Pd metal by β-elimination from PdIEt(bpy).[5k] However, few complexes containing β-hydrogens have been synthesized, so it remains to be established whether β-elimination can occur in Pd^{IV} chemistry. At this early stage, the occurrence of oxidative addition mechanisms other than S$_N$2, and of reactions other than oxidative addition for the interaction of organohalides with Pd^{II} substrates, clearly cannot be discounted for some reactions where Pd^{IV} intermediates have not been detected, and for reaction systems that may potentially be developed in the future. These mechanistic considerations, together with selectivity in reductive elimination, the tendency for dissociation of halogeno ligands, fluxionality in five-coordinate intermediates, and exchange of organic groups between Pd^{IV} and Pd^{II} centers, are relevant to the future development of organic syntheses that may proceed via Pd^{IV} species.

Expanding the Analogy between Phosphorus–Carbon and Carbon–Carbon Double Bonds

François Mathey

Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

It is very difficult to imagine the impressive development of organic chemistry without the existence of π-bonds. Organophosphorus chemistry was limited precisely by such an absence until 1976 when Becker discovered the first stable phosphaalkenes.[1] Since that time, the chemistry of the P=C π-bonds has undergone an explosive development, which has been reviewed recently.[2] A striking parallel soon appeared between the chemistry of phosphaalkenes and alkenes. In essence, this analogy bears the possibility of developing a huge "phosphaorganic" chemistry in which sp^2 phosphorus chemistry would systematically mimic all the aspects of sp^2 carbon chemistry. In this Account, I summarize some experimental evidence that brought to light this analogy with particular emphasis on the results of my research group and on the problems remaining to be solved.

Theoretical Background

Phosphaethylene is characterized by two closely spaced highest occupied molecular orbitals, the HOMO corresponding to the π-bond and the next orbital corresponding to the lone pair.[3] Inversion of these two levels can be observed with appropriate substitutions at phosphorus and carbon, e.g., Me$_3$CP=C(SiMe$_3$)$_2$.[4]

The π-bond appears to be almost apolar whereas the σ-bond displays significant P$^+$–C$^-$ polarity.[5] The π (HOMO) $-\pi^*$ (LUMO) separation is significantly lower than in ethylene.[5] From a thermodynamic standpoint, the P=C π-bond is much weaker than the C=C π-bond, ca. 45 versus 65 kcal/mol.[6] All these data suggest that the P=C double bond will be more reactive than the C=C double bond. A priori, it will be generally possible to duplicate the chemistry of alkenes with phosphaalkenes unless the phosphorus lone pair (NHOMO or HOMO) interferes with the reactions. The relatively low kinetic and thermodynamic stability of the P=C π-bond of course will imply some steric protection by bulky substituents or additional electronic stabilization by conjugating or electron-withdrawing substituents in order to keep the chemistry of these species under control.

Free versus P-Coordinated Phosphaalkenes. The "Phospha-Wittig" Synthesis

We have already underlined the possible interference between the reactivity of the phosphorus lone pair and

François Mathey is Professor of Chemistry at Ecole Polytechnique, Palaiseau (near Paris), France, and "Directeur de Recherche" in Centre National de la Recherche Scientifique (CNRS). He was born in Paris in 1941, studied in Ecole Polytechnique from 1961 to 1963, and then received a Ph.D. in organic chemistry from the University of Paris VI in 1971. He was appointed group leader in Institut National de Recherche Chimique Appliquée (IRCHA) in 1969, left IRCHA for Société Nationale des Poudres et Explosifs (SNPE) in 1980, and finally, joined the faculty at Ecole Polytechnique in 1987 and the CNRS in 1989. His research deals with organophosphorus and transition-metal chemistry.

(1) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.

(2) Appel, R. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; pp 157–219.

(3) Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964. See also: Bock, H.; Bankmann, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 265.

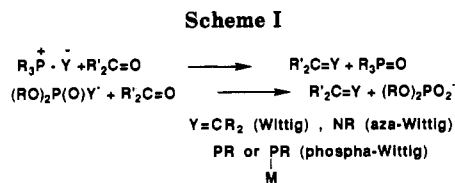(4) Some relevant data are quoted in the following: Schoeller, W. W. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; pp 5–32.

(5) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1985**, 334.

