Carbene-Like Chemistry of Phosphinidene Complexes − Reactions, Applications, and Mechanistic Insights

Koop Lammertsma*[a] and Mark J. M. Vlaar[a]

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The versatile carbene-like chemistry of electrophilic phosphinidene complexes ($R–P=ML_n$) with C=C, C≡C, C=X, and C≡X (X = N, O, S, Si, and P) bonds and aromatics is discussed.

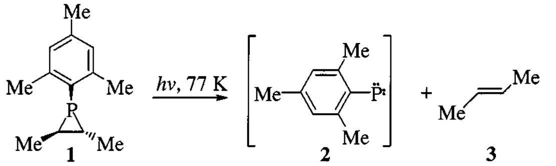
1. Introduction

Phosphinidenes (short: $R-\ddot{P}:$)[1] are the phosphorus analogues of carbenes ($R_2C:$). Because phosphorus is slightly more electropositive than carbon, these low-valent organophosphorus compounds resemble carbenes.[2] When stabilized by a single transition metal group ($RP=ML_n$), they become remarkably versatile reagents. Like the carbene complexes ($R_2C=ML_n$), they are either electrophilic (Fischer-type) or nucleophilic (Schrock-type). Phosphinidenes have been the topic of earlier reviews.[3]

In this Microreview we focus on the rapidly maturing chemistry of the electrophilic phosphinidene complexes. These building blocks are generated in situ. Whereas they have yet to be detected by spectroscopic means, their existence may be inferred from trapping experiments affording a broad array of new compounds. This Microreview is not intended to cover all of these; it aims rather to show their synthetic potential by selected examples and mechanisms, with some emphasis on those produced in our own laboratory. To put the topic into context, we should briefly address the matter of the "free" and the nucleophilic phosphinidenes.

2. Free Phosphinidenes [R−P]

Despite many attempts to detect them, "free" phosphinidenes remained elusive until 1994, when Gaspar and collaborators identified mesitylphosphinidene (**2**) by ESR spectroscopy after irradiation of the mesitylphosphirane **1** at low temperatures.[4] Previous efforts such as the thermal decomposition of cyclopolyphosphanes $(R-P)_n$ and the reduction of dihalophosphanes by alkali metals[5] had failed, but the photolysis of phospholenes,[6] phosphiranes,[6] phosphorus bis(azides),[7] and diphosphenes[8] has been more convincing.



1 **2** **3**

This limited success in generating the free species is undoubtedly due to its triplet ground state, which makes it unconducive to synthetic applications. For example, the singlet−triplet energy separation for the phenyl derivative

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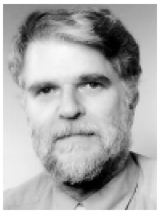
[a] Department of Organic and Inorganic Chemistry, Faculty of Sciences, Vrije Universiteit,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
Fax: (internat.) + 31-20/444-7488
E-mail: lammert@chem.vu.nl



Koop Lammertsma was born in Makkum, The Netherlands, in 1949 and was educated at the Universities of Groningen (M.Sc. 1974) and Amsterdam (Ph.D. 1979). Postdoctoral work with F. Sondheimer (London), P. v. R. Schleyer (Erlangen-Nürnberg), and G. A. Olah (USC) exposed him to physical-organic and computational chemistry. In 1983 he moved to the University of Alabama at Birmingham, USA, becoming Full Professor in 1992. In the same year he served as program officer in the chemistry program of the NSF. In 1996 he moved to the Free University, Amsterdam, The Netherlands, where he has expanded his interest in organophosphorus chemistry.

Mark Vlaar was born in 1973 in Alkmaar, The Netherlands. He obtained his M.Sc. at the University of Amsterdam in 1997 and his Ph.D. at the Free University under the guidance of Koop Lammertsma in 2001.

