

Electrophilic Terminal-Phosphinidene Complexes: Versatile Phosphorus Analogues of Singlet Carbenes

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In memory of Professor *Luigi M. Venanzi*, a highly respected inorganic chemist

Electrophilic and nucleophilic terminal-phosphinidene complexes are compared in terms of electronic structures and reactivities. Various precursors of the unstable electrophilic species [R–P–M] (M = Cr, Mo, W(CO)₅ and Fe(CO)₄) are discussed. The addition reactions of the electrophilic phosphinidene complexes with *Lewis* bases, insertion reactions into O–H, N–H, and activated C–H bonds, and cycloaddition reactions with double and triple bonds are described, as well as some rearrangements and autocondensations. Various applications to the synthesis of new organophosphorus molecules are discussed and techniques available for demetallation are given.

1. Introduction. – Since *Doering's* seminal discovery [1] of the synthesis of 1,1-dichlorocyclopropanes from dichlorocarbenes and alkenes, carbenes have played a central role in organic synthesis. Recent developments include the discovery of stable singlet carbenes [2–4] and the generation of persistent triplet carbenes [5]. Inevitably, it appeared highly desirable to develop a similar chemistry for the corresponding 6-electron species centered upon the P-atom. Of these, electrophilic terminal-phosphinidene complexes [R–P–M] where M stands for a zero-valent transition-metal moiety such as Cr, Mo, W(CO)₅, or Fe(CO)₄ rapidly emerged as the most accessible and versatile P-equivalents of carbenes. Several reviews have already described their chemistry [6–9], but a number of recent and significant results justify an update of the previous accounts. In this report, we shall briefly summarize the earlier data and focus our attention on the more recent ones.

2. Electrophilic vs. Nucleophilic Species. – A phosphinidene ligand [RP] can use either two or four electrons when bonded to a transition-metal center. In the 2-electron mode, it can give either η^1 -bent or μ_2 -pyramidal complexes. In the four-electron mode, it can give linear [R–P=M], μ_2 -planar, μ_3 -tetrahedral, or μ_4 -bipyramidal complexes. From the standpoint of a synthetic chemist, only the two-electron bent species are of major interest. These complexes exist in two varieties, electrophilic and nucleophilic. Their electronic structures parallel those of the electrophilic *Fischer*-type and nucleophilic *Schrock*-type carbene complexes. According to a recent DFT (density-function-theory) study, the nucleophilic type can be viewed as resulting from the combination of two triplets and the electrophilic type of two singlets [10] (*Figs. 1 and 2*).

Hence, the nucleophilic species display a genuine P=M double bond with the more electronegative P-atom carrying the negative charge. Indeed, a DFT/ELF study of

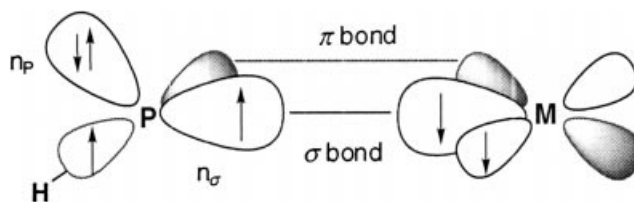


Fig. 1. Electronic structure of nucleophilic terminal-phosphinidene complexes

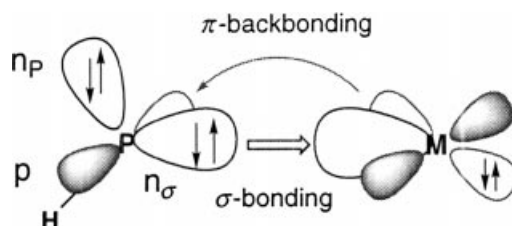


Fig. 2. Electronic structure of electrophilic terminal-phosphinidene complexes

[HP–TiCp₂] [10] indicates that the Ti=P bond is relatively strong at 45.8 kcal mol⁻¹ and that the P-atom carries a negative charge of $-0.33 e$. The LUMO is mainly localized at the Ti-atom. In these species, the P-atom is formally trivalent, and stability is reached whenever a sufficient steric protection is provided. Numerous nucleophilic complexes have been described and characterized by X-ray crystal-structure analysis. They are all derivatives of metals in high oxidation states: Mo^{IV}, W^{IV} [11], Zr^{IV} [12], Ta^V [13], and U^{IV} [14]. The most characteristic reactions of these nucleophilic species are the phospho-*Wittig* reaction with carbonyl compounds [13a][15][16], 1,2-additions with protic reagents [12b][17], and [2 + 2] cycloadditions with alkynes [11d][18] (Scheme 1). As can be seen, this reactivity is quite similar to that of *Schrock* carbene complexes.

Unlike the nucleophilic species, electrophilic phosphinidene complexes are formally derivatives of monovalent P and have never been isolated as stable species. The P–M bond can be described as a σ -dative bond with some π -backbonding and a negligible barrier to rotation. Earlier theoretical data gave conflicting results [19–21]. A better agreement has been reached more recently. A comparison of the calculated

Scheme 1. The Reactivity of Nucleophilic Terminal-Phosphinidene Complexes

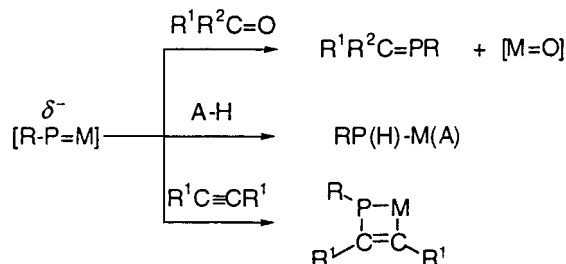


Table 1. DFT Studies of $[H-P-Cr(CO)_5]$

Ref.	Cr–P [Å]	P–H [Å]	Cr–P–H [°]	Δ (singlet-triplet) [kcal mol ⁻¹]	Cr–P bond energy [kcal mol ⁻¹]	Charge at P
[10]	2.332	1.460	103.4	5.46	34.8	+ 0.11 e
[22]	2.271	1.458	102.5	9.5	75.3	~ neutral
[23]	2.268	1.438	103.3	6.0	32.9	+ 0.253 e

data for $[HPCr(CO)_5]$ available from three independent DFT studies is made in Table 1 [10][22][23]. All studies predict a singlet ground state. The second study [22] probably overestimates the π -backbonding, thus leading to a stronger P–Cr bond and a weaker positive charge at the P-atom. Another study [24] correlates the structural and electronic properties of $[RP-Cr(CO)_5]$ with the nature of R. The P–Cr bond strength varies between 30.4 for R = SiH₃ and 51.7 kcal mol⁻¹ for R = NH₂. It is clear from Fig. 2 that the frontier orbitals of the electrophilic phosphinidene complexes are very similar to those of singlet $[CH_2]$ with an in-plane sp² lone pair lying perpendicular to a vacant p orbital. One of the studies [23] confirms the predominant contribution of this p orbital of the P-atom to the LUMO.