(6) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217. Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

Scheme I

$$R_3\overset{+}{P}\cdot\overset{-}{Y} + R'_2C{=}O \longrightarrow R'_2C{=}Y + R_3P{=}O$$

$$(RO)_2P(O)Y^- + R'_2C{=}O \longrightarrow R'_2C{=}Y + (RO)_2PO_2^-$$

$$Y{=}CR_2 \text{ (Wittig)} , \quad NR \text{ (aza-Wittig)}$$

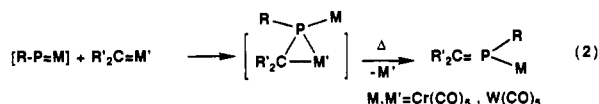$$\underset{\underset{M}{|}}{PR} \text{ or } \underset{\underset{M}{|}}{PR} \text{ (phospha-Wittig)}$$

the reactivity of the P=C π-bond in phosphaalkene chemistry. This kind of problem is almost nonexistent in concerted reactions. In most cases, the incoming reagent easily discriminates between the π-bond and the lone pair. Such is no longer true when 1,2-addition reactions are considered. Most of the electrophiles will tend to react with both the lone pair and the π-bond. The outcome of the reaction will become difficult to predict. Oxidation illustrates that point[7] (eq 1). In

$$(1)$$
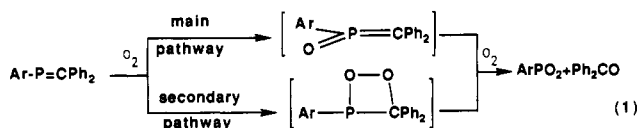
order to perform a selective reaction of the incoming electrophile at the P=C π-bond, it thus becomes necessary to use a mask for the phosphorus lone pair. Complexation at phosphorus by low-valent transition metals is the best solution. The σ-bonding/π-backbonding synergy confers a good stability on the P–M bond and, at the same time, precludes any dramatic changes in the polarity and energetic level of the π-system. Among the various possible complexing groups, the group 6 metal pentacarbonyls [$Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$] immediately proved to be the best choice, combining a ready availability with a sizable stabilizing effect on the P=C π-bond. It was, of course, possible to prepare these phosphaalkene complexes via the complexation of free phosphaalkenes, but in so doing, we would have lost the benefit of the stabilizing effect of the phosphorus complexation. We thus decided to study the synthesis of the P=C double bond directly in the coordination sphere of transition metals.

Our first approach relied on the chemistry of terminal phosphinidene complexes.[8] Since we knew that these transient species easily react with C=C double bonds to give three-membered phosphirane complexes,[9] we attempted a transposition with carbon–metal double bonds. We expected the formation of 4e σ,π-phosphaalkene complexes via a formal [1 + 2] cycloaddition. These species proved to be unstable.[10] They tend to lose the π-bonded metal to give the required P=C double bond[11] (eq 2). We shall see several applications of this approach later.

$$(2)$$

A more general access to phosphaalkene complexes was devised some time later. It relies on the so-called "phospha-Wittig" synthesis. The underlying idea was to transpose the Wittig synthesis of olefins. Scheme I summarizes the known or potential syntheses of alkenes, imines, and phosphaalkenes based upon the Wittig or Horner–Emmons approaches. The success of our idea was conditioned by an easy access to the necessary starting reagents, i.e., the phosphoranylidenephosphines ($R_3P{=}PR$) and the phosphorylphosphines [$(RO)_2P(O)PHR$] or their complexes. Some phosphoranylidenephosphines were known previously, but they are unreactive toward carbonyl compounds, probably because they are stabilized by steric hindrance or by electron-withdrawing substituents.[12] In fact, until now, we have been unable to transpose the Wittig or Horner–Emmons synthesis of alkenes to the synthesis of free phosphaalkenes. The starting reagents are either too unstable or stable but unreactive. The picture changed completely when work was carried out in the coordination sphere of transition metals. We have been able to devise several routes to the starting reagents. Some of them are depicted in eqs 3[13] and 4.[14]   From

$$(3)$$

$$M{=}Fe(CO)_4 , Cr(CO)_5 , W(CO)_5$$

$$(4)$$
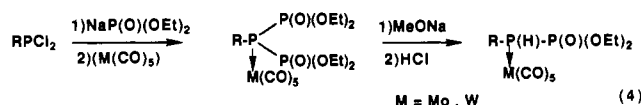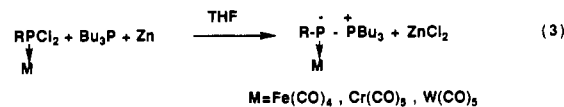
these reagents, it is now very easy to prepare a large series of phosphaalkene complexes by reaction with aldehydes or ketones.[15-17] Several applications of this "phospha-Wittig" synthesis will be quoted in the next sections. At the moment, we have only limited information concerning the mechanism of this reaction, but all the available data point to a Wittig-type pathway with an oxadiphosphetane intermediate.

Some Applications of the Masking of the Phosphaalkene Lone Pair

When one looks at the literature,[2] it immediately appears, if one excludes the concerted cycloadditions, that the number of addition reactions described with phosphaalkenes is surprisingly limited. It mainly includes the addition of protic reagents such as alcohols, secondary amines, and HCl. It is possible to extend the scope of this type of chemistry when masking the phosphorus lone pair. We have seen before (eq 1) that it is impossible to oxidize selectively the phosphaalkene double bond when working with a free lone pair. On the contrary, the epoxidation of the P=C double bond of selected phosphaalkene complexes is very easily

(7) van der Knaap, Th. A.; Klebach, Th. C.; Lourens, R.; Vos, M.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1983**, *105*, 4026.

