-position of the phosphorus atom (structure **A**, Scheme 14).

Scheme 14

b. Simple Phosphaalkenes. While CH_3PCl_2 is stable even at high temperature or over a solid base (VGSR experiments with K_2CO_3),[100] $ClCH_2PH_2$ slowly decomposes at room temperature in the liquid phase to produce HCl and methylidenephosphine polymers.[101] The transient methylidenephosphine $CH_2{=}PH$ was formed by passing $ClCH_2PH_2$ under vacuum over solid K_2CO_3 heated to 150–200 °C (VGSR conditions) and characterized by high-resolution mass spectrometry (HRMS)[102] and photoelectron[103] and IR spectroscopy after condensation of the gaseous flow on a KBr window cooled at 77 K[102] (Scheme 15). Stability of $CH_2{=}PH$ was evaluated by the rapid decrease of the ν_{PH} (2260 cm^{-1}) stretching frequency and the large band at 850 cm^{-1} ($\tau_{1/2} \approx 10$ min on the KBr window in pure form at 77 K). From theoretical calculations,[104] the band at 850 cm^{-1} initially attributed to the $\nu_{C=P}$ could be reassigned to the CH_2 wagging frequency which has a very strong intensity. The $\nu_{C=P}$ stretching frequency observed at 1012 cm^{-1} after reexamination of the IR spectra[105] is in good agreement with the calculated ones

Scheme 15



(1017 cm^{-1}) and the intrinsic value (980 cm^{-1}) which was determinated by Ohno *et al.* for a variety of phosphaalkenes.[95]

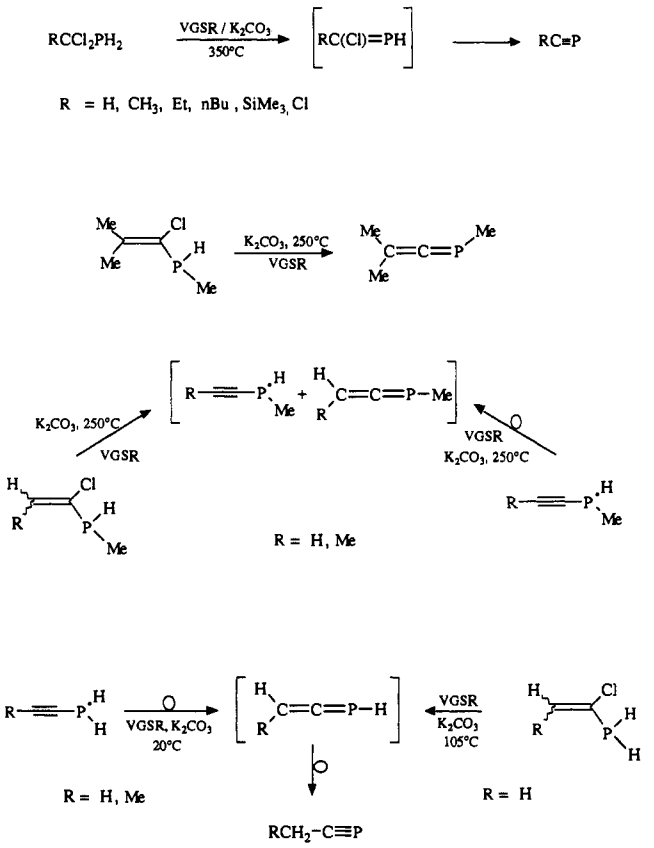
Dehydrochlorination of P- and C-substituted α-chlorophosphines on solid K_2CO_3 occurs at higher temperatures (100–250 °C)[103,106] (Scheme 15). Formation of the corresponding phosphaalkenes was evidenced by IR (77 K) and HRMS[105,106] and for $CH_3C(H)=PH$ by PES.[103] Attempts to characterize the parent compound (R,R' = H) by chemical trapping (2-propanethiol or cyclopentadiene directly condensed with the transient species on the cold trap) or by low-temperature ^{31}P NMR after classical transfer were unsuccessful; oligomerization was the only observed process. However, as it will be further mentioned, ^{31}P NMR and chemical trapping can be carried out when HCl elimination occurs in solution (section IV.A.1). The parent compound and the *C*-methyl derivative have been characterized by photoelectron spectroscopy using a VGSR apparatus directly fitted to the spectrometer.[103]

c. 1-Phosphabutadiene and 2-Phosphabutadiene. Simplest phosphadienes have also been prepared in VGSR conditions. The 2-phosphabutadiene and 1-phosphabutadiene parent compounds are, respectively, formed by 1,2- and 1,4-HCl elimination starting from the corresponding chlorophosphine precursors (Scheme 15) and characterized by IR (77 K), MS, and PE spectroscopy[77] and also ^{31}P and ^{1}H NMR for 2-phosphabutadiene. Small yields of the corresponding thiol adducts are obtained as compared with those obtained when the reaction occurs in solution (section IV.A.1). The 1-phosphabutadienes were also produced by heating the corresponding diallylphosphines under FVT conditions (section III.A.2).

Recent theoretical calculations[107,108] predict that the ring closure of the two phosphadiene parent compounds are nearly thermoneutral and that activation barriers for these transformations are less than 130 kJ mol^{-1}. Although the corresponding dihydrophosphete isomers are not detected, their presence in small amounts is not however excluded.[77]

d. Phosphaalkynes. Unstabilized phosphaalkynes bearing a primary alkyl group or a heteroelement (Cl, $SiMe_3$) were also prepared in good yield by taking advantage of the P–H acidity of α-dichlorophosphines[81] (Scheme 16). The *C*-chlorophosphaalkene intermediates were never detected. Phosphaalkynes are collected by standard procedures and fully characterized by NMR, IR spectroscopy, and mass spectrometry.

Scheme 16



The photoelectron spectrum of the chlorophosphaethyne (R = Cl) generated in the gas phase (VGSR) has been reported.[109] It indicates large interaction between the degenerated P≡C triple bond and the chlorine lone pair. The $\nu_{C\equiv P}$ stretching (77 K) ranges from 1267 cm^{-1} for HC≡P to 1572 cm^{-1} for $Me_3SiC\equiv P$. The half-life of HCP in solution is 6 h at room temperature. For the *C*-alkyl derivatives, a rapid oligomerization is observed in the condensed phase as for HC≡P but they can be kept a few days in solution at room temperature without decomposition. The stability of these compounds, higher than previously reported, can be explained by the absence of byproducts. Thus, this procedure is very efficient for the preparation of an amount of 1 or 2 g of the simplest phosphaalkynes in the pure form.

e. 1-Phosphaallenes. Unstabilized trimethyl-1-phosphaallene was obtained by gas-phase HCl elimination on solid K_2CO_3 starting from the corresponding chlorovinylphosphine. Formation of a mixture of substituted ynephosphines and phosphaallenes in a molar ratio (67/33, R=H and 55/45, R=Me) in the dehydrochlorination of (chlorovinyl)phosphines (R = H, Me) can be rationalized by a tautomeric phosphaallene/ynephosphine equilibrium[110] (Scheme 16).

Phosphaallenes were collected by a standard procedure (section II) and fully characterized at low temperature by ^{1}H, ^{13}C, and ^{31}P NMR and chemical trapping (thiol addition). The observed values are in good

agreement with those reported for the bulky substituted derivatives.[111] Oligomerization was observed upon warming at room temperature. The IR (77 K) absorptions of the *P*-methylphosphaallene derivative (1715 and 869 cm^{-1}) have been assigned respectively to the $\nu_{C=C}$ and $\nu_{C=P}$ stretching frequencies. They are in good agreement with the predicted frequencies established for the parent compound.[112]

All attempts to characterize $H_2C{=}C{=}PH$ by HCl elimination starting from the primary (chlorovinyl)-phosphine were unsuccessful; $CH_3C{\equiv}P$ was the only isolated product. Rearrangement of the phosphaallene intermediate by a 1,3-hydrogen shift rationalizes this result. As will be further discussed (section V.4), these one line two reactions (HCl elimination and 1,3-hydrogen shift) are also observed in solution.

2. Base-Induced Rearrangement (Method D)

The base-induced rearrangement in solution of phosphines bearing an unsaturated group in α-position to the phosphorus will be developed in a special chapter (section V). Rearrangement of volatile secondary ethynylphosphines in the gas phase on solid K_2CO_3 into the corresponding 1-phosphaallenes has been observed. However the transformation is not complete, whatever the conditions. Observation of the two isomers (ethynylphosphine and 1-phosphaallene) in the same molar ratio as precedently reported by HCl elimination of (chlorovinyl)phosphine (section III.C.1) is in favor of a tautomeric equilibrium (Scheme 16).

Phosphapropyne and phosphabutyne were the only products isolated in good yield by passing the corresponding primary ethynylphosphines on solid K_2CO_3 at room temperature; the phosphaallene intermediates were not detected[113] (Scheme 16).

3. Gas-Phase Reductions (Method E)

Chlorophosphaethyne has been produced by gas-phase reduction of Cl_3CPCl_2 over granulated zinc at 530 °C (Scheme 17), and its microwave[114,115] and

Scheme 17

$$CCl_3PCl_2 \xrightarrow[\text{VGSR, 530°C}]{\text{Zn}} Cl\text{-}C{\equiv}P$$

$$Cl_2\text{-}P{-}C{\equiv}C{-}P{-}Cl_2 \xrightarrow[\text{VGSR}]{MgCl_2/MgO/SiO_2} P{\equiv}C{-}C{\equiv}P + P_4 + PCl_3$$

photoelectron[116] spectra have been recorded. The lack of previous success in detecting this species by MWS has been attributed to the expected small dipole moment and to the splittings due to the chlorine nuclear quadrupole moment. By using the rotational and centrifugal distortion constants from a high resolution FTIR study of the 1475-cm^{-1} band of $ClC{\equiv}P$, very weak microwave transitions of $^{35}ClC{\equiv}P$ were detected. The bond lengths were determined to be 1.6635 Å (Cl—C) and 1.554 Å (C≡P). As predicted, the resulting dipole moment of $ClC{\equiv}P$ was found to be very small (0.056 D).

The PES of $ClC{\equiv}P$ shows four peaks. The first band (10.10 eV) corresponds to the ionization of the π molecular orbital and the second (12.94 eV) to the ionization of the σ (P) molecular orbital. These assignments are supported by *ab initio* SFC calculations. Similar PES spectra have been obtained when $ClC{\equiv}P$ was formed by base-induced HCl elimination starting from CCl_3PH_2[117] (section III.C.2).

Different catalysts have been tested as potential dehydrochlorinating agents for phosphorus halides. Gas-phase reaction of $Cl_2PC{\equiv}CPCl_2$ over a solid catalyst (10% $MgCl_2/MgO/SiO_2$) produced predominantly PCl_3 and P_4, but PES and mass spectroscopy have provided evidence of the formation of a small amount of $P{\equiv}CC{\equiv}P$[118] (Scheme 17).

Table 1 and 2 sum up the different gas-phase preparations of phosphaalkenes and phosphaalkynes, respectively. (Only the first detection of the species is mentioned.) Spectroscopic NMR and IR data of these compounds are collected in Table 9 (NMR of phosphaalkenes), Table 10 (NMR of phosphaalkynes), and Table 11 ($\nu_{C\equiv P}$ and $\nu_{C=P}$ stretching).

D. Structural Parameters of the P–C Multiple Bonds

Structural information on the P–C multiple bonds were obtained by microwave and photoelectron spectroscopies.

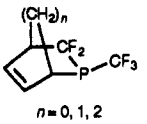
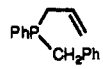
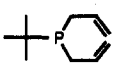
1. Microwave Spectroscopy (MWS)

Microwave spectroscopy (MWS) is a powerful tool for the identification of new compounds since it allows their structural determination. The first identification of numerous phosphaalkene and phosphaalkyne derivatives such as $CH_2{=}PH$,[33] $CH_2{=}PCl$,[33] $CF_2{=}PH$[33] (1976), $PhC{\equiv}P$[53] (1982), and more recently $P{\equiv}C{-}C{\equiv}P$[120] was realized by this technique. For $HC{\equiv}P$, the simplest phosphaalkyne, the MW spectra were obtained as early as 1964.[121a]

In the phosphaalkenes series, the P=C bond length varies between 1.63 to 1.673 Å with an average of 1.67 Å, clearly shorter than that of a typical P–C single bond (1.8–1.9 Å). In Table 3, the structural parameters of $CH_2{=}PH$ are compared with those of other phosphaalkenes. As expected, the substitution of an H on the P atom by a chlorine or a fluorine atom results in a slight shortening of the P=C bond (1.673 Å in $CH_2{=}PH$,[86] 1.658 in $CH_2{=}PCl$,[48] and 1.644 in $CH_2{=}PF$[58]) and an increase in the CPX angle (~6°), probably as a result of enhanced sp^2 hybridization on the P atom. These variations are paralleled by those observed in the corresponding ethene derivatives.[122] For $CH_2{=}PCN$, the somewhat short bond length of the P–X bond (1.788 Å) is likely due to the conjugative interaction between the C–N triple bond and the P lone pair and/or the C–P double bond.[50] The observed shortening of the C–C single bond in $CH_2{=}CHCN$[123] is in agreement with this.