3. Generation of Electrophilic Terminal-Phosphinidene Complexes. – The original access to electrophilic phosphinidene complexes by thermal decomposition of 7-phosphabicyclo[2.2.1]hepta-2,5-diene complexes [25][26] is still the major route to these carbene-like species (Eqn. 1). These complexes are easily obtained by [4 + 2] cycloaddition of the appropriate 1H-phosphole complexes with dimethyl acetylenedicarboxylate [25]. When the 7-phosphatrinorbornadiene complex displays too high a reactivity or too low a stability – see the cases when R = CN [27] or R = PhC≡C [28] – it may be advantageous to use directly the mixture phosphole/acetylenedicarboxylate as the phosphinidene precursor. Typically, when M = W(CO)₅, the decomposition takes place around 50–60° in the presence of CuCl as the catalyst or around 100° without catalyst [29]. It must be noted here that CuCl can alter the course of the reaction of $[R-P-M]$ with the substrate. Whilst this scheme is, in practice, limited to M = Cr, Mo, W(CO)₅, it is extremely versatile concerning the substituent R at the P-atom. A complete list of the $[RP-W(CO)_5]$ species thus generated is given in Table 2. The only observed limitations are for bulky R groups such as ^tBu, the cycloaddition of ZC≡CZ with the 1H-phosphole diene system being prevented, or for amino groups, the electrophilic ZC≡CZ inserting into the P–N bond. A kinetic study of the reactions of one 7-phosphatrinorbornadiene complex with various substrates [40] has shown first-order kinetics in the concentration of the 7-phosphatrinorbornadiene complex and no dependence on the nature of the substrates, thus demonstrating the intermediacy of $[R-P-M]$.

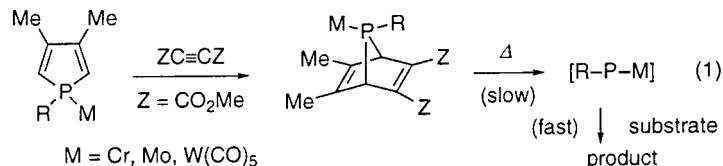
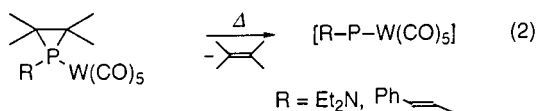


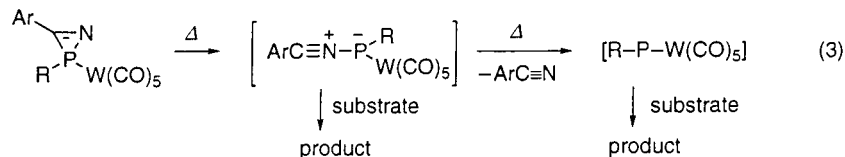
Table 2. $[RP-W(CO)_5]$ as Generated from 7-Phosphatrinorbornadiene Precursors

R	Reactions	Initial ref.	R	Reactions	Initial ref.
Ph	alkenes, alkynes, etc.	[26]	MeO	alkenes, alkynes, etc.	[36]
Me	alkenes, alkynes, etc.	[26]	^t BuO	alkynes	[27]
ClCH ₂	alkynes, dienes, rearrangement	[30]	N≡C	alkynes	[27]
ClCH ₂ CH ₂	alkynes	[31]	9H-fluoren-9-yl	alkynes	[27]
Cl(CH ₂) _n , n = 3–5	Bu ₃ P	[32]	EtOC(O)	alkynes	[27]
CH ₂ =CH(CH ₂) _n , n = 1, 2	alkynes	[33]	CH ₂ CH ₂	alkenes, alkynes, etc.	[37]
CH ₂ =CH(CH ₂) ₃	self-condensation	[33]	CH ₂ CH=CHCH ₂ (Z)	alkynes, dienes	[38]
EtOC(O)CH ₂ CH ₂	alkynes	[34]	CH ₂ =C(Me)	dimerization, dienes	[39]
MeC(O)(CH ₂) _n , n = 1, 3, 4	Bu ₃ P	[35]	PhC≡C	alkynes	[28]

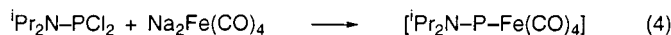
Another route to these phosphinidene complexes involves the thermal decomposition of some selected phosphirane complexes. It has been used to generate aminophosphanylidene [41] and vinylphosphinidene complexes [42] (Eqn. 2).



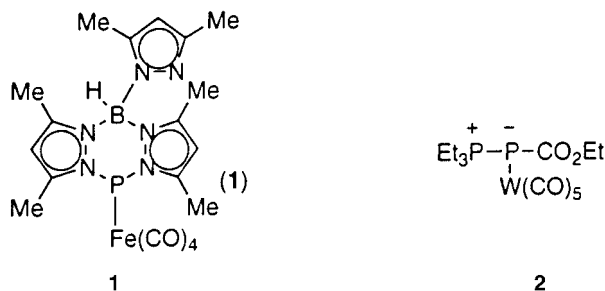
A third route relies on the thermal decomposition of azaphosphirene complexes [43] (Eqn. 3). The initial ring opening leads to a highly reactive 1,3-dipole, which can be trapped by the substrate. If this reaction is relatively slow, the final decomposition product is the terminal-phosphinidene complex which can, in turn, react with the substrate. This route offers the opportunity to study the reactivity of bulky phosphanylidene complexes.