(8) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. Mathey, F. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; pp 33–47.

(9) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(10) Some stable 4e σ,π-phosphaalkene complexes have been described in the literature: Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *293*, 213.

(11) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791.

(12) Burg, A. B.; Mahler, W. *J. Am. Chem. Soc.* **1961**, *83*, 2388. Zurmühlen, F.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 83; *New J. Chem.* **1989**, *13*, 335. Weber, D.; Fluck, E. *Z. Anorg. Allg. Chem.* **1976**, *424*, 103. Schmidpeter, A.; Lochschmidt, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 253.

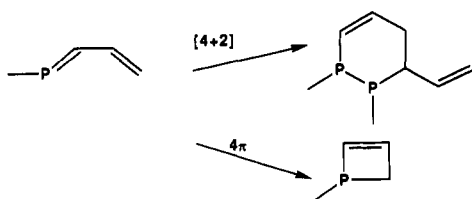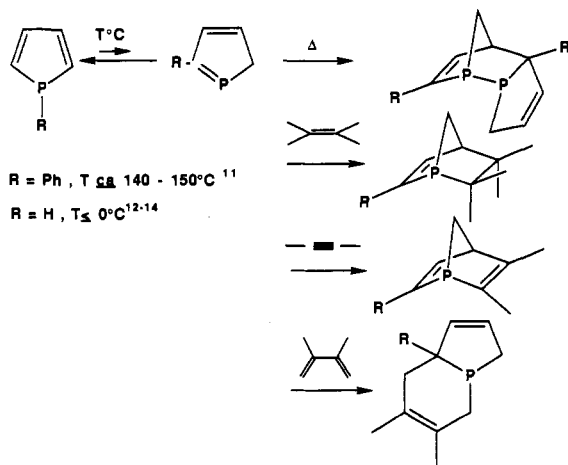(13) Le Floch, P.; Mathey, F. *Synlett* **1990**, 171.

(14) Bauer, S.; Marinetti, A.; Mathey, F. *Heteroat. Chem.* **1991**, *2*, 277.

(15) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382.

(16) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.

(17) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407.

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achieved in spite of the oxidizability of the metal[18] (eq 5). The reaction proceeds with predominant retention

$$\text{Mes} \diagdown \underset{(OC)_5W}{P}{=}C\diagup\overset{H}{\diagdown R} \xrightarrow[\text{THF , 0°C}]{m\text{-ClC}_6\text{H}_4\text{-CO}_3\text{H (1 eq)}} \text{Mes}\diagdown\underset{(OC)_5W}{P}\diagup\overset{O}{\diagdown}C\diagup\overset{H}{\diagdown R} \qquad (5)$$
ca 100 %

of the phosphaalkene stereochemistry as a classical epoxidation. The X-ray crystal structure analysis of one such ring shows that the oxygen atom "sits" on the plane of the former P=C double bond and that the geometry of the phosphaalkene moiety is almost undisturbed apart from the expected lengthening of the P—C bond. The similarity to the structure of oxiranes is obvious. A preliminary chemical study[19] indicates that these oxaphosphirane complexes are opened upon reaction with hydroxide ion to give P(OH)C(OH) glycol-like products. In addition, the ring can be deoxygenated by triphenylphosphine in toluene at 110 °C to restore the P=C double bond. The analogy with oxiranes is striking.

It is well-known in organic chemistry that one of the most versatile syntheses of four-membered rings involves the nonconcerted [2 + 2] cycloaddition between electron-rich and electron-poor alkenes or alkynes. The tendency of phosphaalkenes to dimerize via [2 + 2] cycloaddition to give 1,2- or 1,3-diphosphetanes is well-known,[2] but except for a single example with a silene,[20a] no [2 + 2] cycloadditions with other π-bonds have been described. The "phospha-Wittig" approach gave us an easy access to unstable and very reactive electron-poor P=C double bonds[20b] (eq 6). These electron-poor π-bonds very readily react with electron-rich alkenes or alkynes to give the expected four-membered rings[20b] (eqs 7 and 8).

$$\underset{W(CO)_5}{\overset{\bullet}{R}P}\text{-}P(O)(OEt)_2 + R^1C(O)\text{-}CO_2Et \xrightarrow[-70°C]{THF} [\underset{W(CO)_5}{R\text{-}P}{=}C(R^1)CO_2Et] \qquad (6)$$

$$[\underset{W(CO)_5}{RP}{=}C(R^1)CO_2Et] + R^2CH{=}CHZ \xrightarrow[-70 - +25°C]{THF} \underset{W(CO)_5}{\overset{R^2HC-CHZ}{\underset{RP-C-R^1}{\square}}}_{CO_2Et} \qquad (7)$$

$$[\underset{W(CO)_5}{RP}{=}C(R^1)CO_2Et] + R^2C{\equiv}CZ \xrightarrow[-70 - +25°C]{THF} \underset{W(CO)_5}{\overset{R^2 \diagup\diagdown Z}{\underset{RP{-}\diagup\diagdown}{\square}}}_{CO_2Et}^{R^1} \qquad (8)$$
Z = OEt , NEt$_2$