In the phosphaalkyne series, the P–C triple bond lengths are more or less the same whatever the substituent (1.54 Å) (see Table 4). The dipole moment of $ClC{\equiv}P$ is very small[115] (0.056 D) and indicates that the bond moment of the Cl–C bond is very close to, and oppositely directed to, that of the C–P triple bond. Comparison with the values measured for $HC{\equiv}P$[121a] (μ = 0.392 D) and $FC{\equiv}P$[127] (μ = 0.279 D) implies a change of sign of the dipole moment on going from $HC{\equiv}P$ to $FC{\equiv}P$, as chlorine is intermediate in electronegativity between hydrogen and fluorine. For $N{\equiv}CC{\equiv}P$,[90] the dipole moment is quite large (3.5 D), this value is close to that of $HC{\equiv}CCN$.[90] All these

Table 1. Gas-Phase Generation of Simple Phosphaalkenes and Phosphaallenes

compound	precursor	method[a]	first detection	yield (%)	ref	comments
CH_2=PCl	CH_3PCl_2	A	MWS		33	presence of various amount of HC≡P. Problem with the back-reaction. $\tau_{1/2}$ = 1.5 min at room temp in the gas phase
	CH_3PCl_2	A	^1H, ^{13}C, ^{31}P NMR; chemical trapping	35	35	HCl removing on solid triazine. $\tau_{1/2}$ = 5 min at room temp in solution
	$TmsCH_2PCl_2$	A	MWS		85	
Me(H)C=PCl	$CH_3CH_2PCl_2$	A	^{31}P, ^1H, ^{13}C NMR; chemical trapping	15	35	HCl removing on solid triazine. $\tau_{1/2}$ = 3 min at -20 °C in solution
	$TmsCH(CH_3)PCl_2$	A	^{31}P, ^1H, ^{13}C NMR; chemical trapping	60	35	better yield with elimination of TmsCl, but lower stability of the phosphaalkene (decomposition in solution up to -40 °C)
H_2C=PF	$TmsCH_2PF_2$	A	MWS		58	better yield with elimination of TmsCl
	ClH_2PF_2	A				
CF_2=PH	CF_3PH_2	A	MWS		33	
		C (KOH)	^{19}F, ^{31}P NMR		49	
CF_2=PMe	$Me_3SnP(CF_3)Me$	A	chemical trapping	low	71	
CF_2=PEt	$Me_3SnP(CF_3)Et$	A	chemical trapping	low	71	
F(H)C=PCF_3	$Me_3SnP(CF_3)CF_2H$	A	chemical trapping	low	69	
F_2C=PCF_3	$Me_3SnP(CF_3)_2$	A	MS; ^{19}F NMR; dimerization	≈85	59	
	$(CF_3)_2PH$	C (KOH)	^{19}F, ^{31}P NMR; chemical trapping	low	96	
	$(CF_3)_2PH$	A	^{19}F, dimerization		99	
	 n = 0, 1, 2	A	MS; dimerization and chemical trapping		79	
$(F_3C)_2C$=PCF_2	$Me_3SnP(CF_3)[CF(CF_3)_2]$	A	isomerization into perfluoroalkene (1,3-F shift)		72	perfluorophosphaalkene is only an intermediate
	$CF_3(H)PCF(CF_3)_2$	C (KOH)	isomerization into perfluoroalkene (1,3-F shift)	12	72	perfluorophosphaalkene is only an intermediate
$F_3CC(F)$=PCF_3	$Me_3SnP(CF_3)CF_2CF_3$	A	^{19}F, ^{31}P, NMR; dimer, chemical trapping		68	
F_2C=PC_2F_5	$Me_3SnP(C_2F_5)CF_3$	A	^{19}F, ^{31}P, NMR; dimer, chemical trapping		68	
$CF_3(F)C$=PC_2F_5	$Me_3SnP(C_2F_5)_2$	A	^{19}F, ^{31}P NMR; MS; chemical trapping		67	slow dimerization in solution at room temp
CH_2=PH	$(CH_3)_2PH$	A	MWS		33	
	CH_3PH_2	A	MWS		85	better yields with the silyl derivative
	$Me_3SiCH_2PH_2$	A	MWS		85	
	$ClCH_2PH_2$	C (K_2CO_3)	MS, IR		102	
CH_2=PCH_3	$(CH_3)_2PCl$	A	PES, MS		47	
	$(CH_3)_2POH$	A	PES		82	
	$ClCH_2P(H)Me$	C (K_2CO_3)	MS		106	
CH_2=PCN	$Me_3SiCH_2P(CN)Cl$	A	MWS		50	TmsCl elimination is favored over TmsCN. $\tau_{1/2}$ = 6 s in the gas phase
H_2C=PPh		A	dimerization; cycloaddition reactions	low	76	poor yield in the cycloaddition reactions
$CH_3(H)C$=PH	$ClCH(Me)PH_2$	C (K_2CO_3)	PES		103	
Ph(H)C=PPh		A	dimerization	low	76	
CH_2=CHCH=PH	$ClCH_2CH$=$CHPH_2$	C (K_2CO_3)	IR; MS; PES; chemical trapping		77	
	$(CH_2CH$=$CH_2)_2PH$	A	IR; MS; PES; chemical trapping		77	
CH_2=CHCH=PMe	$(CH_2CH$=$CH_2)_2PMe$	A	IR; MS; PES; chemical trapping		77	
CH_2=CHCH=P^{t}Bu		A	^{31}PNMR; dimerization	low	76	
CH_2=CHCH=PPh		A	^{31}P NMR; dimerization	low	76	
CH_2=CHP=CH_2	CH_2=CHP(H)CH_2Cl	C (K_2CO_3)	^1H, ^{31}P NMR; IR; MS; PES; chemical trapping		77	
H_2C=C=PMe	CH_2=C(Cl)P(H)Me	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; IR; MS	26	110	presence of the corresponding alkynylphosphine (8%)
	HC≡CP(H)Me	D (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; IR; MS	28	110	presence of the corresponding alkynylphosphine (8%)
MeCH=C=PMe	MeCH=C(Cl)P(H)Me	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; IR; MS	32	110	presence of the corresponding alkynylphosphine (45%)
	MeC≡CP(H)Me	D (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; IR; MS	26	110	presence of the corresponding alkynylphosphine (45%)
Me_2C=C=PMe	Me_2C=C(Cl)P(H)Me	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; IR; MS		110	

[a] Method A, FVT; Method C, gas-phase elimination on solid base (VGSR, the base used is indicated in brackets); Method D, gas-phase rearrangement (VGSR, the base used is indicated in brackets).

Table 2. Gas-Phase Generation of Simple Phosphaalkynes

compound	precursor	method[a]	first detection	yield (%)	ref	comments
HC≡P	PH_3 + graphite electrode	electric arc	IR; MS; combustion analysis of $(HC{\equiv}P)_n$ and chemical trapping		14	first detection of a phosphaalkyne derivative
	CH_3PCl_2	A	MWS		33	$CH_2{=}PCl$ was also detected
	CH_3PCl_2	A	MWS;[b] ^1H, ^{31}P, ^{13}C NMR,[c,d] chemical trapping[c,d,e]	30[c]	34,35	KOH,[b] triazine,[c]
					36,45	KOH/K_2CO_3[d] and Et_3N[e] are used to prevent back-reaction, $CH_2{=}PCl$ was also detected.[c] $\tau_{1/2}$ = 5 min at -10 °C in solution
	$^tBuC{\equiv}P$	A	chemical trapping	9	36	low yield and time consuming for the precursor synthesis
	$CH_3P(O)(H)OH$	A	PES		82	
	$HCCl_2PH_2$	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; MS	80	81	this compound exhibits a reasonable stability (6 h in solution)
MeC≡P	$MePCl_2$	A	MWS,[f] PES,[g]	10[f]	40,41	
	$MePCl_2$	A	^1H, ^{13}C, ^{31}P NMR,[c]	30[c]	35,45	triazine[c] and Et_3N[e] were used to prevent back-reaction
			^{31}P, ^1H NMR and chemical trapping[e]	5–8[e]		
	$MeCCl_2PH_2$	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; MS	80	81	this compound exhibits a reasonable stability (>7 d in solution)
	$HC{\equiv}CPH_2$	D (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; MS		113	this compound exhibits a reasonable stability (>7 d in solution)
	$(CH_2{=}CH)_2PH$	A	^{31}P NMR; chemical trapping		80	this compound exhibits a reasonable stability (>7 d in solution)
EtC≡P	$CH_3CH_2CCl_2PH_2$	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; MS,	80	81	this compound exhibits a reasonable stability (>7 d in solution)
^{n}BuC≡P	^{n}BuCCl$_2$PH$_2$	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR, MS	70	81	this compound exhibits a reasonable stability (>7 d in solution)
$CH_2{=}CH{-}C{\equiv}P$	$CH_2{=}CHCH_2PCl_2$	A	MWS		41	
	$H_2C{=}CHCH_2Cl_2 + PCl_3$	B	MWS		44	
PhC≡P	$Ph(Me_3Si)C{=}PCl$	A	MS; ^{13}C, ^{31}P NMR; chemical trapping	high	52	$\tau_{1/2}$ = 7 min at 0 °C in solution
TmsC≡P	$(Tms)_2C{=}PCl$	A	^{31}P, ^{13}C NMR	high	51	
	$TmsCCl_2PH_2$	C (K_2CO_3)	^1H, ^{31}P, ^{13}C NMR; MS	65	81	thus prepared, this compound exhibits a reasonable stability (1 d in solution)
ClC≡P	CCl_3PCl_2	E (Zn)	MWS		114	
	CCl_3PH_2	C (K_2CO_3 or CaO)	^1H, ^{31}P, ^{13}C NMR; MS	60	81	thus prepared, this compound exhibits a reasonable stability (10 h in solution)
FC≡P	CF_3PH_2	C (KOH)	PES		93	
N≡CC≡P	NCN_3 + HCP	B	MWS		90	
P≡CC≡P	$Cl_2PC{\equiv}CPCl_2$	E ($MgCl_2$, MgO, SiO_2)	PES		118	
HC≡CC≡P	$HC{\equiv}CCH_2Cl + PCl_3$	B	MWS		88	
NCC≡CC≡P	$CH_3C{\equiv}CC{\equiv}N + PCl_3$	B	MWS	poor	89	

[a] Method A, FVT; method B, condensation–elimination in the gas phase; method C, gas-phase elimination on solid base (VGSR, the base used is indicated in brackets); method D, gas-phase rearrangement (VGSR, the base used is indicated in brackets); method E, gas-phase reduction (VGSR). [b] Reference 34. [c] Reference 35. [d] Reference 36. [e] Reference 45. [f] Reference 40. [g] Reference 41.

Table 3. Structural Parameters of Simple Phosphaalkenes (from MWS)

compound	year	r(C=P)[a]	r(P—X)[a]	∠CPX[b]	τ[c]	ref
$CH_2{=}PH$	1976	1.670	1.420	100.0		33
	1977	1.670	1.470	98.0		124
	1978	1.632	1.421	108.2		125
	1981	1.671	1.425	95.5	11 min	86
	1981	1.673	1.420	97.4		85
$CH_2{=}PCl$	1976	1.670	2.040	104.0	1.5 min	33
	1982	1.655	2.060	103.3		126
	1984	1.658	2.059	103.7		48
$CH_2{=}PF$	1989	1.644	1.598	104.16		58
$CH_2{=}PCN$	1987	1.658	1.788	101.4	6 s	50
$CF_2{=}PH$	1976	1.671	1.420	100.0	1.3 min	33

[a] Bond lengths (in Å). [b] Bond angles (in deg). [c] Stability in the gas phase.

bond lengths are in agreement with the results of recent interesting theoretical investigations which study the effect of substituents on the C–P triple bond lengths.[128,129] A comparative study of the bond lengths of various RC≡E (E = N, P, As, Sb) is also presented.[129]

Table 4. Structural Parameters of Simple Phosphaalkynes (from MWS)

compound	year	r(C≡P)[a]	r(C_p—X)[a]	μ[b]	ref
HC≡P	1964	1.542	1.066	0.392	121a
	1979	1.542		0.39	40
	1984	1.540	1.066		121b
FC≡P	1980	1.541	1.285	0.279	127
ClC≡P	1990	1.544	1.646		114
	1992	1.554	1.635	0.056	115
$CH_3C{\equiv}P$	1979	1.544	1.465	1.499	40
PhC≡P	1982	1.544[c]	1.467		53
$^tBuC{\equiv}P$	1991	1.540			130
N≡CC≡P	1982	1.547	1.382	3.44	91
HC≡CC≡P	1981	1.544[c]	1.382	0.745	88
$CH_2{=}CHC{\equiv}P$	1981	1.544	1.432	1.181	44
N≡CC≡CC≡P	1985	1.547	1.362	4.3	89

[a] Bond lengths (in Å). [b] Dipole moment (in debye). [c] Values were fixed in the structural determination.

2. Photoelectron Spectroscopy (PES)

Most of the volatile unstabilized phosphaalkenes and phosphaalkynes have been characterized by photo-

Table 5. Calculated and Experimental Ionization Potential of Phosphaalkynes[a]

	calculated IP[b]			experimental IP		
compound	$\pi_{C\equiv P}$[c]	n_P[d]	ref	$\pi_{C\equiv P}$[c]	n_P[d]	ref
HC≡P	10.50	13.42	131			
	10.00	12.6	132	10.79	12.86	132
FC≡P	10.53	13.94	93	10.57	13.55	93
$CH_3C\equiv P$	9.69	12.95	131	9.89	12.19	41
ClC≡P	10.13	13.75	131			
	10.12	13.44	116	10.10	12.94	116
	10.30	13.20	131	10.05	12.98	109
$^tBuC\equiv P$				9.70	11.45	55
	9.46	12.07	54	9.61	11.44	54
$(CH_3)_3SiC\equiv P$				9.90	10.90	55
PhC≡P	8.35, 9.82	12.51	54	8.68, 9.87	11.76	54
				9.80, 10.9	11.90	55

[a] IP (in eV). [b] Calculated IP assuming Koopman's theorem applies. [c] Assignment of the first IP. [d] Assignment of the second IP.

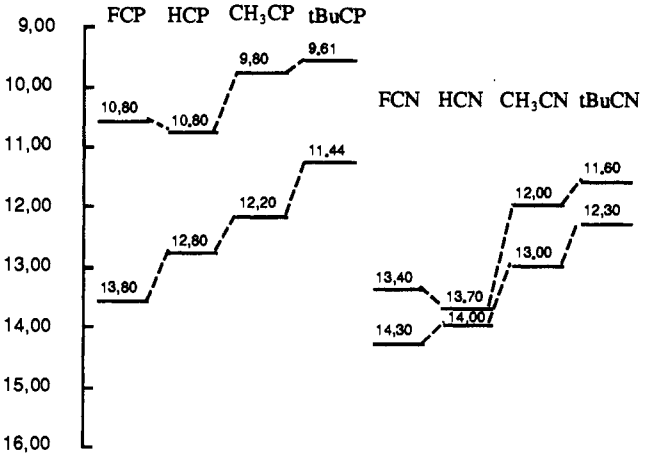


Figure 1. Correlation between vertical ionization potentials of nitriles and phosphaalkynes.

electron spectroscopy. PES is a valuable technique for the analysis and the optimization of numerous gas-phase reactions in flow systems and provides interesting information on the assignment and the values of the highest occupied molecular orbital (HOMO) which are of fundamental significance for the properties and the reactivity of a compound.