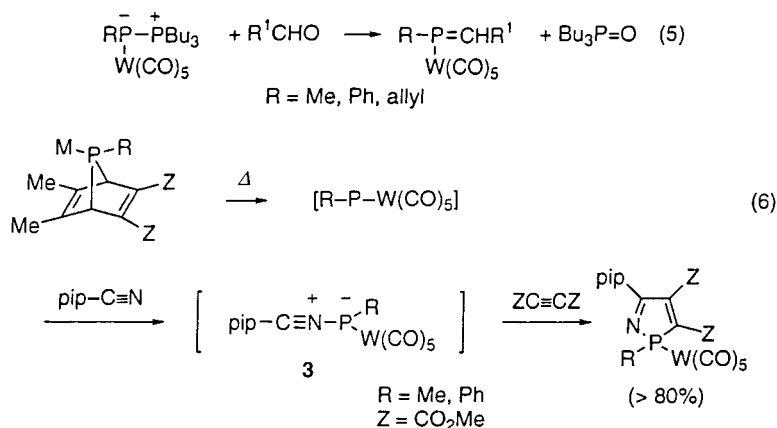
Finally, a fourth route has been recently proposed. It relies on the reaction of an amidodichlorophosphane with Na₂Fe(CO)₄ [44] (Eqn. 4). The electrophilicity of this tetracarbonyl(phosphanylidene)iron complex appears to be lower than that of its $[\text{M}(\text{CO})_5]$ counterparts. It has been trapped by allenes and alkynes [45], but does not react with alkenes.



4. Reactivity. – Unless otherwise noted, all the terminal-phosphinidene complexes discussed hereafter have been generated from the appropriate 7-phosphatrinorbornadiene precursors. As expected for any electrophilic species, $[\text{RP}-\text{M}(\text{CO})_n]$ can give transient or stable adducts with Lewis bases. The intramolecular N adduct **1** has been structurally characterized by Cowley *et al.* [46]. The synthesis relies on the route depicted in Eqn. 4. At 2.274(2) Å, the P–Fe distance corresponds to a single bond.



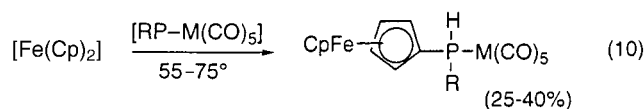
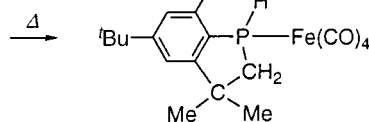
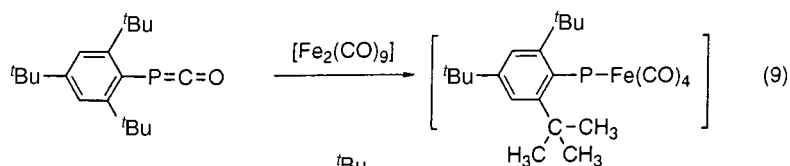
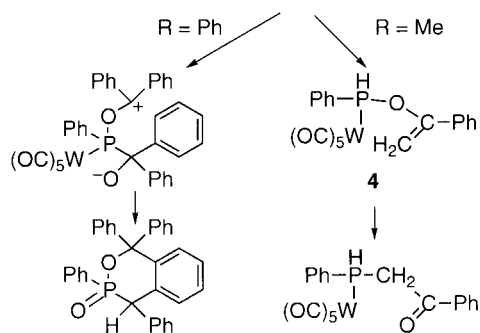
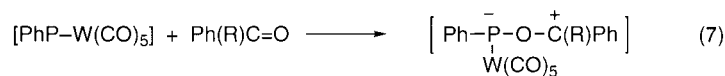
In a similar vein, the trialkylphosphine adduct **2** proved to be sufficiently stable for full characterization [47]. The long P–P bond (2.156(2) Å) and the weak $^1J(\text{P,W})$ coupling constant (107.4 Hz) suggests a zwitterionic structure as shown. When the substituent at the P-atom is a classical alkyl or aryl group, these so-called ‘phospha-Wittig’ reagents react with carbonyl compounds to give phosphalkenes (Eqn. 5). The ‘phospha-Wittig’ reagents can be obtained either by reaction of trialkylphosphanes with the appropriate 7-phosphatrinorbornadiene complexes [47] or by Zn reduction of dihalophosphines in the presence of trialkylphosphanes [48]. The various facets of the ‘phospha-Wittig’ reaction have been reviewed [16]. Unstable transient adducts have been also postulated on the basis of trapping reactions. This is the case with piperidine-1-carbonitrile [49] (Eqn. 6). As can be seen, Eqn. 6 represents the reverse of the reaction described in Eqn. 3. Nitrilium phosphanylides such as **3** have been studied by *Streubel*'s group and display a rich [3 + 2] cycloaddition chemistry towards alkynes, nitriles, and phosphalkynes.



A zwitterionic adduct has also been postulated in the reaction of electrophilic terminal-phosphinidene complexes with ketones [50–52]. The outcome of the reaction depends on the structure of the carbonyl compound. Some examples are described in (Eqn. 7). Products such as **4** can be isolated in some cases. These *Lewis*-acid/base adducts probably also play a role in the reactions of electrophilic phosphanylidenes with water, alcohols, primary and secondary amines, *etc.* [53] (Eqn. 8).