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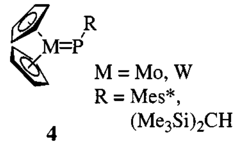
has been estimated at around 24 kcal/mol.[9] The presence of amino and phosphido groups reduces this energy difference and may even favor a singlet ground state,[10] but such species have yet to be developed. So far, only one phosphanylphosphinidene, generated from a phosphanylidene phosphorane, has been reported, but its applicability has yet to be studied.[11]

3. Terminal Phosphinidene Complexes [R−P=M]

Phosphinidenes prefer a singlet ground state when stabilized by a transition metal group. Ab initio studies on $HP=Cr(CO)_5$ in the mid 1980s were ambiguous about its electronic properties,[12] but recent investigations favor a singlet ground state over a triplet one for $HP=M(CO)_5$ (M = Cr, Mo, W) by as much as 10 kcal/mol for the phenyl derivative [M = W].[13] The singlet−triplet energy difference increases with increasing π-donation from the substituent on the phosphorus atom. Whereas the P−M bond is often depicted as dative, it possesses significant π-bonding character.[13a]

Stabilization of the phosphinidene by a transition metal group can give rise either to electrophilic (Fischer-type) or to nucleophilic (Schrock-type) properties, depending largely on the ancillary ligands on the metal atom.[14] Several well-characterized nucleophilic phosphinidene complexes have been reported, but surprisingly little of their chemical behavior has been explored.[15] The first Schrock-type phosphinidenes **4** were synthesized − as *stable* compounds − in 1987 by Lappert's group,[16] who even reported an X-ray structure for $Cp_2Mo=PMes^*$. A few years later, Niecke et al.[17] generated similar amino-substituted derivatives. In the years since, several other *stable* phosphinidene complexes have been obtained with molybdenum,[18] tantalum,[19] tungsten,[20] uranium,[21] and zirconium[22] metal centers. The ^{31}P NMR spectra of these complexes showed resonances at extremely low field, with chemical shifts of up to $\delta = 1007.5$ for an $MoCp(CO)_3$ complex.[18] Most of these species have hardly been investigated, except for the (phosphinidene)zirconium complex **5**. The more noteworthy reactions that Stefan et al.[2d] explored for **5** are those with carbonyl groups to give phosphaalkenes and those with vicinal dichlorides and epoxides to give phosphiranes.



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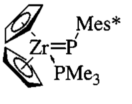

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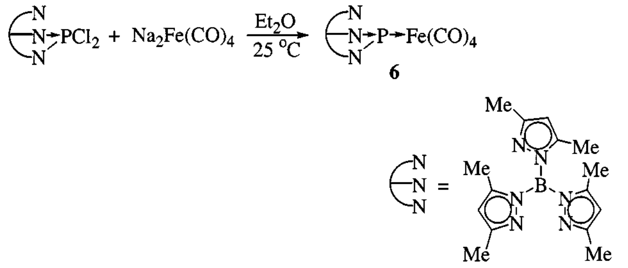
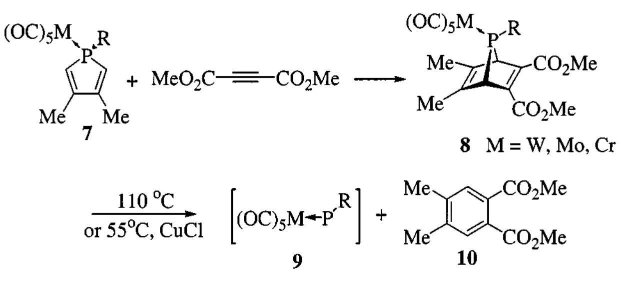
4. Generation of Electrophilic Phosphinidene Complexes

All known electrophilic phosphinidene complexes have transition metal groups bearing carbonyl ligands only, except for the cationic $[Cp^*(Co)_2Fe = P^iPr_2]^+$.[23] So far, only one (**6**) has been isolated;[24] Cowley et al. reported it to have a P−C bond length of 2.274(2) Å and two nearly equivalent P−N bonds of 1.777(7) Å and 1.764(7) Å, which suggests that the phosphorus center is intramolecularly stabilized by Lewis base coordination. Apparently, it does not represent an unencumbered species.



"Free" electrophilic phosphinidene complexes have only been inferred from trapping reactions. Several approaches to these transient species have been followed. Marinetti and Mathey[25] were the first to report a stable precursor in 1982, having found that the hitherto unknown 7-phosphanorbornadiene is effectively stabilized by $M(CO)_5$ (M = Cr, Mo, W) groups. In the same year, they trapped the transient phosphinidene complexes **9** as phosphiranes and phosphirenes by degradation of precursor **8** at ca. 110 °C in the presence of olefins and alkynes, respectively.[26] The temperature could be reduced to ca. 55 °C if CuCl was used as a catalyst, with elimination of the aromatic residue **10** considered to be the driving force for the formation of **9**. 7-Phosphanorbornadiene complexes with a large variety of substituents at the phosphorus atom are accessible.[27] Only those with bulky groups or NR_2 substituents are difficult to access, a fact that has its origin in the sluggish Diels−Alder reaction producing **8**.