In the phosphaalkynes series, the bond having the lowest ionization potential (IP) corresponds to the removal of an electron from a bonding π orbital mainly localized in the C≡P bond. The second band has been assigned as arising from the removal of a nonbonding electron localized at the phosphorus atom (Table 5).

The ionization potential of phosphaalkynes are lower than those of the corresponding nitriles as it can be expected when N is replaced by the less electronegative P atom. This property is reflected in the much more pronounced ligand behavior of the phosphaalkynes in comparison with their nitrogen analogues. In Figure 1, the correlation diagram for the first and second IP values of FC≡P,[93] HC≡P,[132] $CH_3C\equiv P$,[41] and $^tBuC\equiv P$[54] is presented. These values are compared with those of the analogous nitriles FC≡N,[133] HC≡N,[132] $CH_3C\equiv N$,[134] and $^tBuC\equiv P$.[135]

Another important feature is the increased π/n separation in phosphaalkynes series compared with the analogous nitriles.[54] This property has been considered as a quantitative indicator of the reduced overlap in

Table 6. Calculated and Experimental Ionization Potentials of Phosphaalkenes and Phosphabutadienes[a]

	calculated IP[b]			experimental IP		
compound	$\pi_{C=P}$	n_P	ref	$\pi_{C=P}$	n_P	ref
$CH_2{=}PH$	9.63	10.43	141	10.30	10.70	103
	10.18	10.42	142			
$CH_2{=}PCH_3$	9.29	9.92	141	9.69	9.97	47
$H(CH_3)C{=}PH$	9.11	10.26	141	9.75	10.35	103
$CH_2{=}PCl$	9.92	10.95	103	10.05	10.75	37
$CH_2{=}CHP{=}CH_2$	9.08	10.44	77	9.28	9.96	77
$CH_2{=}CHCH{=}PH$	8.65	10.74	77	9.00	10.13	77

[a] IP (in eV). [b] The calculated IP are obtained using the Monstergauss program with a modified 4-31G basis set; IP's are evaluated with Koopman's approximations.

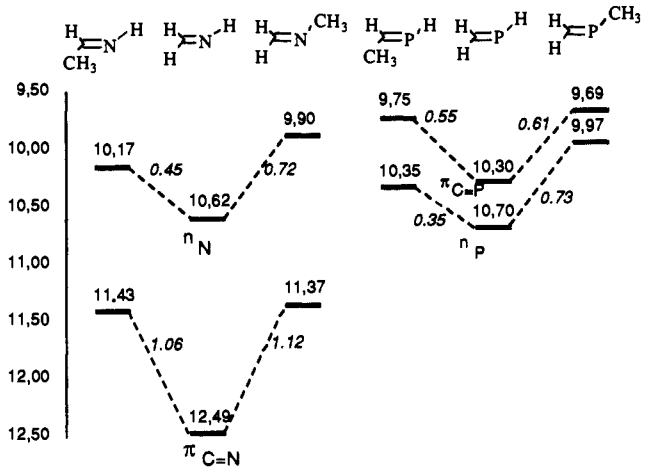


Figure 2. Correlation between vertical ionization potentials of imines and phosphaalkenes.

the p_π phosphaalkynes relative to nitriles.[54] The main effect is the destabilization of the π bonding in the C≡P derivatives. These results are in agreement with *ab initio* SFC calculations on phosphaalkynes RC≡P (R = H, CH_3, F, Cl) reported by N'guyen[131] (Table 5). The replacement of H by any of the considered substituents R destabilizes the π orbitals (by 0.05–0.91 eV). The decreasing order of π orbital energies is H > F > Cl > CH_3 > $(CH_3)_3Si$ > $(CH_3)_3C$ and this destabilization was rationalized in terms of the π-donor ability of substituents (+M effect). For the n orbital energies, the observed ordering F > Cl > H > CH_3 > $(CH_3)_3C$ > $(CH_3)_3Si$ is arising from the electron-withdrawing ability of the substituents (+I effect).[131]

In the case of phosphaalkenes, the vertical $\pi_{P=C}$ and n_P ionization energies are respectively observed at 10.30 and 10.70 eV for phosphaethene and at 9.75 and 10.35 for 1-phosphapropene.[103] These results are in agreement with a previously reported photoelectron study on 2-phosphapropene[47] for which the two closely spaced highest occupied levels correspond to the $\pi_{P=C}$ bond and to the phosphorus lone pair n_P. The HOMO in phosphaalkene derivatives corresponds to the $\pi_{P=C}$ bond (Table 6) in good agreement with theoretical calculations.[24,136-139] The situation is drastically different for the analogous nitrogen derivatives in which the HOMO is localized at nitrogen. In the imines series, a rather significant energy difference between the $\pi_{N=C}$ and n_N orbitals is observed[140] while in the phosphorus series, the $\pi_{C=P}$ orbital is quite close in energy to the P lone pair orbital (10.3 vs 10.7 eV). The lower π/n separation for the P=C with respect to the N=C results

in a destabilization of the π-bonding orbital in the phosphaalkene derivatives. In Figure 2, the correlation diagram for the first and second IP of CH_2=PH, CH_3-CH=PH, and CH_2=PCH_3 is presented. The values are compared with those of the analogous nitrogen derivatives (CH_2=NH, CH_3CH=NH, CH_2=NCH_3).

IV. Liquid-Phase Elimination Reactions (Method F)

A. Lewis Base-Induced HX Elimination (X = F, Cl)

Dehydrohalogenation of halophosphines bearing either an acidic P–H bond (structure A) or an activated C–H bond in the α-position to the phosphorus atom (structure C) is efficiently performed with Lewis bases (Scheme 18). Reactions occur under mild conditions,

Scheme 18

A C

X = Cl, F

E = electron–withdrawing group

often at low temperature. Oligomerization is lowered by low concentration of the reactive species in the medium. The structures of the P–C multiple bond derivatives are usually preserved at low temperature, allowing in most cases their ^{31}P NMR analysis. Reactive species are in most cases efficiently trapped by nucleophiles, dienes, and dipoles. No special equipment is required for these reactions.

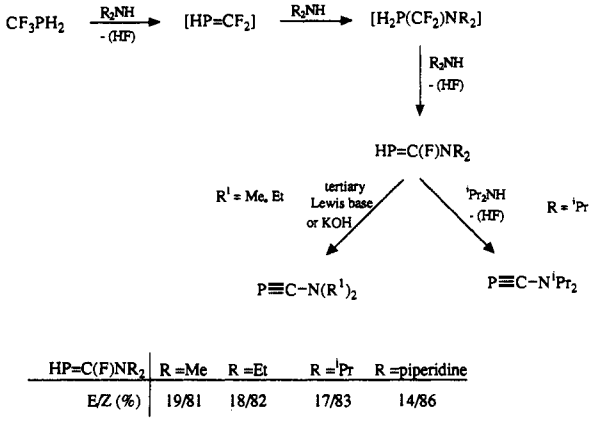
1. Base-Induced HX Elimination from α-Halophosphines

a. From α-(Fluoromethyl)phosphines. As already mentioned (section III.C.1), activation of the P–H bond with a halogen in α-position to the phosphorus is effective. The strategy developed by Grobe *et al.*[143] consists of forming a phosphaalkene intermediate by HF elimination with secondary Lewis bases. *C*-(Dialkylamino)-*C*-perfluorophosphalkenes (R = Me, Et, Pr, piperidine) were formed by a spontaneous addition of amine to the first phosphaalkene intermediate, followed by a second HF elimination. A stable *C*-(diisopropylamino)phosphaalkyne was isolated instead of the expected phosphaalkene when diisopropylamine was used (Scheme 19). With tertiary Lewis bases (NMe_3, NEt_3, quinuclidine) or solid KOH in tetraglyme, the *N*-(methyl- and *N*-(ethylamino)phosphaalkynes were obtained starting from the corresponding phosphaalkenes (Scheme 19).

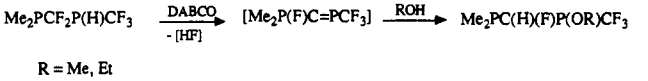
When the HF elimination is induced by a tertiary amine (DABCO), the (dimethylphosphinyl)perfluorophosphaalkene intermediate was formed and trapped with methanol or ethanol[63] (Scheme 19).

b. From α-(Chloromethyl)phosphines. Low-temperature dehydrohalogenation of $ClCH_2PH_2$ using DABCO led to methylidenephosphine.[102] By monitoring the reaction at –50 °C, the ^{31}P chemical shift and $^2J_{PH}$ have been precised. The two methylene hydrogens appear to be nearly equivalent as was already observed

Scheme 19



HP=C(F)NR_2	R =Me	R =Et	R =^{i}Pr	R =piperidine
E/Z (%)	19/81	18/82	17/83	14/86



for other phosphaalkenes bearing a methylene substituent at the phosphorus atom.[133] Methylidenephosphine (CH_2=PH) was unambiguously characterized by chemical trapping with dimethylbutadiene, 2-propanethiol, and H_2O and subsequent oxidation of the adducts (Scheme 20).

This approach was generalized to various P- and C-substituted phosphaalkenes[105,106] (Scheme 19) which were characterized *in situ* by low-temperature ^{31}P NMR. Their stereochemistry was established using the so-called "cis rule" which states that the $^2J_{PH}$ coupling constant is larger when H is cis relative to the phosphorus lone pair.[144] They were also characterized by chemical trapping. As an example, methyl(ethoxycarbonyl)diazaphosphole was obtained in 17% overall yield by a [3 + 2] cycloaddition reaction between the phosphaalkene intermediate and ethyl diazoacetate, followed by aromatization of the adduct in a N-chlorination–elimination sequence using *N*-chlorosuccinimide[105] (Scheme 20).

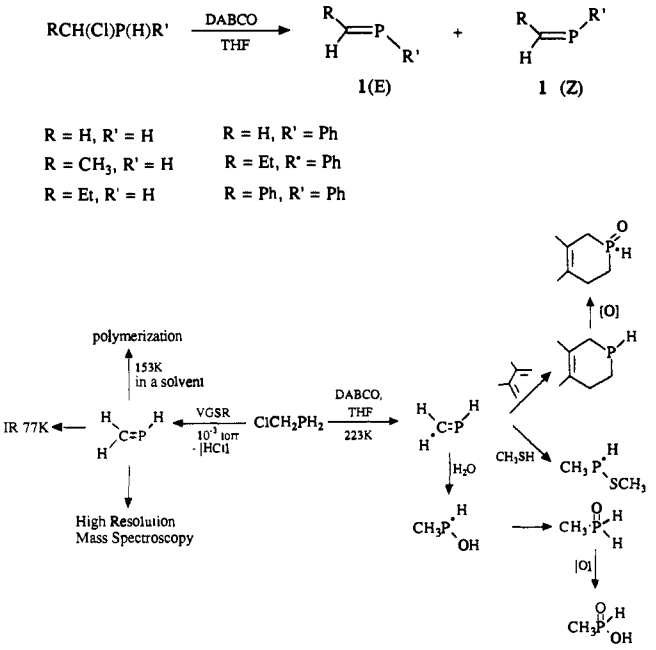
As observed in this example, dehydrochlorination on solid K_2CO_3 (VGSR, section III.C.1) and dehydrochlorination in solution are complementary one to another; with the former, spectroscopic measurements in the gas phase can be performed (IR, PES, MS); the later provides ^{31}P NMR data and gives the opportunity to define the chemical reactivity of the transient species (nucleophilic additions and cycloadditions).

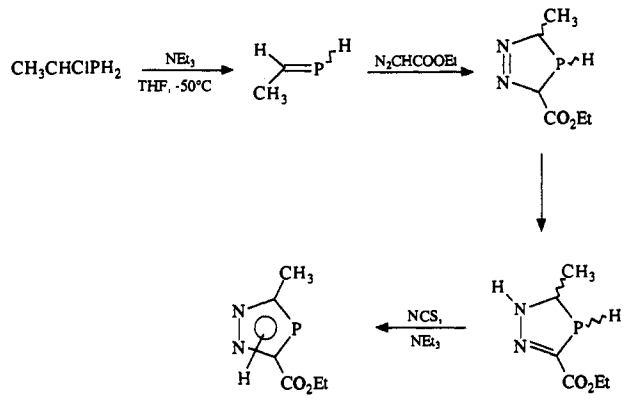
P-Methylphosphaallenes and phosphabutadienes can also be formed by this approach.