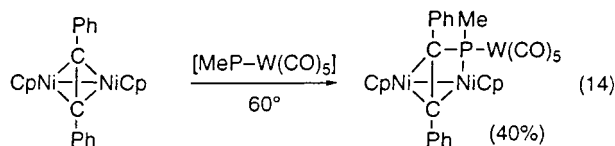
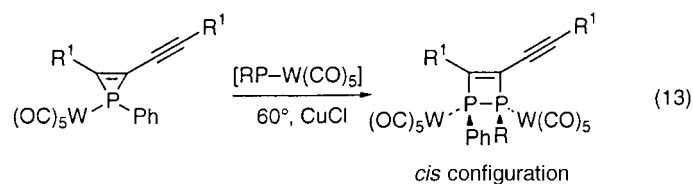
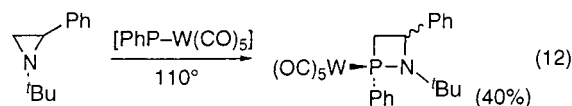
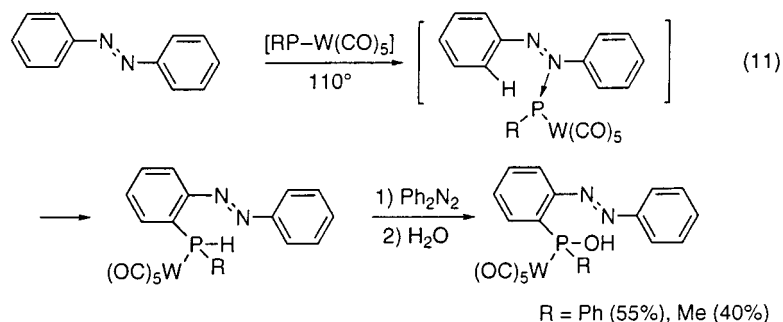
The most attractive insertion reactions are, of course, those involving C–H bonds. Apparently, $[\text{RP}-\text{M}(\text{CO})_5]$ displays an electrophilicity just sufficient for observing such

reactions. The first example was intramolecular [54] (*Eqn. 9*). An intermolecular example was subsequently reported with the electron-rich ferrocene [55] (*Eqn. 10*). Apparently, the reaction does not work with phosphinidene Cr complexes.

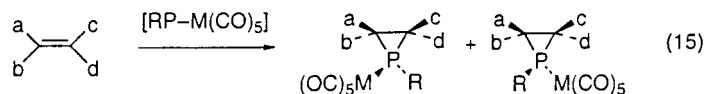


M = Mo, W; R = Ph, Me...

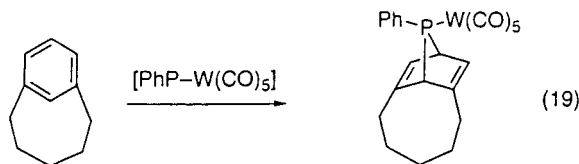
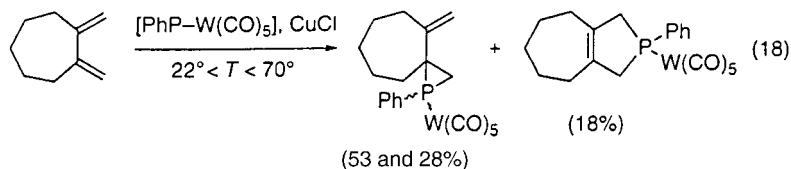
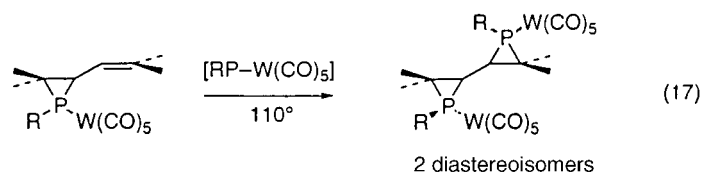
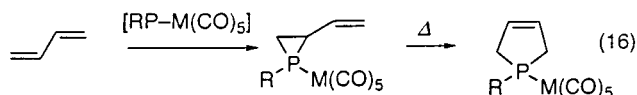
Recently, what appears to be the combination of two steps, the formation of a *Lewis*-acid/base adduct followed by insertion into one of its own vicinal C–H bond, has been discovered for azobenzene [56] (*Eqn. 11*). Another type of insertion occurs with 3-membered heterocycles. Examples have been described with epoxides, aziridines [57], and 2-alkynylphosphirenes [58][59]. Stable insertion products have been obtained in the latter two cases (*Eqns. 12* and *13*). Conjugation to the 2-alkynyl substituent destabilizes the P–C(2) bond of the phosphirene ring. Without this substituent, no phosphanylidene insertion is observed. The *cis* configuration of the insertion product is not fully understood. Finally, an example of phosphinidene insertion into a transition metal–C bond has been described [60a] (*Eqn. 14*).



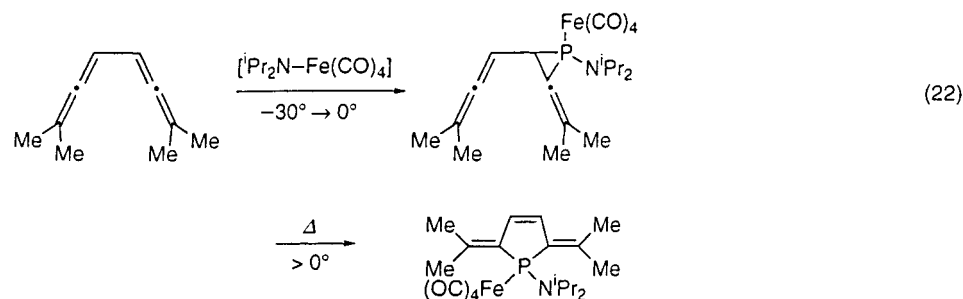
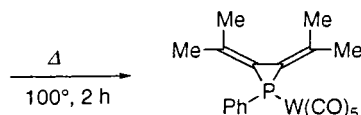
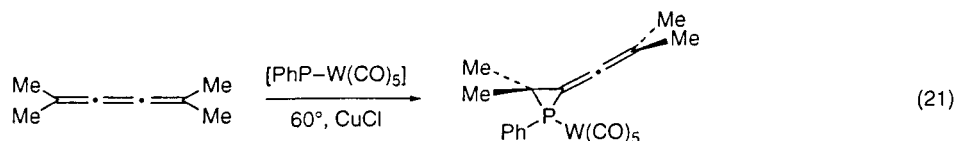
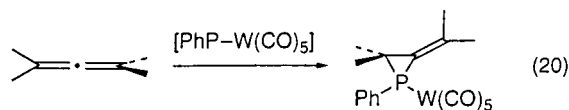
The most striking aspect of the chemistry of these electrophilic terminal-phosphinidene complexes is, without doubt, the wide range of [1 + 2] cycloaddition reactions that they give with a variety of π -bonds. Almost all the alkenes cleanly react with these species to give the corresponding phosphiranes, with the full retention of configuration typical of a concerted reaction [29] (*Eqn. 15*). The range of alkenes includes ethylene itself [60b], methylenecycloalkanes [60b], trinorbornadiene [61], electron-rich olefins such as enol ethers [29] and enamines [62], electron-poor olefins such as acryl acid esters [29], and vinyl halides [63][64]. In some cases, the product phosphirane readily undergoes a ring-opening reaction by hydrolysis (enol ethers, enamines) or upon heating (vinyl halides). We shall discuss this point below. *Lammertsma* and co-workers have quantified the reactivity of terminal-phosphinidene complexes with olefins. Using substituted styrenes as a probe, they have measured the following *Hammett* reaction constants ρ^+ : -0.76 [$\text{PhP}-\text{W}(\text{CO})_5$], -0.60 [$\text{MeP}-\text{W}(\text{CO})_5$], and -0.55 [$\text{MeO}-\text{P}-\text{W}(\text{CO})_5$] [65–67]. From that standpoint, these phosphinidene complexes show a reactivity comparable to that of alkylidenecarbenes. A study of the comparative reactivity of [$\text{PhP}-\text{W}(\text{CO})_5$] towards a range of Me-substituted olefins produced somewhat erratic results that showed no predictable trends [68].