Catalytic reactions using soluble transition-metal catalysts are of great importance in the chemistry of alkenes. The direct transposition of such a chemistry to free phosphaalkenes was doomed to failure since phosphorus lone pairs strongly bind the low-valent and electron-deficient transition-metal centers that form the bulk of the soluble catalysts effectively used with alkenes. Once again, the replacement of free by complexed phosphaalkenes proved to be the solution. When a phosphaalkene complex in which the metal is strongly bound to phosphorus is used,[21] no scrambling

(18) Bauer, S.; Marinetti, A.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1166.

(19) Bauer, S. Dissertation, Ecole Polytechnique, Palaiseau, 1991.

(20) (a) Ford, R. R.; Li, B.-L.; Neilson, R. H.; Thoma, R. J. *Inorg. Chem.* **1985**, *24*, 1993. (b) Marinetti, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1990**, 153.

(21) A few metallic centers such as PtL$_2$ "hesitate" between P- and π-coordination; see: van der Knaap, Th. A.; Bickelhaupt, F.; Kraaykamp, J. G.; van Koten, G.; Bernards, J. P. C.; Edzes, H. T.; Veeman, W. S.; de Boer, E.; Bairends, E. J. *Organometallics* **1984**, *3*, 1804.

between the catalytic and the masking metals occurs and it becomes possible to perform a catalytic transformation of the P=C double bond. This was demonstrated for catalytic hydrogenation using the RhL$_2$ (catalyst)-W(CO)$_5$ (mask) couple[22] (eq 9).

$$\underset{(OC)_5W}{\overset{R}{\diagdown}}P{=}C\diagup\overset{H}{\diagdown R^1} \xrightarrow[\text{Rh(diphos)}^*]{H_2 , 8 \text{ bar , CH}_2\text{Cl}_2 , RT} \underset{(OC)_5W}{\overset{R}{\diagdown}}PH\text{-}CH_2R^1 \qquad (9)$$
R , R^1 = Ph , ^{t}Bu , ^{i}Pr

In some cases, we observed competition between hydrogenation and isomerization of the phosphaalkene complex into the corresponding secondary vinylphosphine complex[22] (eq 10). It seems that the Lewis

$$\underset{(OC)_5W}{\overset{Ph}{\diagdown}}P{=}C\diagup\overset{Me}{\diagdown Me} \xrightarrow[\text{Rh(diphos)}^* , CH_2Cl_2]{H_2 , 8 \text{ bar , RT}} \underset{(OC)_5W}{\overset{Ph}{\diagdown}}PH\text{-}C\diagup\overset{CH_2}{\diagdown Me}$$
3h , 84%

$$\xrightarrow[\text{Rh(diphos)Cl , Me}_2CO]{H_2 , 8 \text{ bar , RT}} \underset{(OC)_5W}{\overset{Ph}{\diagdown}}PH\text{-}CHMe_2 \qquad (10)$$
25 h , 71%

acidity of the medium and of the catalyst favors the isomerization against the hydrogenation. At the moment, we have no detailed information on the catalytic cycles. Deuteration experiments only indicate that selective cis hydrogenation occurs. Indeed, equal *Z/E* isomeric and P*D–C*D diastereomeric ratios were observed during the reactions depicted in eq 11.[22] Finally, using a prochiral phosphaalkene complex and an inducting group as the substituent at phosphorus, it was possible to achieve complete face selectivity during the catalytic hydrogenation of the P=C double bond[23] (eq 12).

$$\underset{(OC)_5W}{\overset{Ph}{\diagdown}}P{=}C\diagup\overset{H}{\diagdown CHMe_2} + D_2 \xrightarrow[CH_2Cl_2]{Rh(diphos)^*} \underset{(OC)_5W}{\overset{Ph}{\diagdown}}PD\text{-}CHD\text{-}CHMe_2 \qquad (11)$$
Z + E

$$\underset{(OC)_5W}{\overset{Men}{\diagdown}}P{=}C\diagup\overset{H}{\diagdown CHMe_2} \xrightarrow[CH_2Cl_2 , L_2Rh^*]{H_2 , 8 \text{ bar ,24h , RT}} \underset{(OC)_5W}{\overset{Men}{\diagdown}}P\diagup\overset{CHMe_2}{\diagdown H} \qquad (12)$$
Men ≡ L-menthyl

pure diastereomer selective attack on the SI face (sp^{2}C as the reference)

Concerted Reactions

Generally speaking, the Woodward–Hoffmann rules can be applied to the various cycloadditions, electrocyclizations, and sigmatropic reactions undergone by P=C-containing systems. Of course, the replacement of carbon by phosphorus in the reacting species lowers the symmetry and weakens some bonds in the transition states. This may induce a loss of stereochemical control, as we shall see later.