P-Methylphosphaallene was prepared by base-induced HCl elimination starting from (chlorovinyl)-methylphosphine. The reaction occurs in solution at 0 °C in the presence of DBU (Scheme 21). A rapid oligomerization is observed in the absence of chemical trapping (^{i}PrSH).[110]

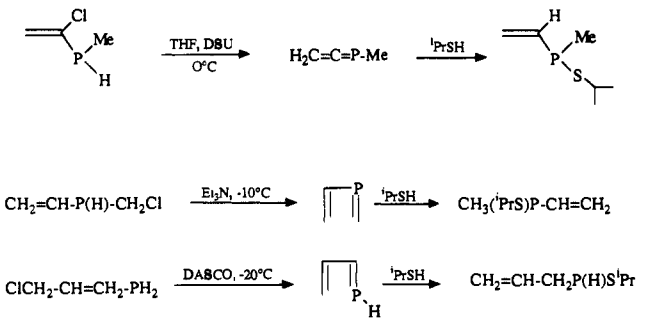
1-Phosphabutadiene (H_2C=CHC(H)=PH) and 2-phosphabutadiene (H_2C=CHP=CH_2) are formed by low-temperature base-induced HCl elimination from the vinylphosphine precursors.[77] 2-Phosphabutadiene was detected by ^{31}P NMR and chemical trapping. 1-Phosphabutadiene, which is a highly reactive species,

Scheme 20





Scheme 21

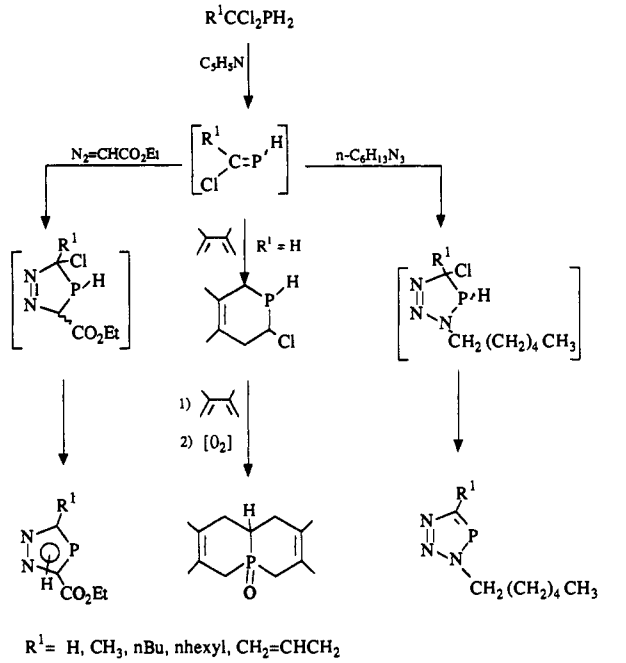


was only characterized in solution by chemical trapping with 2-propanethiol (Scheme 21).

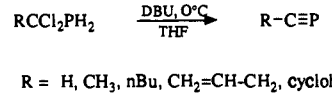
c. From α,α-(Dichloromethyl)phosphines. Depending on the nature of the Lewis base, a mono- or a bisdehydrochlorination can occur leading to the formation of *C*-chlorophosphaalkenes and phosphaalkynes, respectively.

i. Monodehydrochlorination: Access to C-Chlorophosphaalkene Intermediates. By carefully controlling the experimental conditions using a weak base like pyridine, transient *C*-chlorophosphaalkene intermediates are slowly formed by monodehydrochlorination of the corresponding α,α-(dichloromethyl)phosphines.

Scheme 22



R[1]= H, CH_3, nBu, nhexyl, CH_2=$CHCH_2$

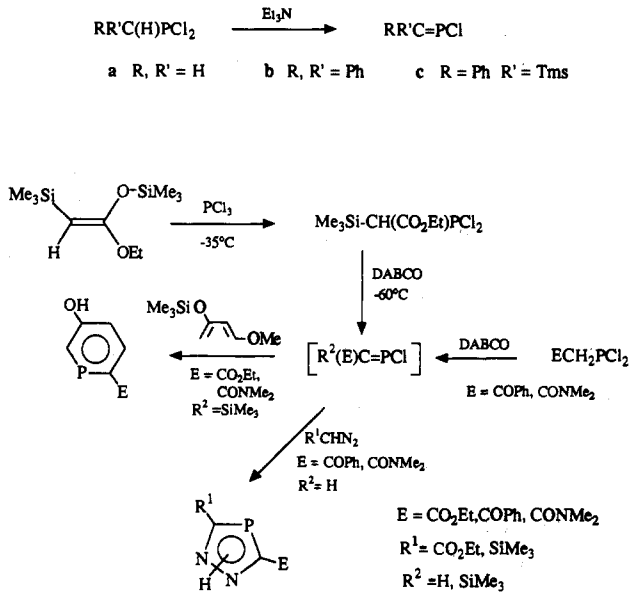


R = H, CH_3, nBu, CH_2=CH-CH_2, cyclohexyl, $Ph(CH_2)_2$

They were only detected by chemical trapping.[145,146] Oligomerization was reduced by the low concentration of the reactive species in the medium. *C*-Chlorotetrahydrophosphorine was isolated when the reaction was performed at room temperature. Symmetrical bisadducts of dimethylbutadiene (R^1 = H) and adducts of ethyl diazoacetate and *n*-hexyl azide have been obtained in a yield ranging from 15 to 40% (Scheme 22). These syntheses are conducted under conventional equipment. α,α-Dichlorophosphine precursors can be considered as synthetic equivalents of RC≡P. This method which is particularly well adapted for the study of high-boiling and functionalized derivatives seems of a general applicability.

ii. Bisdehydrochlorination: Access to Phosphaalkynes. Phosphaalkynes, linked to primary, secondary, or tertiary substituents are efficiently prepared by addition of a strong Lewis base (DBU) to the corresponding α,α-(dichloromethyl)phosphines in an ethereal solution[81,147] (Scheme 22). This method is well suited for the preparation of nonvolatile derivatives such as (cyclohexylethylidyne)phosphine but failed for reactive species (ClC≡P, Me_3SiC≡P, PhC≡P). Since these phosphaalkynes can be efficiently prepared by gas-phase HCl elimination on solid K_2CO_3 from the same precursors (VGSR, section III.C.1), the two HCl elimination procedures are complementary to each other. They constitute a very efficient route to various phosphaalkynes linked to a heteroelement (Cl, Me_3Si) (gas-phase reactions) or to a primary or a secondary substituent (gas-phase and liquid-phase reactions). Phosphaalkynes can be kept several months in a 5% molar solution in a freezer (−20 °C). Oligomerization is observed upon warming the neat product to room temperature.

Scheme 23



2. Base-Induced HX Elimination from Acidic α-CH P-Chlorophosphines

Dehydrochlorination of *P*-chlorophosphine derivatives with Lewis bases can also be efficiently accomplished with phosphines bearing an acidic C–H in the α-position. Activation by electron-withdrawing groups E like phenyl, trimethylsilyl, ethoxycarbonyl, or chlorine bonded to the carbon in α-position to the phosphorus (structure C) have been generally used, but the vinyl and phosphonio groups are also efficient.

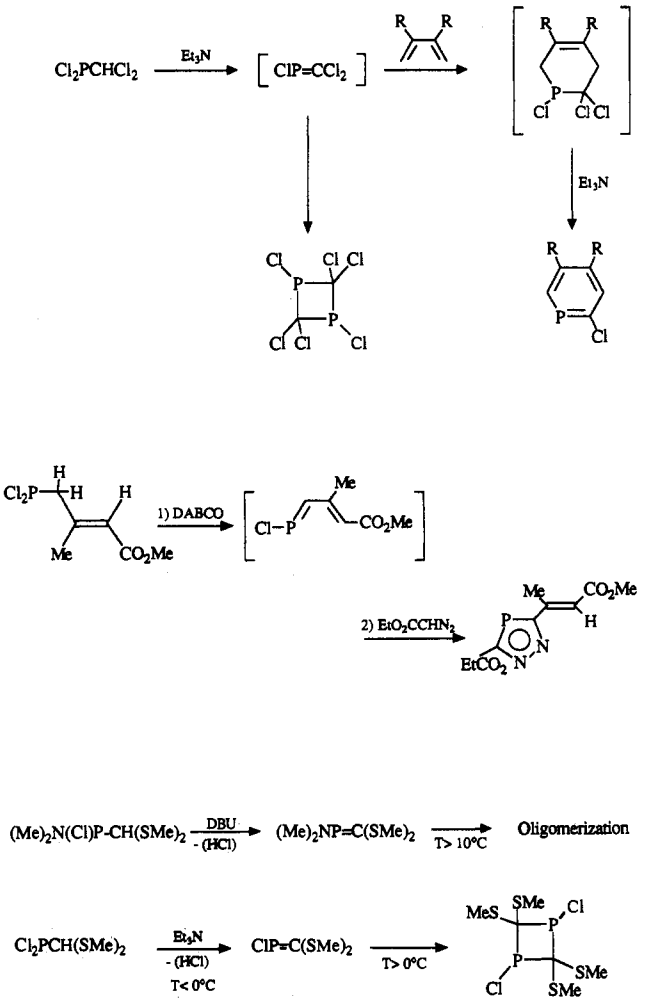
a. *P*-Chlorophosphaalkenes. Stable *P*-chlorophosphaalkenes are formed by HCl elimination of dichlorophosphines bearing a phenyl or a silyl group[148] and are characterized by NMR and elemental analysis. The unstable parent compound (R = R′ = H), also formed by this approach, has only been characterized by ^{31}P NMR (Scheme 23).

A transient *P*-chlorophosphaalkene bearing an ethoxycarbonyl function on the carbon atom has been generated by condensation of a silylated ketene acetal on PCl_3 followed by dehydrochlorination of the dichlorophosphine precursor by a Lewis base (DABCO). 2-Substituted 4-hydroxyphosphinines and functionalized diazaphospholes were formed by trapping this intermediate with the Danieshefsky's diene[149] or diazo compounds, respectively.[150,151] (Scheme 23).

Other phosphaalkenes bearing a dimethylacetamido ($CONMe_2$) or a benzoyl (COPh) group have also been evidenced by chemical trapping[150] (Scheme 23). Thus, dichlorophosphines ($Cl_2PCH(E)SiMe_3$) and *P*-chlorophosphaalkenes (ClP = C(E)$SiMe_3$) and ClP=C(E)H bearing an electron-withdrawing group E can be considered as synthetic equivalents of the corresponding phosphaalkynes (P≡CE).[56,57,149,150,152]

A similar chemical behavior was observed with Cl_2PCHCl_2. Weak Lewis bases were able to induce dehydrochlorination of the *C,C*-dichloro-*P*-chlorophosphine percursors. In the absence of trapping agent, the transient phosphaalkene spontaneously dimerizes.[153] [4 + 2] cycloaddition reactions were observed in the presence of differently substituted butadienes. 2-Chlorophosphorins, formed by aromatization of the primary adduct intermediates, are isolated in *ca.* 35% yield[154,155] (Scheme 24). Extension of this reaction to the *C,C*-dibromo- and *C,C*-diiodo-*P*-halophosphine derivatives has allowed functionalization of the phosphorin system at the 2-position.[156,157]

Scheme 24

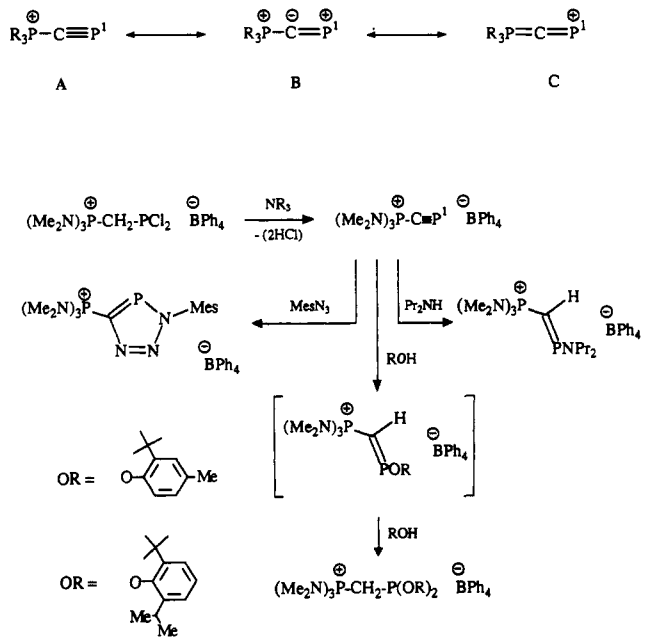


Allylic protons in α-position to the PCl_2 group are also very acidic. A transient *P*-chlorophosphadiene was formed by low-temperature 1,2-dehydrochlorination of a [(methoxycarbonyl)allyl]dichlorophosphine and was trapped in a [3 + 2] cycloaddition by ethyl diazoacetate.[158] The (ethoxycarbonyl)vinyldiazaphosphole adduct was fully characterized (Scheme 24).

[Bis(alkylthio)methyl]phosphines are dehydrochlorinated by Lewis base (NEt_3) (Scheme 24). The stability of the corresponding methylidenephosphines depends on the steric influence of the substituents. (Diethylamino)phosphaalkene rapidly polymerizes above 10 °C and the *P*-chloro derivative dimerizes in ether above 0 °C.[159] The low-temperature substitution of the chlorine by various substituents opens the way to the synthesis of new P-substituted methylidenephosphines.[159]

b. Phosphonio-Substituted Phosphaalkynes. The C–H acidity can also be induced by the presence of a phosphonio group. [Tris(dimethylamino)phosphonio]phosphaalkyne was formed by low-temperature addition of an excess of DABCO or Et_3N to the corresponding phosphonium salt.[160] Oligomerization occurs on heating. The structure was assumed by low-temperature ^{31}P NMR. Chemical shifts are in good

Scheme 25



agreement with those calculated by means of the IGLO method.[161] The low field chemical shift (δ_P = 190.4) can be explained by the important contribution of the resonance forms (**B** and **C**) to the electronic ground state (Scheme 25).

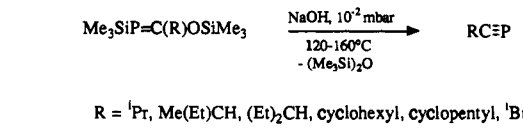
Chemical proof for the assigned structures were obtained by chemical trapping reactions. Addition of diisopropylamine quantitatively yielded the (phosphavinyl)phosphonium salt. This unusual 1,2-addition outlines the activation of the carbon–phosphorus triple bond by the phosphonium group. The phosphonium salts were isolated by addition of substituted phenols. Finally, regioselective [2 + 3] cycloaddition with mesityl azide yielded the corresponding triazaphosphole[160] (Scheme 25).

B. Elimination of the R_3SiOY Group (Y = $SiMe_3$, Me)

1. Hexamethyldisiloxane Elimination (Y = $SiMe_3$)

a. Hexamethyldisiloxane Elimination from the Enolic Form of Phosphaalkenes. The base-induced elimination of hexamethyldisiloxane from suitable P-silylated phosphaalkene precursors, first reported in 1981 by Becker[162] and extended more recently by Regitz *et al.*,[6,119,163] constitutes a very efficient route to phosphaalkynes (Scheme 26).