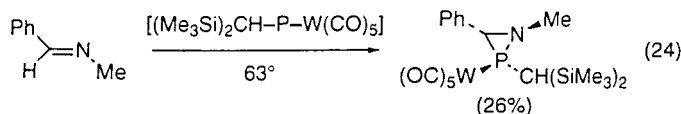
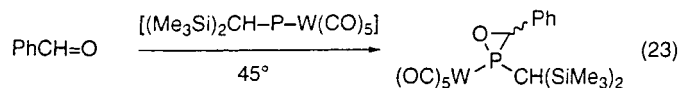
The reactivity toward conjugated dienes has also been investigated in some depth. In the initial report [29], it was shown that the normal reaction pathway starts by a [1 + 2] cycloaddition to give a 2-vinylphosphirane, which then rearranges upon heating to give a phospholene (Eqn. 16). This scheme has been investigated in more depth by *Lammertsma* and co-workers. Depending upon the configuration of the vinylphosphirane, the ring expansion takes place either *via* a concerted [1,3] sigmatropic shift with inversion of configuration at the P-atom or *via* a biradical pathway. The presence of CuCl seems to favor the concerted pathway [69–72]. Two alternative reaction courses have also been observed. If the 2-vinylphosphirane displays sufficient thermal stability, it is possible to graft a second phosphinidene unit onto the vinylic double bond to get a 2,2'-biphosphirane [73] (Eqn. 17). If the diene is constrained to a *s-cis* conformation, then a direct [1 + 4] cycloaddition can be observed [74] (Eqn. 18). The ratios between the [1 + 2] and [1 + 4] cycloaddition products are essentially temperature independent, thus showing that the [1 + 4] adduct is not formed by rearrangement of the [1 + 2] adducts. A similar [1 + 4] cycloaddition has also been observed with a strained benzene derivative whose cyclic delocalization is partly disrupted by the geometrical distortion of the ring [75] (Eqn. 19).

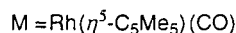
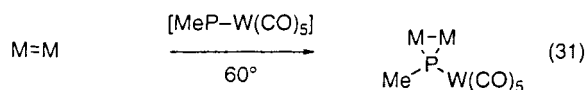
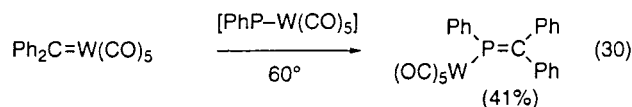


In the same vein, allenes and cumulenes react cleanly with terminal-phosphinidene complexes to give 2-alkylidene phosphiranes [76] and phosphat[3]radialenes [77], respectively (Eqns. 20 and 21). Finally, a [Fe(phosphinidene)(CO)₄] complex, prepared as shown in Eqn. 4, has been condensed with allenes and diallenes [44] (Eqn. 22).

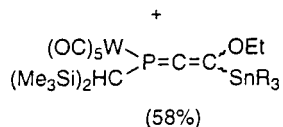
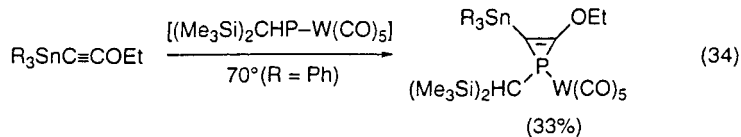
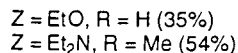
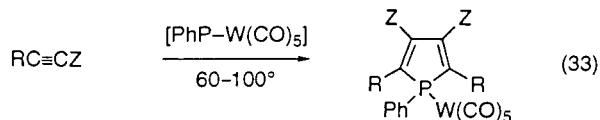
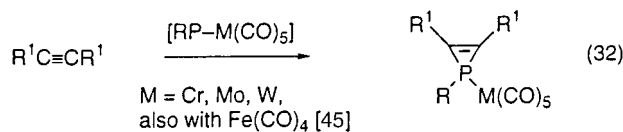


Terminal-phosphinidene complexes have also been allowed to react with numerous double bonds involving heteroatoms. With polar double bonds, the initial formation of a zwitterionic adduct whose further evolution can lead to several products, only one of them being the expected three-membered ring, is always theoretically possible. The reaction with aldehydes and ketones is quite illustrative. With nonbulky substituents at the P-atom, a variety of products is obtained (as already discussed above) (*Eqn. 7*). With a very bulky substituent, a three-membered oxaphosphirane ring has, nevertheless, been isolated by *Streubel et al.* [43][52] (*Eqn. 23*). The bulky phosphinidene complex is generated by the azaphosphirene route (*Eqn. 3*). The same approach leads to a decomplexed thiaphosphirane in 13% yield from $(\text{PhCH}_2\text{S})(\text{Me}_2\text{N})\text{C}=\text{S}$ [78]. The case of imines is identical. A bulky phosphinidene complex gives the expected [1 + 2] cycloadduct [52] (*Eqn. 24*). With ordinary substituents, the reaction is more complex and gives a variety of four- and five-membered rings, probably resulting from insertion into an initially formed [1 + 2] cycloadduct [79] (*Eqn. 25*).