[4 + 2] Cycloadditions. What is known in the literature concerning the prototypical [4 + 2] cycloadditions between conjugated dienes and phosphaalkenes is summarized in a recent reference.[24] It is well established that, in most cases, the cycloaddition takes place with retention of the phosphaalkene stereochemistry. In some cases, however, a subsequent loss of stereochemistry can occur without cycloreversion via

(22) de Vaumas, R.; Marinetti, A.; Mathey, F. *J. Organomet. Chem.* **1991**, *413*, 411.

(23) de Vaumas, R.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1992**, *114*, 261.

(24) Abbari, P.; Cosquer, P.; Tonnard, F.; Yeung Lam Ko, Y. Y. C.; Carrié, R. *Tetrahedron* **1991**, *47*, 71.

Scheme II

Scheme III
The Reactivity of 2H-Phospholes

R = Ph , T ca 140 - 150°C [11]

R = H , T≤ 0°C [12-14]

Scheme IV

Scheme V

a pyramidal inversion at phosphorus.[25] Besides, some phosphaalkenes with electronegative substituents such as ClP=C(Ph)SiMe$_3$ or CF$_3$P=CHF seem not to obey the general rule and to react with dienes via a nonconcerted two-step mechanism.[26] With cyclopentadiene and phosphaalkenes, only the adducts with the P-substituents in the endo position are formed.[27]

If the picture is now almost completely clarified when phosphorus is introduced in the ene component, the introduction of phosphorus in the diene component causes several problems. As a general rule, 2-phosphadienes tend to react exclusively as nonconjugated phosphaalkenes. The [4 + 2] cycloaddition is a high-energy process compared to the 1,2-additions or [2,n] cycloadditions onto the P=C double bond which lead to a favorable increase of the phosphorus coordination number. On the other hand, 1-phosphadienes are obviously very powerful dienes but they are so reactive that it is difficult to find adequate model compounds. When they are not completely deactivated by bulky substituents at phosphorus, they tend to give [4 + 2] dimers or 1,2-dihydrophosphetes via 4π-electrocyclization (Scheme II). We will discuss this topic in the next section.

When we discovered the 1H-phosphole–2H-phosphole equilibrium,[28-31] we soon realized that we held the accessible and reactive 1-phosphadienes that could allow

a systematic study of the reactivity of this type of species. We will discuss later the nature of this equilibrium. Here, it suffices to say that this equilibrium is displaced toward the 1H-phospholes; however, since 2H-phospholes are far more reactive than 1H-phospholes, the reagents "see" only the 2H isomers. The chemistry of these species[32] is summarized in Scheme III. The dimerization[29-31] and the reaction with alkenes[33] yielded some useful information.

The structure of the 3,4-dimethyl-2H-phosphole dimer was established by X-ray analysis.[30] It shows long and weak P–P and C–C connecting bonds. The former dienophilic unit is in the endo position. Upon heating, the dimerization is reversible and the kinetic endo dimer is transformed into the thermodynamic exo dimer.[31] All these data are strictly analogous to those concerning the dimerization of cyclopentadiene. This is a strong argument in favor of a concerted [4 + 2] cycloaddition. The endo preference, in particular, can be associated with secondary favorable overlaps between the HOMO and LUMO lobes at the nonreacting sp^2 carbons in the forming dimer. Moreover, the exclusive formation of the P–P dimer can be rationalized easily if we assume that the reaction is under frontier orbital control. Indeed, both the HOMO and the LUMO are probably highly localized at phosphorus although no precise calculation has been performed until now.[34]

The reaction of 2H-phospholes with cis- and trans-1,2-disubstituted-alkenes[33] allowed us to deepen our insight. With the cis-alkenes, the monitoring of the [4 + 2] cycloaddition by ^{31}P NMR initially showed the exclusive formation of the cis adducts. However, on further heating, the stereochemistry was lost and the thermodynamically more stable trans adducts started

(25) Appel, R.; Knoch, F.; Zimmermann, R. *Chem. Ber.* **1985**, *118*, 814.
(26) Casser, C. Dissertation, University of Bonn, 1985, cited in ref 2. Althoff, U.; Grobe, J.; Le Van, D.; Würthwein, E.-U. *Z. Naturforsch.* **1989**, *44b*, 175.
(27) Appel, R.; Menzel, J.; Knoch, F. *Chem. Ber.* **1985**, *118*, 4068.
(28) Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.
(29) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 511.
(30) de Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1272.
(31) Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871.