Scheme 26



The reaction can occur in solution using solid KOH or NaOH, but the slow addition of phosphaalkenes under reduced pressure on solid NaOH at 110/160 °C in the absence of solvent constitutes the best procedure for the preparation of volatile derivatives. Phosphaalkynes with tertiary substituents are stable and can be handled in air without decomposition. In pure form, derivatives bearing secondary substituents tend to polymerize and consequently must be stored at low temperature (−30 °C). The required high stability of the precursors and that of the products in the conditions of the reaction (T > 120 °C) limit the extent of this method: access to derivatives bearing a primary substituent is limited to stabilized derivatives.

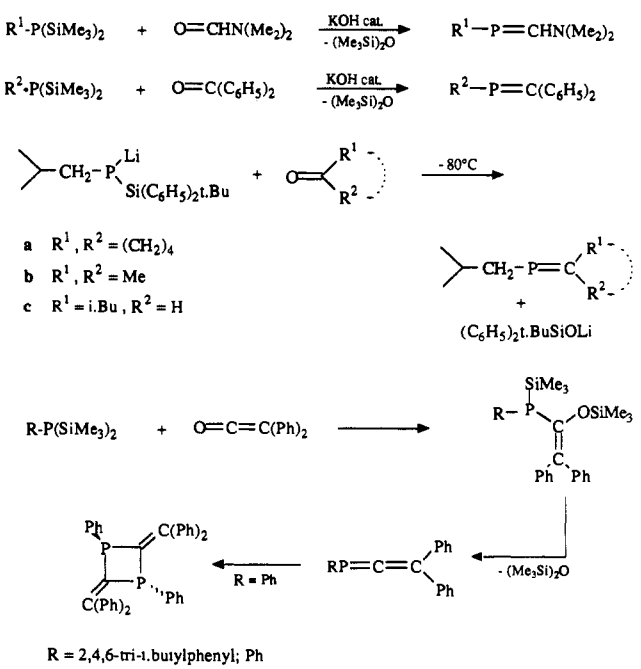
b. Peterson-Type Phosphaolefination. Olefins can be efficiently prepared by condensation of ketones onto bis(trimethylsilyl)alkanes (Peterson olefination).[164] This reaction has been extended to the synthesis of phosphaalkenes in a so-called "phospha-Peterson" reaction.[165,166] In absence of base, reaction of alkyl- or arylbis(trimethylsilyl)phosphines with dimethylformamide or benzophenone proceeds slowly. The shortening of the reaction time by introducing a catalytic amount of KOH favors a silyl phosphide intermediate (Scheme 27). Phosphaalkenes bearing a mesityl group on phosphorus are stable. Dimerization and formation of the corresponding diphosphetane are observed with the corresponding *P*-phenyl and *P*-methyl derivatives.

This reaction was extended to the synthesis of simple alkyl-substituted phosphaalkenes by stabilizing the intermediate phosphide ion with a bulky silyl group. Thus, low-temperature condensation of (diphenyl-*tert*-butylsilyl)isobutylphosphide on cyclohexanone or acetone leads to the corresponding transient cyclohexylidenephosphine (R^1, R^2 = $(CH_2)_4$) or propylidenephosphine (R^1, R^2 = Me) which were characterized by ^{31}P NMR and chemical trapping.[167] The two isomers of isobutylidenephosphine (R^1, R^2 = ^{i}Bu) were also observed when starting from isobutyraldehyde (Scheme 27). Due to the unresolved $^2J_{PH}$ coupling constant, the stereochemistry was not defined.

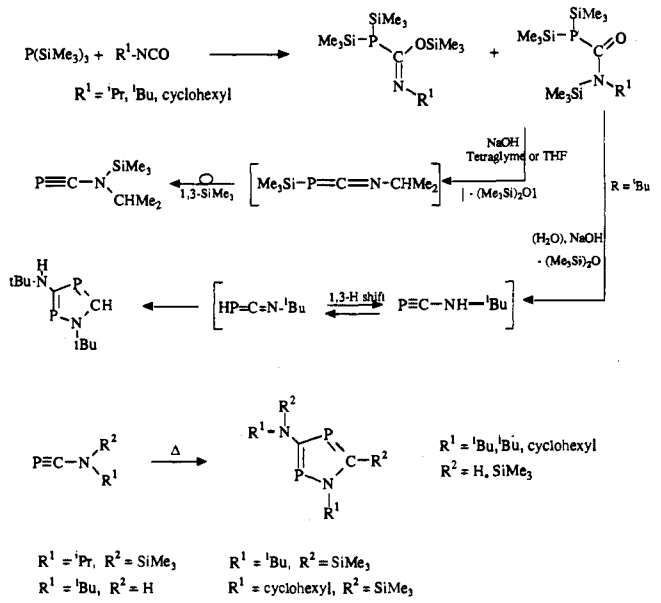
Stable 1,3-diphosphaallenes were observed by treatment of disilylphosphines with diphenyl ketene. Only the dimeric structure was observed starting from the *P*-phenyl derivative[168] (Scheme 27).

A stable amino-substituted phosphaalkyne was formed by NaOH-induced elimination of hexamethyldisiloxane from the adduct of tris(trimethylsilyl)-

Scheme 27



Scheme 28



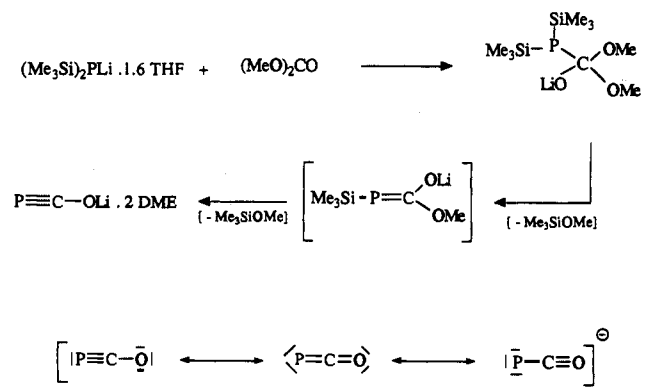
phosphine and isopropyl isocyanate.[169] The formation of the P≡CN structure can be explained by the formation of a transient 1-aza-3-phosphaallene, which rapidly rearranges via a 1,3-$SiMe_3$ shift (section V). If moist sodium hydroxide was used, a cyclic dimeric structure, the 1-aza-2,4-diphosphole (R = ^{t}Bu) was observed. A simple iminophosphaallene, in equilibrium with primary aminophosphaalkyne (1,3-H shift), is involved.[170] Other dimeric structures have been observed by heating stable aminophosphaalkynes (Scheme 28). The mechanism of these dimerizations is not well established so far.[171]

2. Elimination of Me_3SiOCH_3

[(Lithiooxy)methylidyne]phosphine–2 DME is formed by reaction of lithium bis(trimethylsilyl)-phosphide–1.6 THF with an excess of dimethyl carbonate[172] (Scheme 29). The mechanism is up to now poorly understood. The lithiooxy-*P*-(trimethylsilyl)-phosphaalkene is probably an intermediate in this reaction but its detection by NMR was unsuccessful.

The upfield ^{31}P NMR chemical shift of the P≡CO$^-$ structure (δ = −384 ppm) and the one of the corresponding hydroxy derivative P≡COH (δ = −392 ppm) are the consequence of the π-donor properties of alkoxy group and the important contribution of the mesomeric

Scheme 29



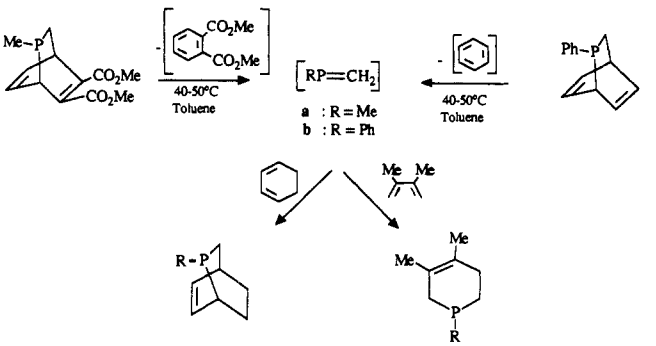
PC≡O structure (Scheme 29). The X-ray structure confirms these results: its was observed an extremely short C–O bond length (1.198 Å) compared to the standard value of a single C–O bond (1.39 Å).

C. Thermal Elimination in Solution

1. Retro [4 + 2] Cycloadditions

Phosphaalkenes can also be formed in solution. However due to the high reactivity of the P=C bond, they have been in most cases characterized by chemical trapping. For example, cycloadducts bearing a single P–C bond are valuable synthetic equivalents of phosphaalkenes in solution. Upon heating 2-phosphabicyclo-[2.2.2]octadiene in solution under very mild conditions (T < 50 °C) in the presence of various dienes as trapping agents, the corresponding cycloadducts are formed in good yield.[173] The process was free of interfering side reactions. ^{31}P NMR signals are in good agreement with the proposed structure. Further characterization of the adducts was accomplished by conversion into their methiodides. Main reactions are collected in Scheme 30.

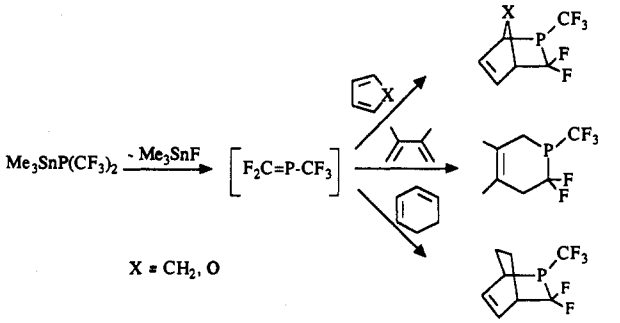
Scheme 30



2. R_3SnF Elimination

Stannylphosphines can be used in a one-pot procedure as a perfluorophosphaalkene equivalent[60,70] in Diels–Alder-type reactions upon heating at moderate temperatures (50–100 °C) in the presence of an excess of diene (Scheme 31). The yield of the cycloadducts

Scheme 31

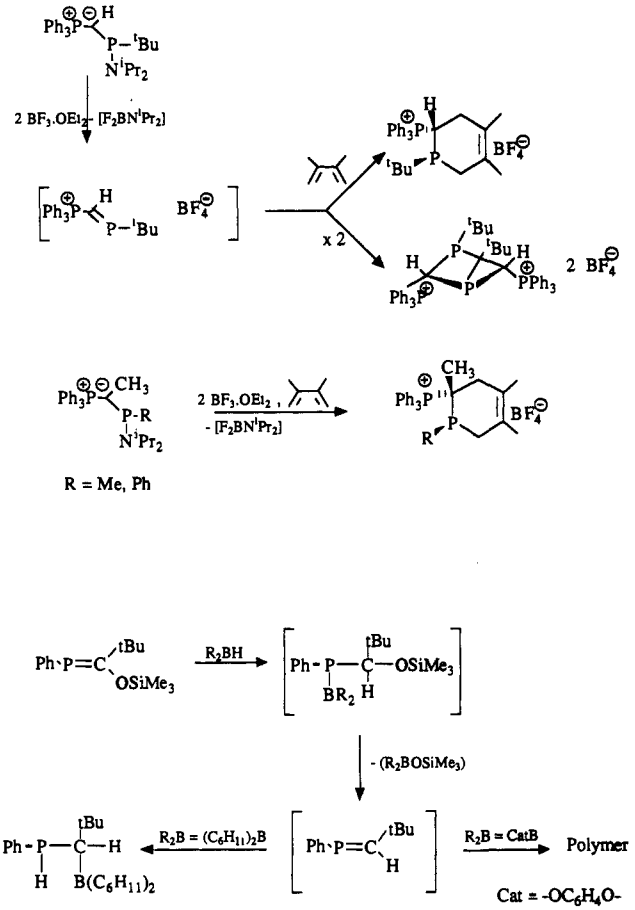


(20–90%) depends on the nature of the stannylphosphine substituents and thus on the stability of the intermediate phosphaalkenes. The conformers and diastereoisomers are formed in a similar ratio as found for the [4 + 2] cycloaddition of the isolated P=C system (section III.A.3).

D. Elimination Involving Lewis Acids

2-Phosphonio-substituted 1-phosphaalkenes were obtained in good yield by reaction of [[(diisopropylamino)phosphino]methylene]triphenylphosphorane with 2 equiv of $BF_3{\cdot}OEt_2$ or $AlCl_3$. The *P*-alkyl-substituted derivative dimerizes spontaneously and was only characterized by chemical trapping in a [4 + 2] cycloaddition with dimethylbutadiene. The head to tail dimer was also observed[174] (Scheme 32).

Scheme 32

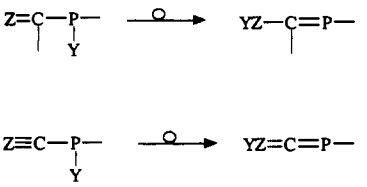


An interesting result concerning the reactivity of phosphaalkenes with boron derivatives has been reported by Ionkin *et al.*[175] Adducts (1:1) with P–B bond were obtained by hydroboration of *P*-phenyl-*C*-[*tert*-butyl[(trimethylsilyl)oxy]methylidene]phosphine with catecholborane or dicyclohexylborane. The reaction takes place at room temperature, but heating to 50–60 °C for 1–2 h is needed for its completion. This adduct underwent a spontaneous β-elimination of [(trimethylsilyl)oxy]borane leading to the formation of a nacked phosphaalkene which tends to polymerize (Scheme 32). This derivative was trapped with an excess of dialkylborane. The hydroboration regiochemistry of the phosphaalkene precursor is strongly affected by the trimethylsiloxy group which determines the β position for the boron atom, either exclusively (reaction with catecholborane) or predominantly (reaction with the more active dicyclohexylborane).