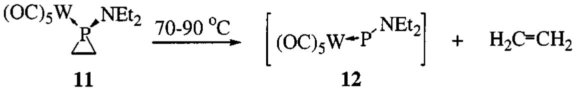
Besides these trapping products, the formation of transient electrophilic phosphinidene complexes is supported by the following observations:

(1) Cheletropic elimination of 7-phosphanorbornadiene complex **8** in the presence of various trapping reagents is a first order process that depends only on the concentration of the precursor and not on the concentration and nature of the trapping substrate.[28]

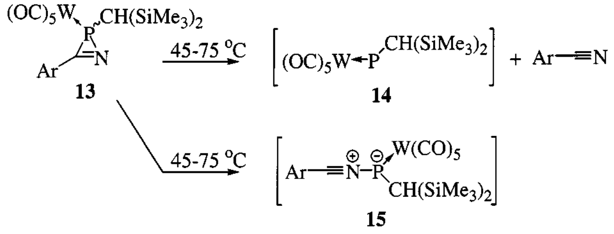
(2) 1,2-Addition to *Z*- and *E*-olefins proceeds with complete retention of configuration, suggesting a concerted reaction of a carbene-like singlet species.[29]

(3) Small and negative Hammett reaction constants of −0.76, −0.60, and −0.55 for additions to styrenes of $PhPW(CO)_5$,[30] $MePW(CO)_5$,[31] and $MeOPW(CO)_5$,[32] respectively, corroborate their electrophilic nature.

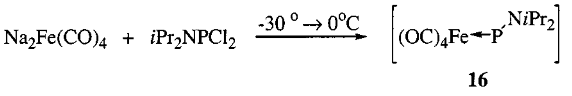
Amino-substituted phosphinidene complexes **12** are accessible through thermal decomposition of amino-phosphiranes **11**.[33] Unfortunately, the synthesis of these precursors is laborious and they have therefore not found wide applicability. Phosphirane complexes can be applied to (re)generate phosphinidenes, but higher temperatures are required, making them much less desirable precursors than the 7-phosphanorbornadienes.[28,34,35]



Streubel's group[36] developed a different route to generate an amino-substituted phosphinidene complex (**14**) by thermally cleaving the azaphosphirene ring **13**. Reactions that successfully trapped the phosphinidene, however, also showed that transient nitrilium phosphane ylides **15** can be formed as well.[37]



More recently, Lammertsma's group[38] has developed a rather different route to amino-substituted phosphinidenes, based on earlier work by King on P/Fe clusters.[39] The method relies on condensation of an aminodichlorophosphane with $Na_2Fe(CO)_4$ (Collman's reagent). Complexed phosphinidene **16** is generated below ambient temperatures and can be trapped with alkynes and alkenes.

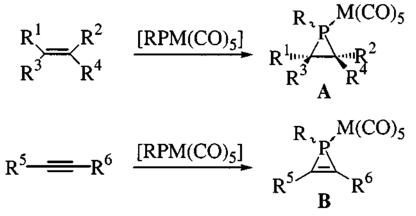


5. Reactions of Electrophilic Phosphinidene Complexes

The emphasis throughout the remainder of this Microreview is on the most widely employed phosphinidenes, those generated from $W(CO)_5$ complexed 7-phosphanorbornadienes. We concentrate on cycloadditions to π-bonds, apparent insertions into σ-bonds, and P-ylides formed from addition to lone pairs. These reactions are reviewed by a functional group approach that takes in C=C, C≡C, C=X, and C≡X bonds.