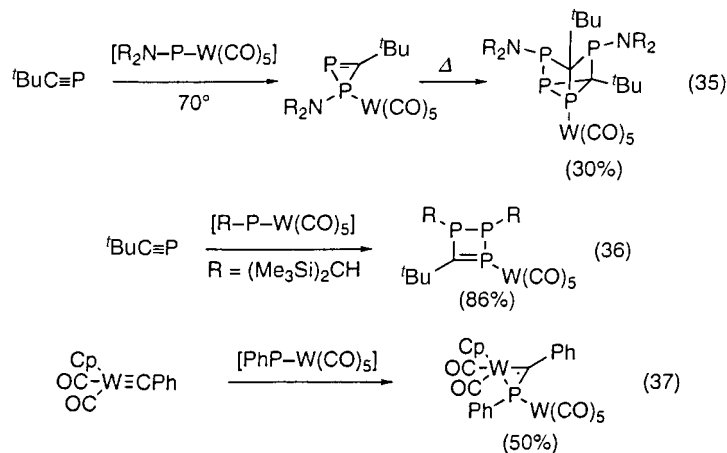




A very rich cycloaddition chemistry has also been developed with triple bonds. The [1 + 2] cycloaddition between alkynes and terminal-phosphinidene complexes is very general [26] (*Eqn. 32*). In fact, it provided the first synthesis of the phosphirene ring. The range of alkynes includes acetylene itself [86], mono- and disubstituted alkynes [26], and electron-poor alkynes such as phenyl propiolate [87]. The bulky phosphanylidene complex whose synthesis is depicted in *Eqn. 3* and reactivity in *Eqns. 23* and *24* tolerates a wide range of functional groups such as alkoxy, silyl, stannyl, and alkoxycarbonyl substituents [88–91]. The reaction with acetylenedicarboxylate has not been observed with other phosphinidene complexes [88]. It suggests some ambiphilic behavior in this species. A concerted mechanism is almost certainly at work in these [1 + 2] cycloadditions although an alternative dipolar pathway is conceivable for highly polarized alkynes. Indeed, other products appear when electron-releasing substituents such as alkoxy or amino are present at the alkyne [90][92] (*Eqns. 33* and *34*). A similar [1 + 2] cycloaddition takes place with the first C≡C triple bond of conjugated diynes. Then, the second phosphinidene unit either inserts as shown in *Eqn. 13* [58][59], or gives a 2,2'-biphosphirene [93], according to the nature of the diyne substituents. Their influence is not understood at present.

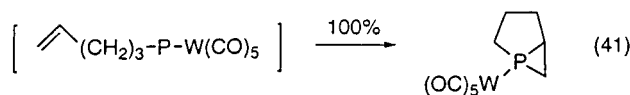
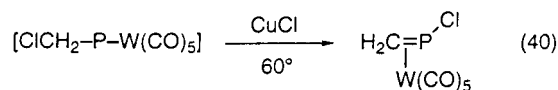
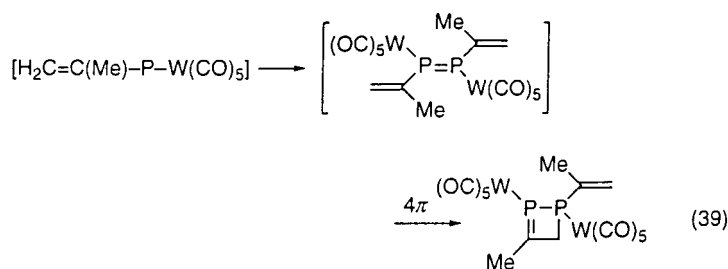
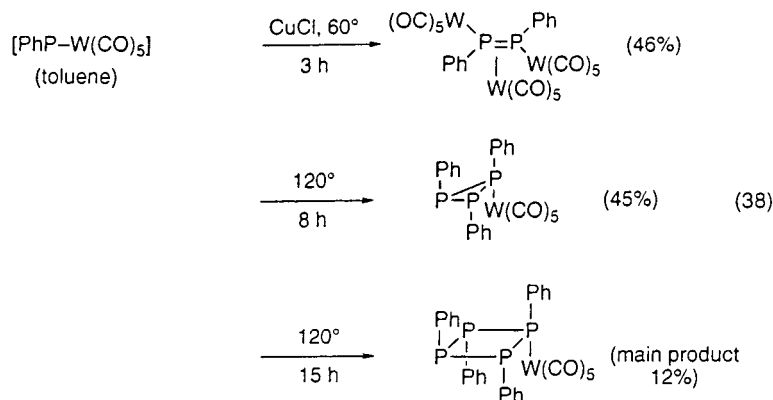


A similar [1 + 2] cycloaddition chemistry has also been developed with some heteroatom-containing triple bonds. An aminophosphinidene complex generated as shown in *Eqn. 2* has been allowed to react with (*tert*-butyl)phosphaacetylene [94] (*Eqn. 35*). The initially formed 1,2-diphosphirene evolves slowly to give a polycyclic cage product. A different evolution leading to a 1,2,3-triphosphete is observed with *Streubel's* bulky phosphinidene complex [95] (*Eqn. 36*). The triphosphete is probably formed *via* the insertion of a second phosphinidene unit into the P–P bond of the initial diphosphirene. With other bulky substitution schemes, the initial diphosphirene is stable. A carbyne complex has also been shown to give the expected stable metallaphosphirene by reaction with a terminal-phosphinidene complex [96] (*Eqn. 37*).