V. Rearrangement Reactions (Method G)

The majority of the rearrangements allowing an access to phosphaalkenes and phosphaalkynes proceeds from

Scheme 33

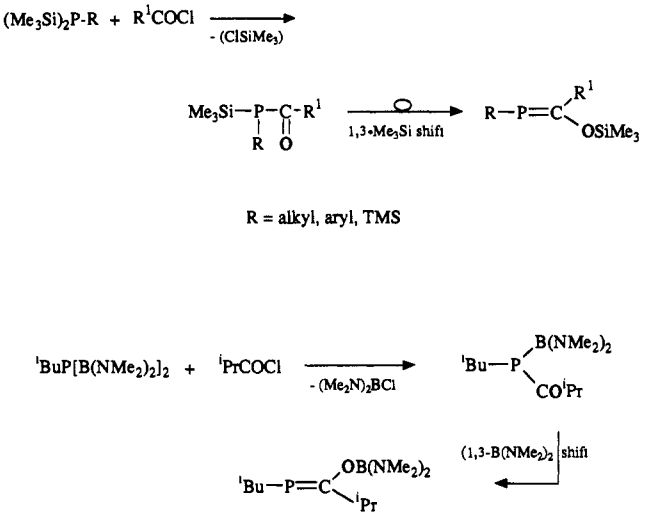


phosphine precursors bearing an unsaturated function in the α-position (Scheme 33).

A. Synthetic Routes to Phosphaalkenes via a 1,3-Y Shift (Z = O; Y = $SiMe_3$, $B(NR_2)_2$, Li)

The discovery by Becker in 1976 of the rearrangement under mild conditions of *P*-silyl-substituted pivaloylphosphines into the thermodynamically more stable O-isomers strongly stimulated the development of low-coordinated derivatives[120] (Scheme 34).

Scheme 34

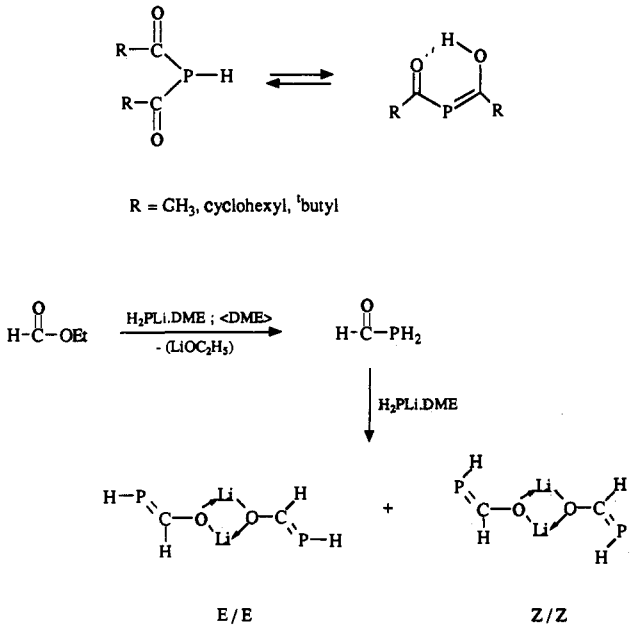


A large variety of stable phosphaalkenes bearing various substituents on the phosphorus and on the carbon have been thus prepared.[8] The P-silylated derivatives (R = $SiMe_3$), obtained by condensation of tris(trimethylsilyl)phosphine with acyl chloride are important intermediates for the preparation of phosphaalkynes.[119,162,163]

Organoborane derivatives of (isopropylacyl)phosphines have been recently obtained by low-temperature condensation of a bis(diorganoborylated) alkylphosphine with acyl chloride. Rearrangement into the corresponding O-isomer occurs upon heating at room temperature.[176] Only stable derivatives have been prepared by this approach up to now (Scheme 34).

As in the case of classical keto–enol tautomerism, the enolic form of diacylphosphines can be stabilized by chelation[177] (Scheme 35). The enolic form of the simple formyl phosphine is formed by addition of the lithium dihydrogenophosphide–DME complex to ethyl formate in a 2:1 molar ratio. Characteristic NMR data show the presence of the *E*/*E*- and *Z*/*Z*-isomers. The structure has to be considered as a dimer forming a four membered Li–O–Li–O ring[172] (Scheme 35).

Scheme 35

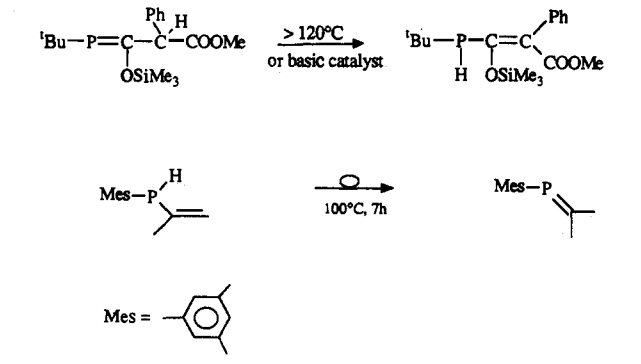


B. Vinylphosphine/Phosphaalkene Rearrangement (1,3-Hydrogen Shift)

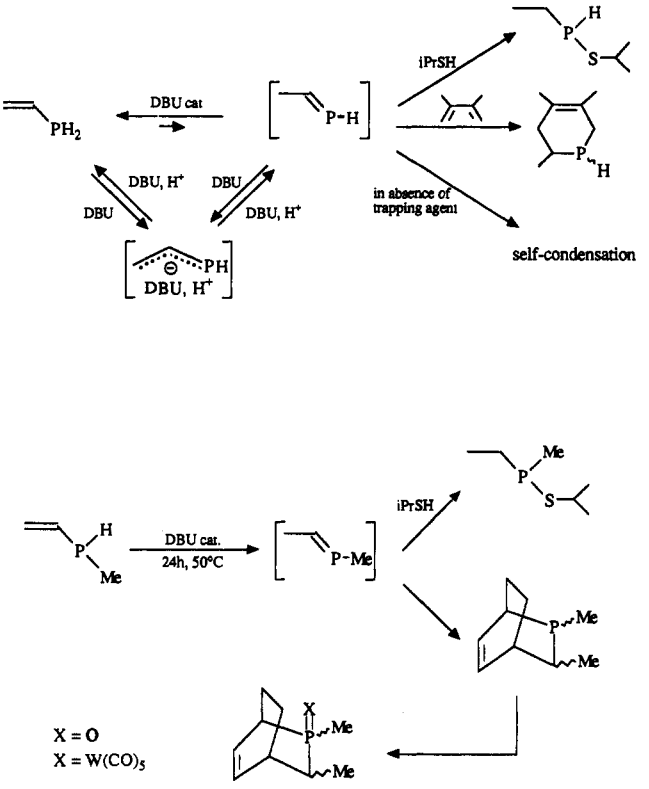
1,3-Hydrogen shift in heteroallyl systems containing two carbon atoms and a heteroatom (oxygen, nitrogen, sulfur, etc.) has played a fundamental role in the understanding of acid–base catalysis and constitutes the essential steps in many important chemical reactions. Theoretical investigations have shown that the energy difference between vinylphosphine and the corresponding $CH_3CH{=}PH$ isomer is not very significant, the vinylphosphine being however the energetically favored isomer. Because of the low-energy difference, interconversion of these two levels can be expected with appropriate substitutions at phosphorus or carbon.[141,178] The barrier for the phosphaalkene/vinylphosphine interconversion (1,3-hydrogen shift) was calculated to be 437.5 kJ mol^{-1}.

The first phosphaalkene/vinylphosphine rearrangement was observed in 1982 by Kolodyazhnyi *et al.*[179] (Scheme 36). The required presence of the ethoxycarbonyl group as an electron-acceptor substituent and acceleration of the reaction in the presence of triethylamine indicates that the rearrangement depends on the C–H acidity of the β-carbon atom. It has further demonstrated on other examples that addition of a catalytic amount of DBU strongly accelerates the reaction.[180]

Scheme 36



Scheme 37



Generalization of this rearrangement[181–185] indicates that the studied *P*-alkylvinylphosphine precursors are thermodynamically more stable than the dicoordinated phosphorus isomers. The first vinylphosphine/phosphaalkene rearrangement was observed by Mathey *et al.*[186] (Scheme 36). The higher thermodynamic stability of the observed mesitylphosphaalkene compared with that the one of the vinylphosphine counterpart can be explain by a (p_π–p_π) conjugation between the P=C bond and the aryl group.

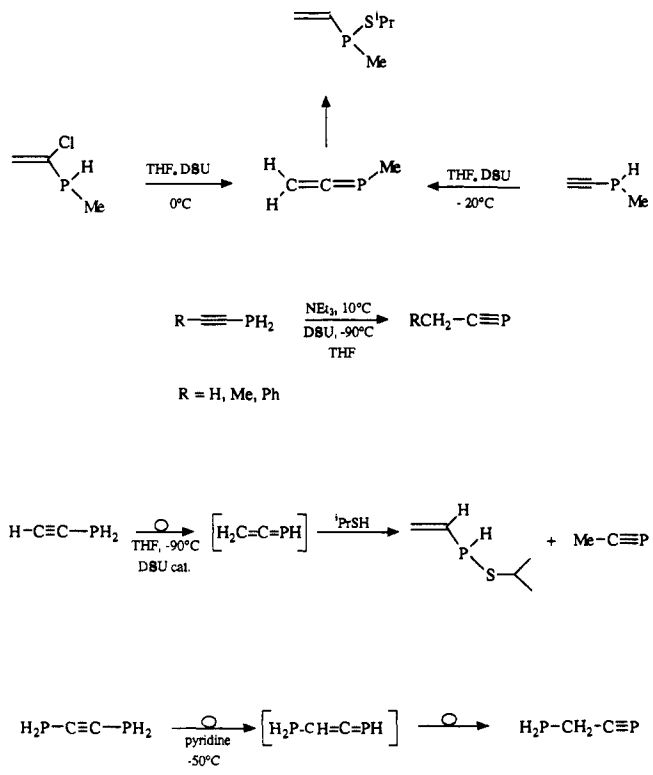
A 1,3-hydrogen shift was also observed for the simplest vinyl phosphines.[187,188] The rearrangement of $CH_2{=}CHPH_2$ to 1-phosphapropene occurs at −10 °C in the presence of a catalytic amount of DBU. A phosphaallyl anion was postulated as an intermediate.[189] Slow polymerization was observed in the absence of trapping agent. A [4 + 2] cycloadduct was obtained in the presence of an excess of dimethylbutadiene (Scheme 37). The high yield of this reaction can be explained by the very low concentration of the transient species in the medium. These results are in favor of a tautomeric equilibrium, the vinylphosphine being thermodynamically more stable than the phosphaalkene, in good agreement with theoretical calculations.[141,178]

The temperature of the rearrangement is dependent upon the P–H acidity; vinylphosphine rearranges at 20 °C while the rearrangement of the *P*-methylvinylphosphine is only observed at 50 °C. Adducts of cyclohexadiene and 2-propanethiol are obtained in good yields (Scheme 37).

C. Secondary Ethynylphosphine/Phosphaallene Rearrangement (1,3-Hydrogen Shift)

1-Phosphaallenes have been widely studied.[9] Derivatives stabilized by sterically demanding groups have

Scheme 38



been prepared through reactions of phosphaketenes with methylene phosphoranes[111] or silylated phosphines.[168] Efforts to apply this later approach to the generation of 1-phosphaallenes bearing a less bulky substituent at the phosphorus atom led to the corresponding dimer.[168] The synthetic utility of these methods is restricted by the hard to access starting materials.

By analogy with the propargylic rearrangement, Märkl *et al.* developed another approach which involves the base-induced rearrangement of stable *P*-aryl-1-alkynylphosphines.[190-192] Independently unstabilized 1-phosphaallenes have been prepared by the same pathway starting from simple secondary ethynylphosphines.[110] Thus, *P*-methyl-1-phosphaallene is formed by base induced rearrangement of ethynylphosphine with DBU at low temperature and characterized by ^{31}P NMR (δ_P = 42.0 ppm, $^3J_{PH}$ = 26 Hz) and chemical trapping (Scheme 38). An independent route which involves a 1,2-HCl elimination of the (chlorovinyl)-phosphine precursor confirms the structure (Scheme 16, section III.C). *P*-Methylphosphaallene oligomerizes on warming up the solution to −20 °C.

Extension of this reaction to the C-substituted (one or two methyl groups) derivatives was described.[110] The formation of the CH_2=C=PH intermediate in the base-induced rearrangement of ethynylphosphine is developed in the following section.

D. Primary Ethynylphosphine/Phosphaalkyne Rearrangement

1. Ethynylphosphine

Phosphaalkynes were obtained in good yield in solution by low-temperature base-induced rearrangement of primary ethynylphosphines in solution (NEt_3, 10 °C or DBU, −90 °C)[113] as well as in the gas-phase (VGSR, K_2CO_3, 20 °C, Scheme 38). For the parent compound, the phosphaallene intermediate, formed by a 1,3-hydrogen shift, was evidenced by an unequivocal synthesis (dehydrochlorination of the (chlorovinyl)-phosphine) and chemical trapping. The P–H acidity of the two phosphines (HC≡CPH_2 and H_2C=C=PH) can explain the mild conditions which are needed for the two 1,3-hydrogen shifts. The phosphaalkynes can be kept several days at room temperature in the crude solution, but oligomerization is observed in the absence of solvent.