(32) 2H-Phospholes can be stabilized either by complexation or by bulky substituents: Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. Zurmühlen, F.; Regitz, M. *J. Organomet. Chem.* **1987**, *332*, C1.
(33) Le Goff, P.; Mathey, F.; Ricard, L. *J. Org. Chem.* **1989**, *54*, 4754.
(34) A similar explanation has been provided for the formation of 1,2-diphosphetanes by dimerization of some phosphaalkenes: Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1982**, 569.

to appear. Addition of tolan (PhC≡CPh) to the mixture caused the quantitative formation of the corresponding 1-phosphanorbornadiene. Our explanation is that the initial [4 + 2] concerted cycloaddition is followed by a nonconcerted cycloreversion beginning with the homolytic cleavage of the relatively weak P–C bond (ca. 65 kcal/mol). Scheme IV summarizes the proposed mechanism.

4π- and 6π-Electrocyclizations. The 4π-electrocyclization of 1-phosphadienes was independently discovered by Neilson[35] and ourselves[11] (eqs 13 and 14). We later found that this electrocyclization could be reversible under certain conditions[36] so that 1,2-dihydrophosphetes could be used as masked 1-phosphadienes in [4 + 2] cycloaddition reactions with alkenes, alkynes, and carbonyl compounds (Scheme V).

(13)

(14)
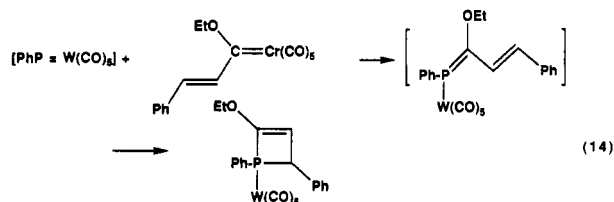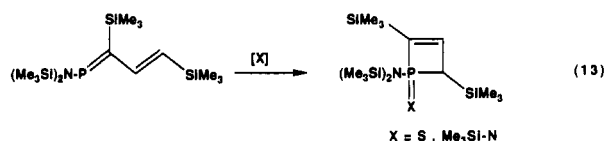
The likelihood of a nonconcerted mechanism being at work in the reaction of dimethyl maleate with a free 1,2-dihydrophosphete[37] should be pointed out here. A zwitterionic compound resulting from the nucleophilic attack of the lone pair at phosphorus onto the C=C double bond is probably initially formed, and then the cleavage of the ring can proceed. The masking of the lone pair by complexation thus plays an indirect but critical role in our experiments.[36]

We have studied the stereochemistry of this reversible cyclization of 1-phosphadiene P complexes. In order to establish the stereochemistry of these elusive species, we have trapped them by η⁴-complexation with the Fe(CO)₃ complexing group[38] (eq 15). On the other hand, we have also allowed the cyclization to proceed and established the stereochemistry of the resulting 1,2-dihydrophosphete[38] (eq 16). From these two experiments, it appeared that the cyclization is conrotatory, as expected from the Woodward–Hoffmann rules.

(15)

(16)
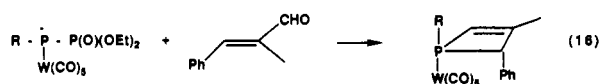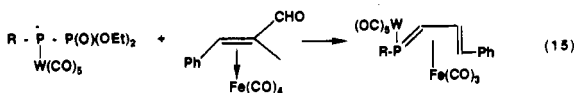
We have established a similar result for 1,4-diphosphadienes. Except when they are substituted by very bulky groups,[39] 1,4-diphosphadienes tend to cyclize

to give the corresponding 1,2-dihydro-1,2-diphosphetes.[40] We have shown, on the P,P-dicomplexed species, that this cyclization could be reversible and have trapped the resulting open-chain dienes by [4 + 2] cycloaddition with various reagents.[41] From the structures of the starting 1,2-dihydrophosphetes and the final [4 + 2] cycloadducts, it appeared, once again, that this cycloreversion follows the Woodward–Hoffmann rules (eq 17).

(17)
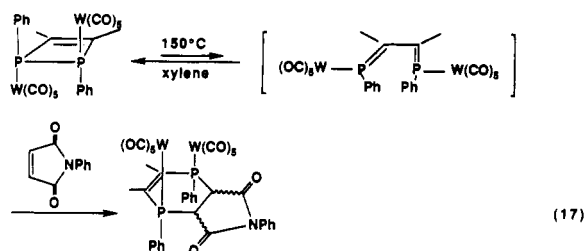
It was logical to extend this first series of data concerning the 4π-electrocyclization of 1-phosphabutadienes to the 6π-electrocyclization of 1-phosphahexatrienes. The necessary backbone was obtained via the phosphinidene–carbene coupling already used for the synthesis of 1-phosphadienes according to eq 14. As expected, the electrocyclization proceeds instantly, but we have no data concerning its stereochemistry at the moment[42] (eq 18).