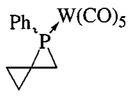
5.1 Reaction with C=C and C≡C Bonds

$R-P=M(CO)_5$ (**9**), generated in situ, reacts with olefins to form phosphiranes **A**.[29] Likewise, its 1,2-addition with acetylenes yields 1*H*-phosphirenes **B**.[26] Mathey[29,33] has shown that $R-P=W(CO)_5$ in some cases transfers from a phosphirane to an acetylenic bond to give a phosphirene. Apparently, the unsaturated three-membered ring is thermodynamically favored over the saturated one. In this context we note that **9** is a potent synthon, as illustrated by its reaction with unsubstituted ethylene.[40] The 21.3 kcal·mol^{-1} strain energy for the parent uncomplexed phosphirane C_2PH_5, calculated by the G2(MP2) ab initio method, is – as expected – smaller than the 28.0 kcal·mol^{-1} for cyclopropane, calculated at the same level of theory.[41]



Olefins

A large number of phosphiranes **A** has already been reported to result from the 1,2-addition to C=C bonds. There appears to be little or no difference in selectivity between simple olefins such as 1- and 2-butene, isobutylene, and tri- and tetramethylethylene,[42] but some discrimination in reactivity exists between differently sized methylenecycloalkanes.[40] Addition of $Ph-P=W(CO)_5$ to exocyclic C=C bonds has also been recognized as a convenient method for the synthesis of more highly strained spirofused polycycles such as the complexed phospaspiropentane **19**[40] and the phospa[3]triangulane **20**.[41] Strain energies, computed at G3(MP2) for the uncomplexed parent systems, give an excess strain per spirocarbon of 5.3 kcal·mol^{-1}.[41] This is less than the 8.6 kcal·mol^{-1} relating to the corresponding hydrocarbons, [*n*]triangulanes,[43] since phosphirane is less strained than cyclopropane.



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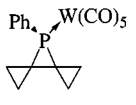

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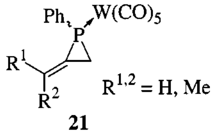

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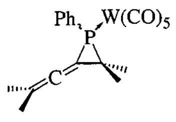

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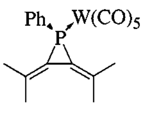

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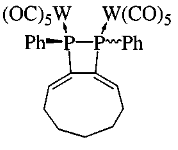

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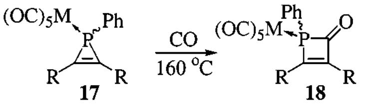
Phosphiranes with exocyclic C=C bonds have also been reported to result from the addition of $PhPW(CO)_5$ to unsaturated hydrocarbons. Methylenephosphiranes **21** are obtained from allene and its methylated derivatives,[44] whereas addition to cumulenes results in addition to a terminal C=C bond to give **22**, which subsequently rearranges to a phospha[3]radialene **23**.[45] This reaction has similarly been reported for a less highly substituted cyclic cumulene, in which case an additional Ph−P=W(CO)$_5$ inserts into the C−P bond of the three-membered ring to give a mixture of *syn*- and *anti*-phospha[4]radialenes **24**.[45]

Metal Decomplexation

Whereas the transition metal group is crucial in stabilizing the phosphinidenes, it is less important for the 1,2 adducts. Consequently, the transition metal group can be removed to give the less stable, "free" three-membered ring structures. Several approaches have been reported, although none of them is uniformly applicable.

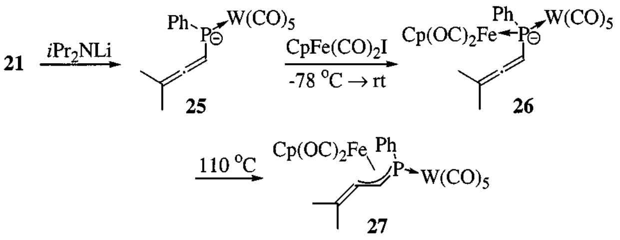
The W(CO)$_5$ complexed phosphirenes **B** can be decomplexed by selective oxidation of the tungsten atom with iodine to weaken the W−P bond, followed by addition of *N*-methylimidazole to displace the phosphirene.[46] So far, only one phosphirane (**21**), containing one sp^2-hybridized ring carbon atom, has been reported to have been liberated from the W(CO)$_5$ group by this method.[44] Another method to remove the transition metal group uses exchange of the phosphira(e)ne ring for a bidentate phosphorus ligand.[47] Removal of M(CO)$_5$ by exchange of a phosphirene **17** for carbon monoxide proved unsuccessful, as the CO inserted into the P−C bond to give the phosphorus analogue of an unsaturated β-lactam **18**.[48] Such a 1,2-dihydro-1-phosphet-2-one complex also results from the reaction between diethylamine and the phosphirene obtained from the 1,2-addition of (Me$_3$Si)$_2$HC−P=W(CO)$_5$ to dimethyl acetylenedicarboxylate.[49]