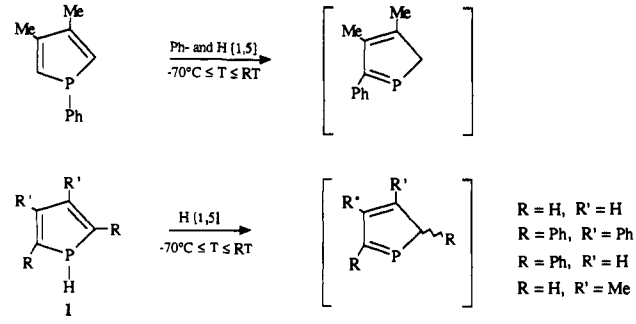
2. Ethynyldiphosphine

3-Phosphino-1-phosphapropyne is the sole isolated product in the reaction of ethynylphosphine with a catalytic amount of pyridine at −50 °C (Scheme 38). The reaction involves an ethynylphosphine/phosphaalkyne rearrangement via a transient phosphaallene which has not been characterized.[193]

E. 1,5-Hydrogen Shift

The 1*H*- and 2*H*-phospholes isomerization was described in 1981 by Mathey[194] and widely developed later. The rearrangement occurs at a temperature higher than 150 °C for the P-substituted phospholes and at low temperature when P-unsubstituted derivatives are involved[195] (Scheme 39). The 1-phosphadiene intermediate are unstable and highly reactive species which were identified by chemical trapping with various agents. Mechanism of this rearrangement and extended applications have been recently reviewed and are therefore excluded from this article.[12]

Scheme 39



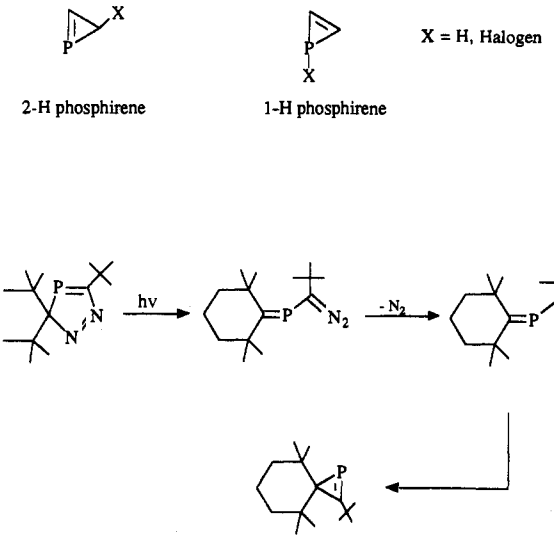
F. 1,3-Chlorine Shift

From *ab initio* calculations, 2*H*-phosphirene is more stable than 1*H*-phosphirene, but the relative stability of these isomers is reversed with halogen substitution[196-198] (Scheme 40).

The first 2*H*-phosphirene, prepared by photolysis of a spiro diazaphosphole[199] is a stable compound which can be handled in air (Scheme 40). Attempts to prepare simple 2*H*-phosphirenes by thermal or base-induced $ClSiMe_3$ elimination have been unsuccessful to date.[200]

Transient 2-chloro-2*H*-phosphirenes are formed in the reaction of chlorocarbenes with phosphaalkynes. They rearrange rapidly via a 1,3-chlorine shift to the

Scheme 40

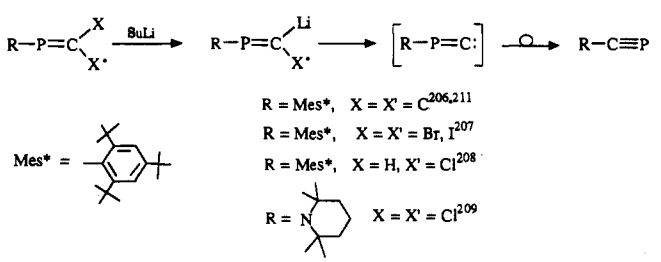


more stable 1-chloro-1*H*-phosphirene[201,202] in good agreement with theoretical calculations (Scheme 40).

G. RP=C/RC≡P Rearrangement

Theoretical calculations predict that HP=C is a transition state rather than a short-lived intermediate.[203,204] The existence of linear HPC seems however to be supported by other calculations, but the local minimum is merely 9.66 kJ below the transition state.[205] Several groups have used stabilized dihalophosphaalkenes as starting material for the synthesis of phosphaalkynes. The formation occurs after addition of BuLi[206-209] or $(Ph_3)_3PPd$.[210] This transformation was interpreted as a multistep process involving a carbenoid species, the generation of RP=C and its subsequent rearrangement into phosphaalkyne (Scheme 41).

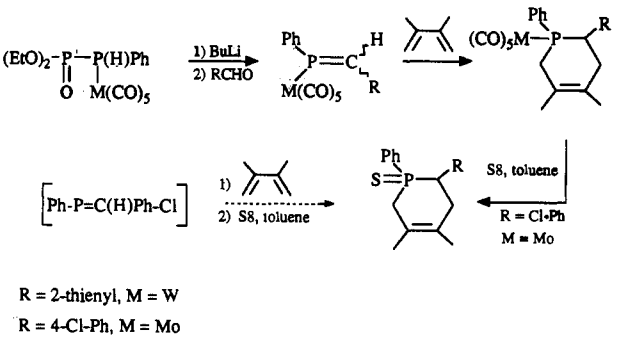
Scheme 41



VI. Phospha-Wittig Route

Mathey and Marinetti have developed an original route to PC double bonds which transforms a carbonyl compound into a phosphaalkene complex by a so-called "phospha-Wittig" reaction[212-214] (Scheme 42).

Scheme 42



This method has wide applicability. Reaction occurs with ketones and saturated and unsaturated aldehydes. The reactivity of these complexes with respect to their free counterparts is preserved or usefully modified. With ketones, the expected phosphaalkene complexes can be isolated but they tend to be unstable with aldehydes. With the later, the P–C double bond was allowed to react *in situ* with nucleophiles and dienes (Scheme 42). This method can serve as an original route to free cyclic phosphines by breaking the P–M bond of the $PMo(CO)_5$ complexes with sulfur in toluene.[213] Thus, this sequence which involves phospha-Wittig reaction, cycloaddition, and cleavage of the P–M bond allows one

Scheme 43

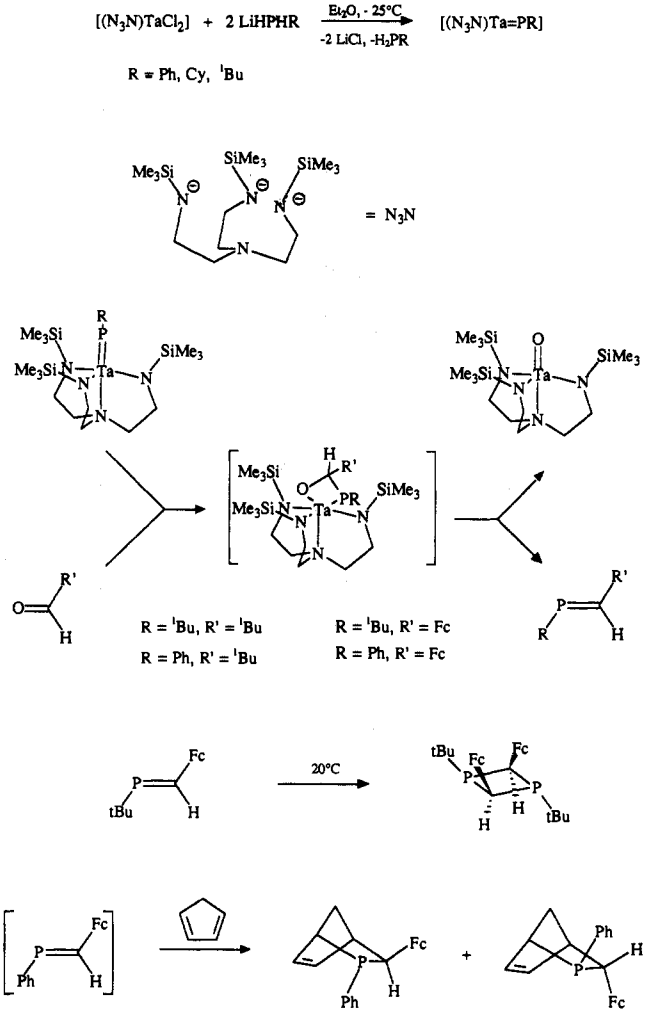


Table 7. Liquid-Phase Generation of Simple Phosphaalkenes

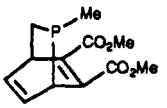
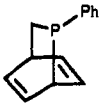
compound	precursor	method[a]	first detection	yield in adduct (%)	ref	comments
CH_2=PH	$ClCH_2PH_2$	F	^{31}P NMR; MS; chemical trapping (cycloadditions, thiol and H_2O additions)		102	decomposition in the solid state at 77K
MeC(H)=PH	$ClCH(CH_3)PH_2$	F	^{31}P NMR; MS; chemical trapping (cycloadditions)		105, 106	
	CH_2=$CHPH_2$	G	chemical trapping		188	
EtC(H)=PH	ClCH(Et)PH_2	F	^{31}P NMR; MS; chemical trapping		105, 106	
ClC(H)=PH	$HCCl_2PH_2$	F	chemical trapping (cycloadditions)	good	145	all the ClC(R)=PH phosphaalkenes are useful intermediates for the synthesis of various cycloadducts without special equipment
ClC(Me)=PH	$CH_3CCl_2PH_2$	F	chemical trapping (cycloadditions)	36–40	146	(see above)
ClC(^{n}Bu)=PH	^{n}BuCCl_2PH_2	F	chemical trapping (cycloadditions)	33–36	146	(see above)
ClC(n-pentyl)=PH	(n-pentyl)CCl_2PH_2	F	chemical trapping (cycloadditions)	35	146	(see above)
TmsC(Cl)=PH	TmsCCl_2PH_2	F	chemical trapping (cycloadditions)	15–20	146	(see above)
PhC(Cl)=PH	$PhCCl_2PH_2$	F	chemical trapping (cycloadditions)	20	146	(see above)
$PhCH_2C$(Cl)=PH	$PhCH_2CCl_2PH_2$	F	chemical trapping (cycloadditions)	30–35	146	(see above)
PhSC(Cl)=PH	$PhSCCl_2PH_2$	F	chemical trapping (cycloadditions)	20	146	(see above)
CH_2=$CHCH_2C$(Cl)=PH	CH_2=$CHCH_2CCl_2PH_2$	F	chemical trapping (cycloadditions)	30–40	146	(see above)
CF_2=PH	CF_3PH_2	F	chemical trapping with R_2NH		143	
CH_2=PMe		F	chemical trapping (cycloadditions)		173	very efficient procedure but the synthesis of the precursor is time consuming
Me(H)C=PMe	CH_2=CHP(H)Me	G	chemical trapping (cycloadditions and thiol addition)	>70	187,188	simple and efficient approach; good yield in cycloadducts
Ph_2NC(H)=PMe	$MeP(SiMe_3)_2$ + O=$CHNPh_2$	F	dimerization		165,166	
CH_2=PPh	$ClCH_2P$(H)Ph	F	^{31}P NMR		105,106	
		F	chemical trapping (cycloaddition)	good	173	better yield in cycloadducts with the retro Diels-Alder reaction
EtC(H)=PPh	ClCH(Et)PH(Ph)	F	^{31}P NMR		105,106	
PhC(H)=PPh	ClCH(Ph)P(H)Ph	F	^{31}P NMR		105,106	
PH_2C=PPh	$PhP(SiMe_3)_2$ + O=CPh_2	F	dimerization		165,166	
Ph_2NCH=PPh	$PhP(SiMe_3)_2$ + O=$CHNPh_2$	F	dimerization		165,166	
^{t}Bu(H)C=PPh	tBu(OSiMe_3)C=PPh + R_2BH	F	chemical trapping with R_2BH		175	
Me_2P(F)C=PCF_3	Me_2PCF_2P(H)CF_3	F	chemical trapping with an alcohol	40	63a	
F_2C=PCF_3	$Me_3SnP(CF_3)_2$	F	chemical trapping (cycloadditions)		60,70	
CH_2=PCl	CH_3PCl_2	F	^{31}P NMR		148	
Ph_2C=PCl	Ph_2C(H)PCl_2	F	^{31}P NMR		148	
Ph(Tms)C=PCl	Ph(Tms)$CHPCl_2$	F	^{31}P, ^{1}H, ^{13}C NMR		148	
Tms(CO_2R)C=PCl	$Me_3SiCH(COOR)PCl_2$	F	chemical trapping	70	149	
$(MeS)_2C$=PCl	$(MeS)_2CHPCl_2$	F	^{31}P NMR; dimerization	90	159	
Cl_2C=PCl	Cl_2PCHCl_2	F	dimerization; chemical trapping (cycloadditions)	72	153	general access to α-functionalized phospha-benzenes by a [4 + 2] cycloaddition-dehydrochlorination sequence
I_2C=PCl	I_2CH=PCl_2	F	chemical trapping (cycloadditions)	33	157	general access to α-functionalized phospha-benzenes by a [4 + 2] cycloaddition-dehydrochlorination sequence

Table 7 (Continued)

compound	precursor	method[a]	first detection	yield in adduct (%)	ref	comments
$Br_2C{=}PBr$	$Br_2CH{=}P(Br)_2$	F	chemical trapping (cycloadditions)	43	155	general access to α-functionalized phospha-benzenes by a [4 + 2] cycloaddition-dehydrochlorination sequence
$Me_2NC(F){=}PH$	$Me_2NCF_2PH_2$	F	IR, MS, ^{31}P, ^{1}H, ^{13}C NMR	42	143	
$Et_2NC(F){=}PH$	$Et_2NCF_2PH_2$	F	IR, MS, ^{31}P, ^{1}H, ^{13}C NMR	60	143	
$Pr_2NC(F){=}PH$	$Pr_2NCF_2PH_2$	F	IR, MS, ^{31}P, ^{1}H, ^{13}C NMR	54	143	
$(CH_2)_5NC(F){=}PH$	$(CH_2)_5N\text{-}CF_2\text{-}PH_2$	F	IR, MS, ^{31}P, ^{1}H, ^{13}C NMR	40	143	
$Ph_3P^+C(H){=}P^tBu,\ BF_4^-$	$Ph_3P^+\text{-}\text{-}C(H)P(^tBu)N^iPr_2$	F	chemical trapping (cycloaddition); dimer	good	174	
$CH_2{=}CHC(H){=}PH$	$CH_2{=}CHCH(Cl)PH_2$	F	chemical trapping		77	
$CH_2{=}CHP{=}CH_2$	$CH_2{=}CHPHCH_2Cl$	F	^{31}P, ^{1}H NMR; IR; chemical trapping		77	
$(MeO_2C)CH_2{=}C(Me)\text{-}CH{=}PCl$	$(MeO_2C)CH_2{=}C(Me)\text{-}CH_2PCl_2$	F	^{31}P NMR; chemical trapping		158	
$CH_2{=}C{=}PH$	$CH_2{=}C(Cl)PH_2$	F	chemical trapping (thiol)		113	can also be prepared in the gas-phase (VGSR)
	$HC{\equiv}CPH_2$	G	chemical trapping (thiol)		113	can also be prepared in the gas-phase (VGSR)
$CH_2{=}C{=}PMe$	$CH_2{=}C(Cl)P(H)Me$	F	chemical trapping (thiol)		110	can also be prepared in the gas-phase (VGSR)
	$HC{\equiv}CP(H)Me$	G	^{31}P NMR; chemical trapping		110	can also be prepared in the gas-phase (VGSR)
$Ph_2C{=}C{=}PPh$	$PhP(SiMe_3)_2 + O{=}C{=}C(Ph)_2$	D	dimer		168	

[a] Method F, liquid-phase base-induced elimination; method G, liquid-phase rearrangement.