(18)
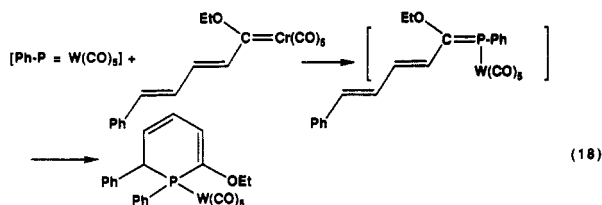
[1,5] Sigmatropic Shifts. Phospholes have a pyramidal ground state because the aromatic stabilization of the transient planar state is insufficient to overcome the large pyramidal inversion barrier of tricoordinated phosphorus.[43] As a result, phospholes have a low aromaticity and resemble cyclopentadiene more than pyrrole. A significant overlap exists between the σ-orbital corresponding to the P–R exocyclic bond and the π-system. [1,5] sigmatropic shifts of the P–R substituents thus become relatively easy. They lead to 2H- and 3H-phospholes (eq 19). From our data,[28-31,44,45] we

(19)
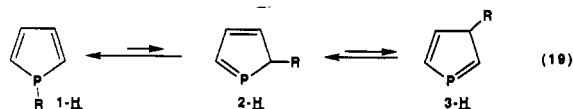
derive the following order of migrating ability for the R substituents: H > SiMe₃ > PR₂ > sp carbon > sp² carbon > sp³ carbon. 2,5- and 3,4-substitutions of the phosphole ring significantly displace the equilibria against the formation of 2H- and 3H-phospholes. As expected for a concerted shift, the same atom remains grafted to the phospholyl ring during the entire reaction

(35) Boyd, B. A.; Thoma, R. J.; Neilson, R. H. *Tetrahedron Lett.* **1987**, 28, 6121.

(36) Tran Huy, N. H.; Mathey, F. *Tetrahedron Lett.* **1988**, 29, 3077.

(37) Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1649.

(38) Marinetti, A.; Ricard, L.; Mathey, F. *Organometallics* **1990**, 9, 788.

(39) Appel, R.; Hünerbein, J.; Siabalis, N. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 779.

(40) Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, 21, 1923.

(41) Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, 9, 1363.

(42) Tran Huy, N. H.; Mathey, F.; Ricard, L. *Tetrahedron Lett.* **1988**, 29, 4289.

(43) This problem is discussed in depth in the following: Mathey, F. *Chem. Rev.* **1988**, 88, 429.

(44) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, 5, 1413.

(45) Bevierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.*, in press.

pathway. When the substituent is a substituted aryl or heteroaryl group, this means that the substitution scheme of the group is preserved during the migration. Two examples, eqs 20[46] and 21,[45] illustrate that point.


(20)

(21)
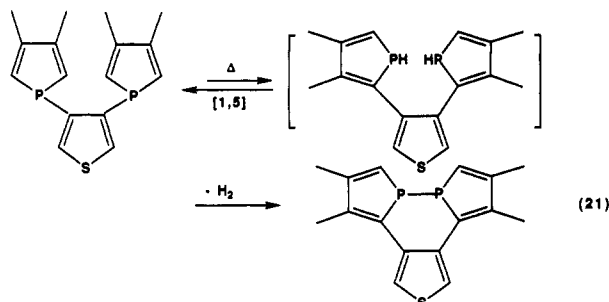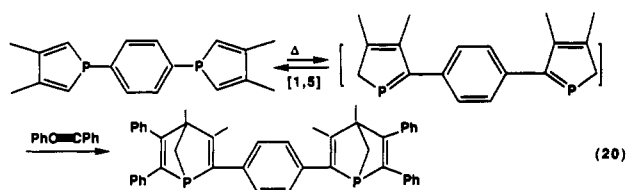
1,1'-Biphospholyls represent a special case. Both rings can migrate around each other to create original structures as shown in eqs 22[45] and 23.[47,48]


(22)

(23)

Ar = Ph ,[47] [48]
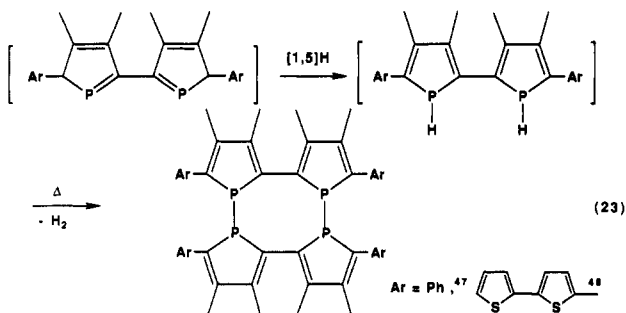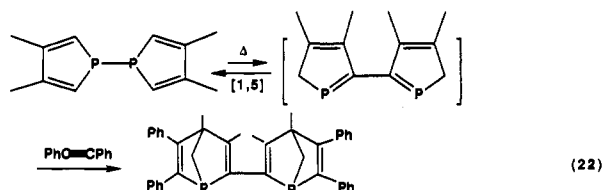
Together with the data of Appel on the [3,3] phospha-Cope rearrangements,[2] these results fully establish that it is possible to substitute carbon by phosphorus in the backbone of any unsaturated hydrocarbon undergoing a concerted sigmatropic reorganization.