M = W, Mo, Cr; R = Ph, Et

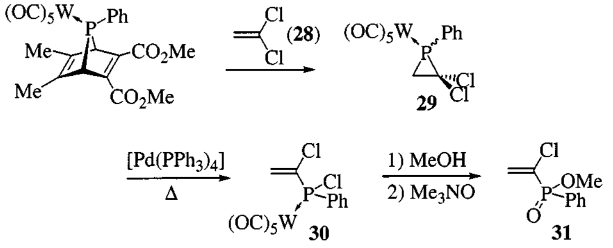
Ring-Opening Reactions

Complex **21** (R^{1,2} = Me) is susceptible to ring-opening reactions. For example, metallation with lithium diisopropylamide (LDA) gives allenylphosphide ion **25**, which, on complexation with CpFe(CO)$_2$I (**26**) and subsequent heating, results in (1,2,3-η)-1-phosphabutadienyl complex **27**.[50] Likewise, 1-phosphapentadienyl complexes have been obtained from treatment of vinylphosphiranes with LDA with subsequent trapping of the resulting 1-phosphapentadienide complex with methyl iodide, HCl, or CpFe(CO)$_2$I.[51] Ring-opening of **21** by heating with Ru$_3$(CO)$_{12}$ was shown to give the phosphorus analogue of a trimethylenemethane complex.[52] Examples of ring-opening reactions for substituted phosphiranes are discussed in the next section.

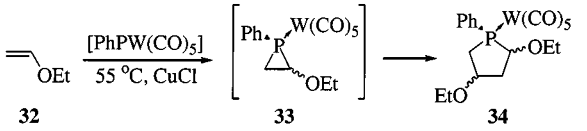


Olefins and Alkynes with Electron-Donating Substituents

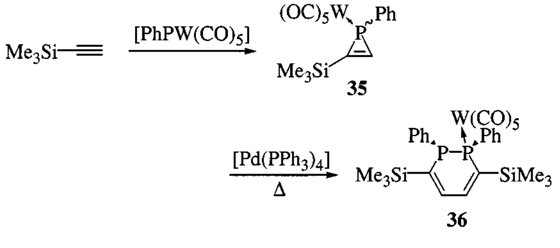
2-Halophosphiranes **29** are formed from the addition of complexed phosphinidenes to haloalkenes **28**. Thermal or Pd-catalyzed ring-opening proceeds with retention of the alkene stereochemistry.[53] The P−Cl substituent in the resulting vinyl−phosphorus compounds **30** is readily replaced by a methoxy group. The complexing metal atom can be removed by oxidation with trimethylamine *N*-oxide to give **31**.



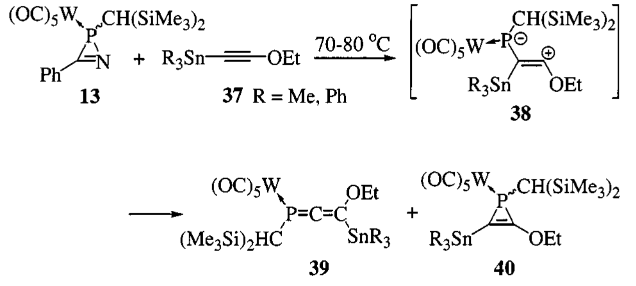
Treatment of PhPW(CO)$_5$ with ethyl vinyl ether (**32**) presumably results in the transient phosphirane **33**, which reacts with a second equivalent of olefin to give the formal [1+2+2] adduct, phospholane **34**.[29] Similarly, treatment with electron-rich alkynes yields five-membered ring phospholes.[54] In this case, when the phosphinidene complex with the bulky CH(SiMe$_3$)$_2$ substituent was used, it was possible to isolate the intermediate 1,2 adduct.[55]