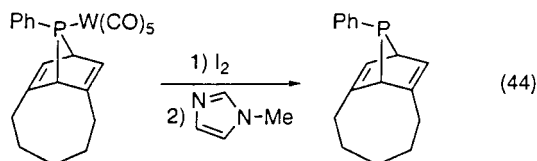
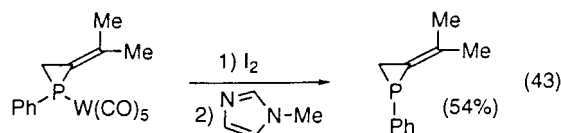
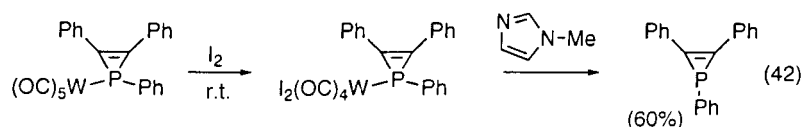
Finally, one last question remains to be addressed: what is the fate of an electrophilic terminal-phosphinidene complex when no trapping reagent is present in the reaction medium? The study has been carried out with $[\text{PhP}-\text{W}(\text{CO})_5]$ [40][97]. A dimer, a trimer, or a tetramer can be obtained depending on the experimental conditions (*Eqn. 38*). This chemistry can be used for synthetic purposes, as shown in *Eqn. 39* [39]; the obtained heterocycle was previously unknown. In some other cases, a reorganization or autocondensation can lead to a stable isolable monomeric product. This is the case with the chloromethyl species [30][98] (*Eqn. 40*). The rearrangement does not take place in the absence of CuCl, which plays the role of halogen carrier. The chlorophosphaalkene is η^2 -complexed but shows reactivity typical of a η^1 -P complex *via* its double bond when treated with alcohols or conjugated dienes. Free $\text{CH}_2=\text{P}(\text{Cl})$ is a highly unstable molecule. The other known example of autocondensation involves an intramolecular reaction with a C=C bond [33] (*Eqn. 41*).

5. Applications. – As shown in the preceding sections, electrophilic terminal-phosphinidene complexes combine easy access, large range of substituents, and an impressive array of reactions with organic or organometallic molecules. Thus, potentially, they constitute a powerful tool for making new organophosphorus molecules. However, to be fully effective, their chemistry needs to be coupled to

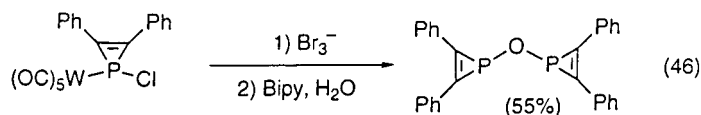
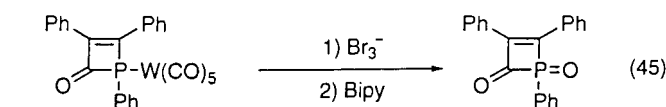


efficient decomplexation techniques. Indeed, whilst the complexing groups are useful for tuning the electrophilicity and the lifetime of the phosphinidene moiety and for increasing the stability and the tractability of the reaction products, they must be removed if useful ligands or bioactive molecules are the final targets of the synthetic work.

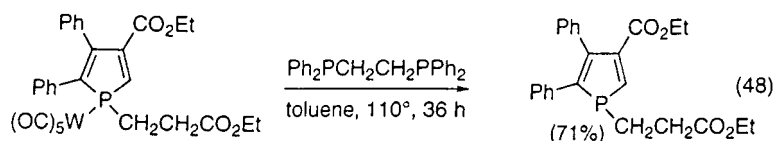
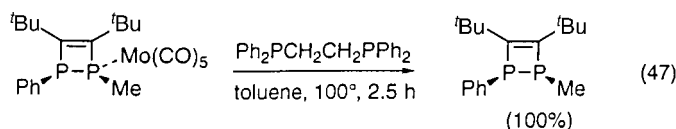
In practice, the most effective complexing group is the pentacarbonyltungsten unit. As might be expected, this is also the one that gives the strongest bond to the P-atom. At the moment, three decomplexation techniques have been applied with some success to its removal. The oldest method involves an oxidation of W^0 to W^{II} by I_2 which weakens the P–W bond, followed by a displacement of the P-ligand by 1-methyl-1*H*-imidazole. This technique allowed the isolation of the first trivalent phosphirene [99] (*Eqn. 42*). Other uses include the synthesis of an unstable 2-alkylidenephosphirane [76] and of the first relatively stable trivalent 7-phosphatrinorbornadiene [100] (*Eqns. 43 and 44*). The 7-phosphatrinorbornadiene is characterized by a ^{31}P -NMR resonance at very low field (δ 112.5).

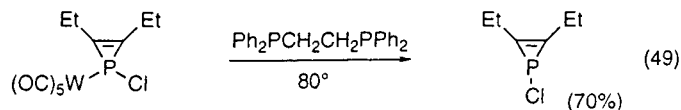


In a variant of this first technique, pyridinium tribromide is used as the halogenation reagent and 2,2'-bipyridine for the displacement. Two examples illustrate this method [101][102] (*Eqns. 45 and 46*).

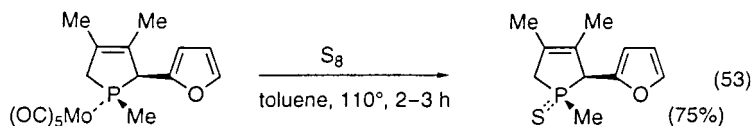
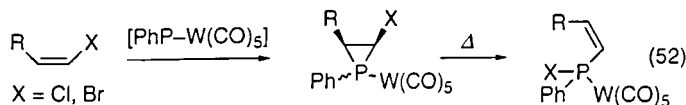
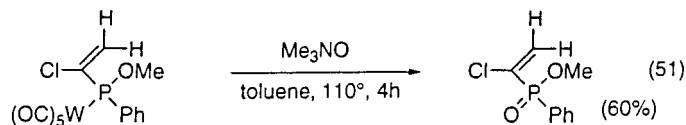
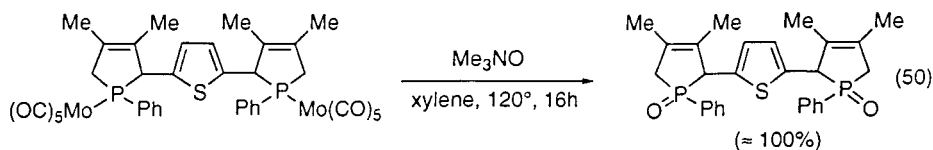


As is clear from *Eqn. 45*, this type of technique suffers from the potential for oxidizing the trivalent P-center. To solve this problem, another method has been proposed. It relies on the displacement of the P-ligand by a chelating bidentate diphosphine such as $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and, of course, can be applied only to the displacement of monodentate ligands. Its feasibility was first demonstrated with a pentacarbonylmolybdenum complex [103] (*Eqn. 47*); the demetallation proceeded with retention of configuration at the P-atom. This method has been applied to a bifunctional phosphole [34] and to a 1-chlorophosphirane with small substituents [86] (*Eqns. 48 and 49*).