Phosphaallylic Chemistry

As C=C double bonds, P=C double bonds activate the α-CH bonds. We have gathered several preliminary data showing that it is possible to develop what could be called "phosphaallylic" chemistry. For example, a striking result was obtained while the chemistry of secondary vinylphosphines was being studied. In some cases, a spontaneous isomerization takes place, giving phosphaalkenes[49] (eq 24). This result demonstrates that a phosphaalkene can be thermodynamically more


(24)

Mes = 2,4,6-Me$_3$C$_6$H$_4$
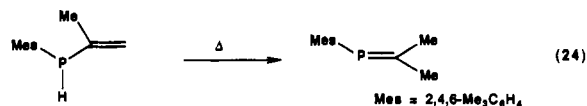
stable than the isomeric 3-coordinate phosphorus compound. In the same vein, Appel[2] has demonstrated that it is possible to shift the [3,3] phospha-Cope equilibria toward the dicoordinate phosphorus compounds at the expense of the tricoordinate species by using bulky substituents at phosphorus. At the moment, we know that this isomerization does not involve radicals as we had at first thought (neither light nor AIBN influenced the speed of the reaction) and that the speed of the conversion decreases with the concentration of the secondary vinylphosphine. A self-ionization bimolecular mechanism is, at the moment, the most likely explanation. It is interesting to note that the reverse reaction has been shown to occur on selected phosphaalkene complexes[16] (eq 25).

(25)

DBO = Diazabicyclo[2.2.2]-octane
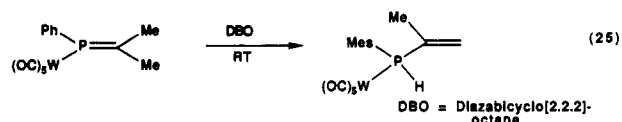
In some instances, the secondary vinylphosphine complex reacts with the P=C double bond to give a biphosphine complex[50] (eq 26). All of this chemistry very likely involves either free or coordinated phosphaallylic anions. While these anions have not been

(26)
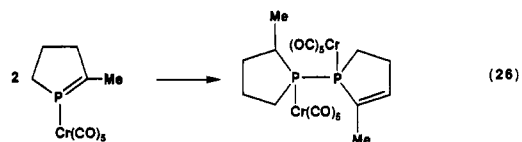
characterized as such, they have been stabilized as η^3-complexes with various transition metals.[51] The analogy with allylic chemistry is completed with a first example of S_N2' substitution[52] (eq 27).

(27)
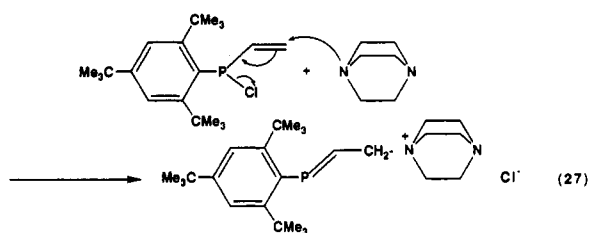
Conclusion

As can be seen from the data collected in this Account and in the review of Appel,[2] it is clear that the analogy between the chemistry of P=C and C=C double bonds is very deep. Of course, at the moment, several mechanistic details concerning the reactions of phosphaalkenes or their complexes have not yet been investigated. Nevertheless, on the basis of what we already know, we

(46) Mercier, F.; Mathey, F. *Heteroat. Chem.* **1990**, *1*, 187.

(47) Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077.

(48) Bevierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 655.

(49) Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 2397.

(50) Marinetti, A.; Le Floch, P.; Mathey, F. *Organometallics* **1991**, *10*, 1190.

(51) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955. Hugel-Le Goff, C.; Mercier, F.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1989**, *363*, 325. Mercier, F.; Mathey, F. *Organometallics* **1990**, *9*, 863. Mercier, F.; Hugel-Le Goff, C.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1990**, *389*, 389. Lang, H.; Leise, M. *J. Organomet. Chem.* **1990**, *393*, C17. Weber, L.; Lücke, E.; Müller, A.; Bögge, H. Z. *Anorg. Allg. Chem.* **1990**, *583*, 91.

(52) Mercier, F.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 5269.

can forecast a great extension for this new chemistry. In itself, the possibility of transposing the catalytic transformations of alkenes to phosphaalkenes represents a wide field of investigation: hydroformylation, metathesis, polymerization, ... It seems that the diagonal analogy between carbon and phosphorus is more effective than the vertical analogy between carbon and silicon.[53]

(53) Some aspects of this carbon–silicon analogy are discussed in a very recent review: Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 902.