Heating of phosphirene complexes in the presence of terminal acetylenes and Pd(PPh$_3$)$_4$ as catalyst also gives complexed phospholes,[56] but in the absence of added acetylene the single *C*-substituted phosphirene **35** undergoes an Ni- or Pd-catalyzed *head*-to-*head* dimerization, with loss of a W(CO)$_5$ group, to yield the six-membered 1,2-dihydro-1,2-diphosphinines **36**.[57] Azaphosphirene complex **13** dimerizes under similar conditions in a *head*-to-*tail* fashion.[58]

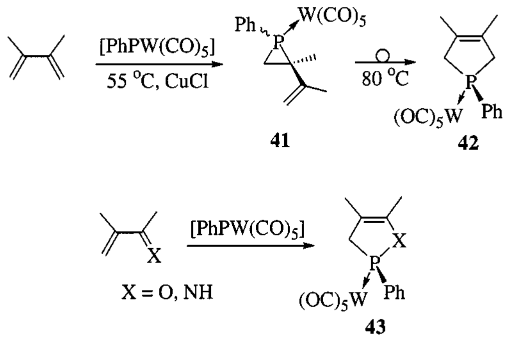


Treatment of complexed phosphinidenes generated from **13** with 1-ethoxy-2-(triorganostannyl)acetylene (**37**) follows a different pathway. Phosphaallene derivative **39**, obtained in addition to the expected 1,2 adduct **40**, is believed to result from rearrangement of the intermediate zwitterion **38**.[59]

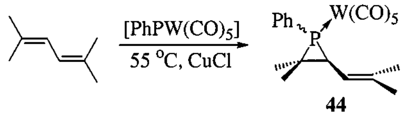


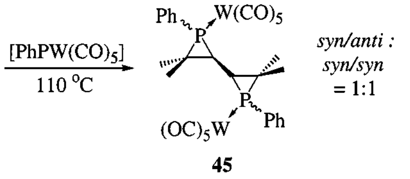
5.2 Reaction with Conjugated C=C and C≡C Bonds

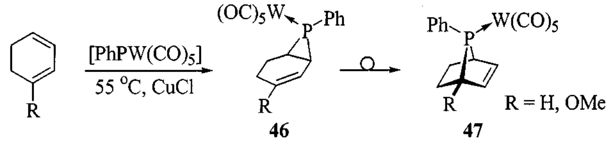
Mathey and Marinetti[29] showed that $PhPW(CO)_5$ reacts with 2,3-dimethylbutadiene to give 1,2-addition product **41**, which upon heating rearranges to give the five-membered ring phospholene **42**. Likewise, the phosphinidene reacts with α,β-unsaturated ketones[29] and 1-azadienes[60] to give oxa- and azaphospholenes **43**, respectively, although no intermediate products could be detected.



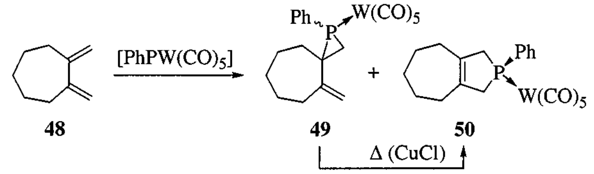
Lammertsma et al.[61] found that treatment with 1,5-dimethyl-2,4-hexadiene also resulted in vinylphosphiranes **44**, but that these did not rearrange. Instead a second 1,2-addition occurred with additional phosphinidene to give 2,2′-biphosphiranes **45**. They also reported that 1,3-cyclohexadienes yielded vinylphosphiranes **46**, which rearranged by a [1,3]-sigmatropic shift to phospholenes **47** with complete inversion at the phosphorus atom,[62] suggesting a concerted process, whereas the 1,2 adducts of both smaller and larger cyclic 1,3-dienes only epimerized at the phosphorus center, ultimately resulting in the formation of only the *anti* isomer.[63]