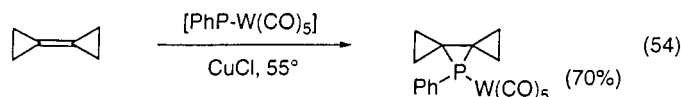


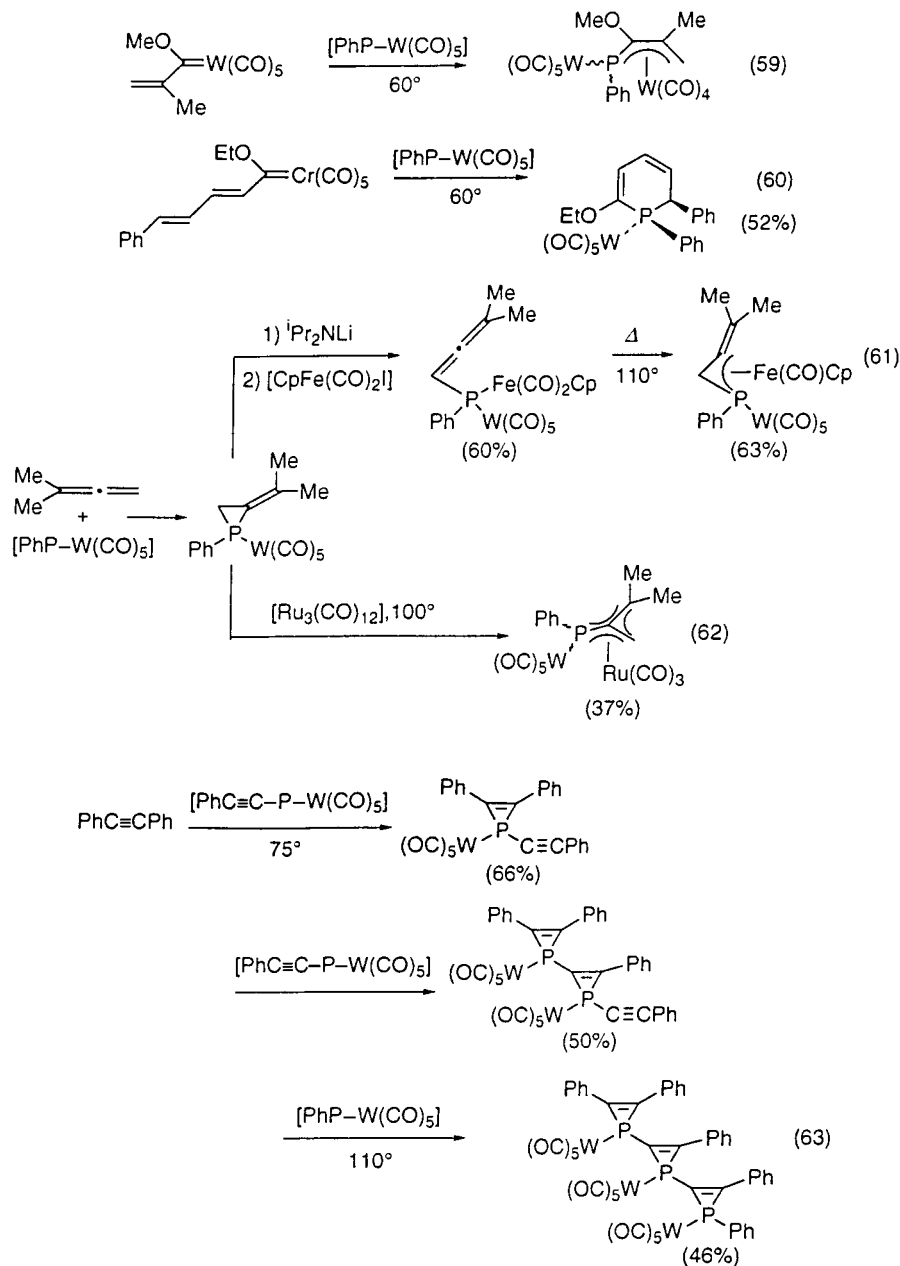


The third group of methods involves oxidative conditions. Trimethylamine oxide has been shown to be the reagent of choice for the conversion of $[\text{P}-\text{Mo}(\text{CO})_5]$ or $[\text{P}-\text{W}(\text{CO})_5]$ complexes into the corresponding phosphoryl compounds [64][104] (*Eqns. 50 and 51*). *Eqn. 51* corresponds to the last step of a process that allows the insertion of a phosphinidene unit into the C–X bond of a vinyl halide with retention of the alkene configuration (*Eqn. 52*). The [1,3] migration of X from C to P appears to be a concerted process. In the case of $[\text{P}-\text{Mo}(\text{CO})_5]$ complexes, sulfurization is another mild oxidation method [105] (*Eqn. 53*). All these oxidation methods can be applied to the demetallation of $[\text{P}-\text{Fe}(\text{CO})_4]$ complexes.



We have already seen in *Sect. 4* that, on several occasions, the electrophilic terminal-phosphinidene complexes have allowed the discovery of new structures. The most striking case is, of course, the preparation of the first phosphirenes although these rings are now accessible by other routes. Other examples are described in *Eqns. 11, 19, 29, 35, 36, 39, and 41*. Additional examples will be briefly discussed now. In the phosphirane field, the synthesis of the first phosphapha[3]triangulane [106] and of parent chlorophosphirane [32] deserve attention (*Eqns. 54 and 55*). No other routes to these species are presently known.





With the exception of this last example, the new structures that have been synthesized by the phosphinidene-complex route are still relatively simple. However, in view of its sophistication combined with its mildness, selectivity, and effectiveness, this route is nicely adapted to the synthesis of highly complex organophosphorus structures. Grafting P-atoms into complex molecules will certainly be the most significant

application of all this work. In these cases, the phosphinidene-complex route will be highly competitive with the more classical syntheses of the P–C bond.

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