Table 8. Liquid-Phase Generation of Simple Phosphaalkynes

compound	precursor	method	first detection	yield (%)	ref	comments
$HC{\equiv}P$	$HCCl_2PH_2$	F	IR; ^{1}H, ^{31}P, ^{13}C NMR		81	very efficient method to prepare phosphaalkynes for analysis and synthetic purpose. $\tau_{1/2}$ = 6 h in solution at room temp
$MeC{\equiv}P$	$MeCCl_2PH_2$	F	IR; ^{1}H, ^{31}P, ^{13}C NMR		81	stable several months at -20 °C in solution
	$HC{\equiv}CPH_2$	G	^{1}H, ^{13}C, ^{31}P NMR; IR; MS; chemical trapping	>90	113	can also be prepared by rearrangement under VGSR conditions (Can be kept several days in solution at RT)
$^nBuC{\equiv}P$	$^nBuCCl_2PH_2$	F	^{1}H, ^{13}C, ^{31}P NMR; IR; MS		81	(see above)
$C_6H_{11}C{\equiv}P$	$C_6H_{11}CCl_2PH_2$	F	^{1}H, ^{13}C, ^{31}P NMR; IR		147	(see above)
	$(Me_3SiO)(C_6H_{11})C{=}PSiMe_3$	F	^{13}C, ^{31}P NMR	28	163	very efficient method for the preparation of volatile phosphaalkynes with a secondary or a tertiary carbon in α position (stable in solution)
$EtC{\equiv}P$	$MeC{\equiv}CPH_2$	G	^{1}H, ^{13}C, ^{31}P NMR; IR; MS	>90	113	$\tau_{1/2}$ = 7 d in solution at room temp
$Et_2CHC{\equiv}P$	$(Me_3SiO)(Et_2CH)C{=}PSiMe_3$	F	^{13}C, ^{31}P NMR	49	163	very efficient method for the preparation of volatile phosphaalkynes with a secondary or a tertiary carbon in α-position; stored at -30 °C
$Me(Et)CHC{\equiv}P$	$(Me_3SiO)(Et_2CH)C{=}PSiMe_3$	F	^{13}C, ^{31}P NMR	41	163	stored at -30 °C in pure form
$^iPrC{\equiv}P$	$(Me_3SiO)(^iPr)C{=}PSiMe_3$	F	^{13}C, ^{31}P NMR; IR	63	119	stored at -30 °C in pure form
$^tBuCH_2C{\equiv}P$	$(Me_3SiO)(^tBuCH_2)C{=}PSiMe_3$	F	^{13}C, ^{31}P NMR	75	119	compounds with a primary carbon in α-position must be stabilized (stored at -30 °C in pure form)
$PhC{\equiv}P$	$Ph(Tms)C{=}PCl$	F	chemical trapping		51	stable 7 min at 0 °C
$PhCH_2C{\equiv}P$	$PhC{\equiv}CPH_2$	G	^{1}H, ^{13}C, ^{31}P NMR	>90	113	stable several hours in solution
$CH_2{=}CHCH_2C{\equiv}P$	$CH_2{=}CHCH_2CCl_2PH_2$	F	^{1}H, ^{13}C, ^{31}P NMR		147	stable several hours in solution
$H_2PCH_2C{\equiv}P$	$H_2PC{\equiv}CPH_2$	G	^{31}P, ^{1}H, ^{13}C NMR; chemical trapping		193	
$^tBuN(H)C{\equiv}P$	$(Me_3Si)_3P + tBuNC{=}O$	F	dimer		171	
$(Me_2N)_3P^+C{\equiv}P,\ BPh_4^-$	$(Me_2N)_3P^+CH_2PCl_2,\ BPh_4^-$	F	chemical trapping ^{31}P NMR		160	
$2DME{\cdot}LiOC{\equiv}P$	$(Me_3Si)_2PLi{\cdot}THF + (MeO)_2C{=}O$	F	^{31}P, ^{13}C NMR	87	172	

[a] Method F, liquid-phase base-induced elimination; method G, liquid-phase rearrangement.

Table 9. Selected Spectroscopic NMR Data and Stability of Simple Phosphaalkenes

structure	method[a]	δ 31P Z	δ 31P E	δ 13C Z	δ 13C E	$^1J_{CP}$ Z	$^1J_{CP}$ E	stability	ref
CH_2=PH	C	231						30 min at 77K (dec)	102
MeCH=PH	C	192	186						105
EtCH=PH	C	179	181						105
Me_2C=PH	C	175							105
$Me_2NC(F)$=PH	F	-99.9	-99.0	199.6	200.6	87.7	65.1	stored at -30 °C	143
$Et_2NC(F)$=PH	F	-99.1	-99.9	198.9	199.5	89.2	66.4	stored at -30 °C	143
$Pr_2NC(F)$=PH	F	-97.7	-98.4	200.0	200.5	88.4	66.4	stored at -30 °C	143
$(CH2)_5NC(F)$=PH	F	-101	-103.2	199.2	199.9	86.7	65.5		143
H_2C=PPh	C	266						NMR at -40 °C	106
MeCH=PPh	C	232						NMR at -40 °C	106
EtCH=PPh	C	229	233					NMR at -40 °C	106
PhCH=PPh	C	215						NMR at -40 °C	106
CF_2=PH	C	-61.4						NMR at -80 °C	49
CH_2=PCl	A	300.4		163.0		58.1		$\tau_{1/2}$ = 5 min at RT in solution	35
$CH_3C(H)$=PCl	A	265.0	266.5	174.9		60.6		$\tau_{1/2}$ = 3 min at -20 °C in solution	35
Ph_2C=PCl	F	273							148
$Tms(CO_2Et)C$=PCl	F	213						dec at $T > -40$ °C	150
CF_2=PCF_3	C	18						25 °C, 10 h	96
$(CF_3)CF$=PCF_3	A	134.6		196.2		50.8			68
$(CF_3)CH$=PC_2F_5	A	132							67
CF_2C=PC_2F_5	A	16.8		199.7		71.6			68
CH_2=PCH=CH_2	C	268.1						NMR at -50 °C	77
CH_2=CHCH=PPh	A	205.7[b]	191.5[b]						76,78
CH_2=CHCH=P^{t}Bu	A	205.7[b]	204.4[b]						76,78
CH_2=C=PMe	C	42		250.4		24.6		NMR at -50 °C	110
MeC(H)=C=PMe	C	45,3		247.2		24.5		dec $T > -20$ °C	110
Me_2C=C=PMe	C	39		209.0		23.8		dec $T > -20$ °C	110

[a] Method A, FVT; method C, gas-phase elimination (VGSR); method F, liquid-phase elimination. [b] The stereochemistry of the two isomers were not attributed.

Table 10. Selected Spectroscopic NMR Data of Simple Phosphaalkynes

compound	method[a]	δ 31P	δ 13C	$^1J_{CP}$	ref	compound	method[a]	δ 31P	δ 13C	$^1J_{CP}$	ref
HC≡P	electric arc	-32	154.0	54	216	$PhCH_2C$≡P	G	-53.2	170.6	46.2	113
	C	-32.0	158.0	56	35,81	CH_2=$CHCH_2C$≡P	G	-57	173.8	45	147
MeC≡P	C,G	-61.0	170.8	49	35,81,113	ClC≡P	C	-116	126.4	17	81
EtC≡P	C,G	-62.0	177.0	44	81,113	FC≡P	C	-223.4			49
^{n}BuC≡P	C	-59.0	176.4	43	81	Me_3SiC≡P	A	+96	201.4	14	51
^{i}PrC≡P	F	-64.0	183.4	41.3	119		C	+99	201.9	13	81
Me(Et)CHC≡P	F	-59.3			163	^{t}BuC≡P	F	-68	184.8	38.5	162
Et_2CHC≡P	F	-53.9	179.4	41.3	163	Me_2NC≡P	F	-124.6			143
^{t}BuCH_2C≡P	F	-51.4	173.7	45.5	119	Et_2NC≡P	F	-119.9			143
$C_6H_{11}C$≡P	F	-62.0	179.7	41.3	163	$^i Pr_2NC$≡P	F	-99.6	152.2	14.7	143
PhC≡P	A	-32.0	164.9	48.3	52	$(Me_2N)_3P^+C$≡P, BPh_4^-	F	59			160

[a] Method A, FVT; method C, gas-phase elimination (VGSR); method F, liquid-phase elimination; method G, liquid-phase rearrangement.

Table 11. Selected IR Data of Simple Phosphaalkynes and Phosphaalkenes

phosphaalkynes	method[a]	$\nu_{C\equiv P}$ (cm^{-1})	ref	phosphaalkenes	method	$\nu_{C=P}$ (cm^{-1})	ref
HC≡P	electric arc	1279[b]	121b,217	CH_2=PH	A	850[e]	102
MeC≡P	A	1558.7[d]	43	CF_2=PH	C	1349.5[d]	95
EtC≡P	C	1552[c]	81	CH_2=PCl	C	979.7[d]	95
nBuC≡P	C	1545[c]	81	CF_2=PCF_3	C	1365.3[d]	95
iPrC≡P	F	1528	119	CH_2=PCH=CH_2	A	978[b]	77
PhC≡P	A	1565[b]	218	CH_2=CHCH=PH	A	968[b]	77
ClC≡P	C	1460[b]	81	CH_2=CHCH=PMe	A	968[b]	77
FC≡P	C	1671[d]	218a	CH_2=C=PMe	C	869[c]	110
Me_3SiC≡P	C	1572[b]	81	$Me_2NC(F)$=PH	F	1302[d]	143
$^i Pr_2NC$≡P	F	1642[d]	143	$Et_2NC(F)$=PH	F	1323[d]	143
				$Pr_2NC(F)$=PH	F	1302[d]	143
				$(CH_2)_5NC(F)$=PH	F	1292[d]	143

[a] Method A, FVT; method C, gas-phase elimination; method F, liquid-phase elimination. [b] Film 77 K. [c] CCl_4, room temp. [d] Gas-phase. [e] This value has been corrected (ν = 1012 cm^{-1}), see ref 105.

to get indirectly access to the cycloadducts of an unstabilized phosphaalkene (PhP=C(H)PhCl).

A direct route to free phosphaalkenes is to use the terminal phosphinidene complexes as phospha-Wittig

reagents. The lack of a general synthetic approach to these intermediates has for a long time delayed their utilization. Schrock *et al.*[215] describe the first stable examples of electron-rich phosphinidene tantalum complexes. This stability is assumed by a ligand of the N^3N type bearing three R^3Si substituents (Scheme 43). Treatment of tantalum dichloride with 2 equiv of LiPHR afforded in good yield the corresponding phosphinidene. Structure was confirmed by NMR and by X-ray diffraction study. The stability is such that the compound with R=Ph can be heated for 12 h at 100 °C without observable decomposition.

Aldehydes react with the corresponding phosphinidene complex to provide both stable and reactive phosphaalkenes together with the corresponding oxotantalum complex (Scheme 43). The *C*-ferrocenyl compound (R = ^{t}Bu) is stable for short periods at 20 °C but ultimately dimerizes to 1,3-diphosphetane. *P*-Phenyl-*C*-ferrocenylphosphaalkene is too unstable to be observed at 25 °C; it was trapped with excess of cyclopentadiene (Scheme 43). The two isomers (1:1 mixture) resulting from the addition of the (*E*)-phosphaalkene to cyclopentadiene are observed. This reaction represents a new and general synthetic route to phosphaalkenes.

Tables 7 and 8 sum up, respectively, the different preparations of phosphaalkenes and phosphaalkynes in solution (only the first detection is mentioned).

Selected NMR data of simple phosphaalkenes and phosphaalkynes produced either in the gas-phase or in the liquid-phase are joined together in Tables 9 and 10, IR data ($\nu_{C=P}$ and $\nu_{C\equiv P}$) in Table 11.

VII. Concluding Remarks

Unstabilized P–C multiple bonds can be efficiently prepared either in the gas phase by using FVT and VGSR techniques or in solution without special equipment. The gas-phase syntheses are mainly of analytical significance while the reactions in solution open the way to synthetic applications. The best situation is given when both the gas-phase and the liquid-phase procedures can be used. To wholly include these intermediates as useful building blocks in the development of organophosphorus chemistry, several routes presented in this review are promising, in particular the base-induced elimination of hexamethyldisiloxane and hydrogen halides and the base-induced rearrangement of unsaturated phosphines. In both cases, precursors are easily available and the reactivity, including that of the parent compounds, can be controlled by lowering the reaction temperature and the concentration of the species in the medium. Special attention should be given to the phospha-Wittig route; the direct transformation of aldehydes into phosphaalkenes under mild conditions can stimulate new developments both in organophosphorus and organometallic chemistry.

Acknowledgments

We express our thanks to our co-workers whose contributions have been reviewed here. The pioneering experiments were carried out by B. Pellerin, J. L. Cabioch, and X. Morise. Various new approaches including rearrangements were developed by J. C. Guillemin, T. Janati, and A. C. Gaumont. Many of the most recent results can also be found in doctoral thesis. This work has been supported by the CNRS.

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