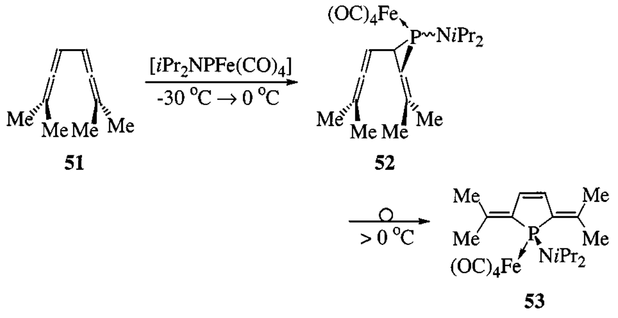




Treatment of $PhPW(CO)_5$ with *cisoid* dienes such as **48** gives the corresponding phospholenes **50** by direct 1,4-addition.[64] However, this route, similarly to the reaction of dihalocarbenes, is in competition with the 1,2-addition/rearrangement pathway. A kinetic study suggested a biradicaloid mechanism for the thermal rearrangement of the 1,2-addition product **49** to **50** and a concerted pathway for the CuCl-catalyzed process.[65]

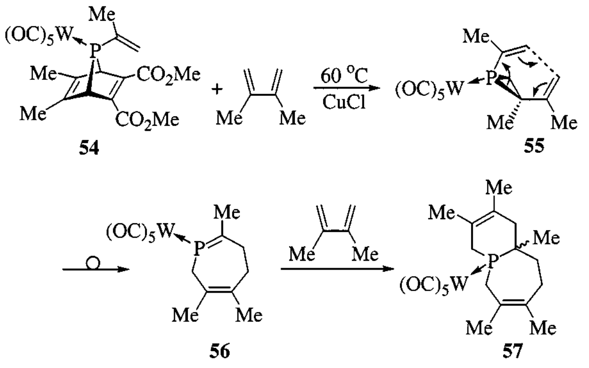


A similar reactivity pattern has been reported for the reaction between an iron-complexed phosphinidene and diallene **51**.[38a] Ab initio calculations showed that reaction at a conjugated double bond is favored by 6 kcal·mol^{-1} over reaction at a terminal one. The rearrangement of the initially formed 1,2 adduct **52** to the conjugated phospholene **53** is exothermic by 40 kcal·mol^{-1}.

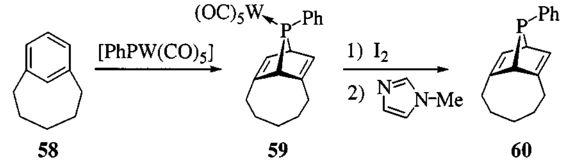


A rather different pathway is followed when a vinyl-substituted phosphinidene complex is treated with dienes. For example, thermal decomposition of 7-phosphanorbornadiene complex **54** in the presence of excess 2,3-dimethylbutadiene yields **57**. The formation of this bicyclic product was explained as resulting from a [3,3]-phospha-Cope rearrangement of the initially formed 1,2 adduct **55**, followed by a

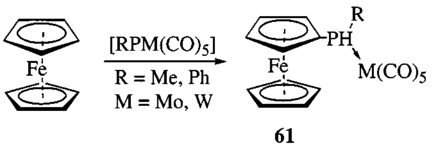
Diels−Alder reaction between the P=C bond of **56** and additional diene.[66]



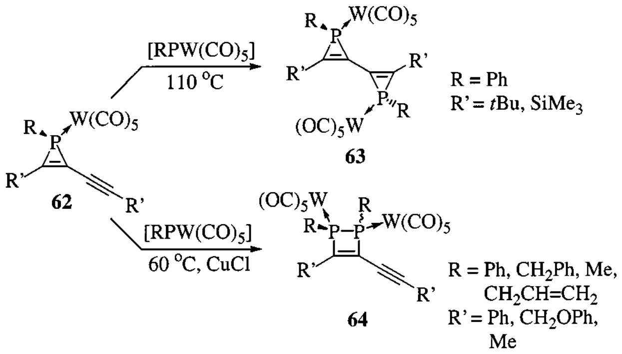
The first and so far only reported addition of a complexed phosphinidene to an aromatic compound is the reaction between PhPW(CO)$_5$ and [5]metacyclophane (**58**) to give the genuine 1,4-addition product **59**.[67] Decomplexation of the W(CO)$_5$ group by I$_2$ oxidation and *N*-methylimidazole ligand exchange resulted in the unique, moderately stable, free 7λ^3-phosphanorbornadiene **60**.[68] The unfavorable thermodynamics for retro-addition of PhP to restore the highly strained **58** explain the relative stability of this phosphanorbornadiene.

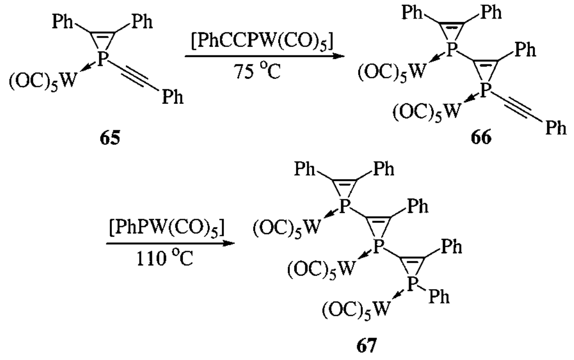


The only other reported reaction between a terminal phosphinidene complex and an aromatic compound is the C−H bond insertion of one of the electron-rich cyclopentadienyl rings of ferrocene to give **61**. Its formation illustrates the electrophilicity of the phosphinidene complex.[69]



The susceptibility of conjugated diynes toward multiple additions appears to be dependent on the reaction conditions. Catenated biphosphirene **63** is formed from the initial 1,2 adduct **62** when RPW(CO)$_5$ is generated at 110 °C,[70] while C−P bond insertion occurs to give 1,2-diphosphete **64** at 60 °C when CuCl is used as catalyst,[71] although the nature of the substituents plays a role as well. Tran Huy et al.[72] reported a different approach towards polyphosphirenes involving catenation of the rings through C−P bonds. For this they used a phosphinidene complex bearing an alkyne substituent (generated in situ) to form **65** and **66**. The extended structure **67** results from addition of PhPW(CO)$_5$.

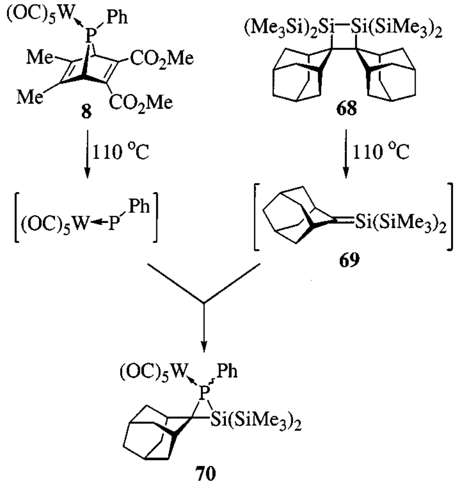




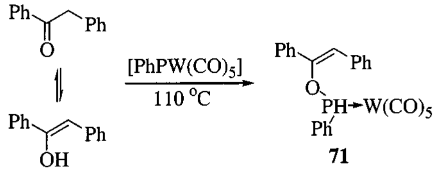
5.3 Reaction with C=X and C≡X Bonds

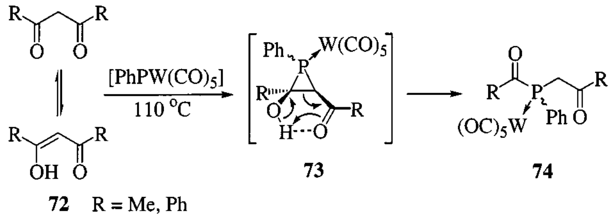
Electrophilic phosphinidene complexes react in extremely diverse ways with unsaturated bonds containing heteroatoms.

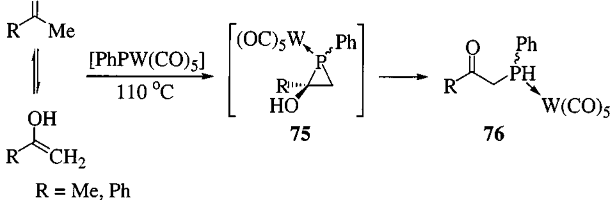
An extraordinary CPSi ring structure results from the 1,2-addition of transient PhPW(CO)$_5$ to the congested silene **69**, generated in situ. Simply heating a mixture of phosphinidene precursor **8** [M = W] and silene dimer **68** at 110 °C gives phosphasilirane **70**, for which an X-ray structure was reported.[73] The G3(MP2) strain energy for the parent phosphasilirane CH$_5$PSi of 26.5 kcal·mol^{-1} is similar to that of cyclopropane.



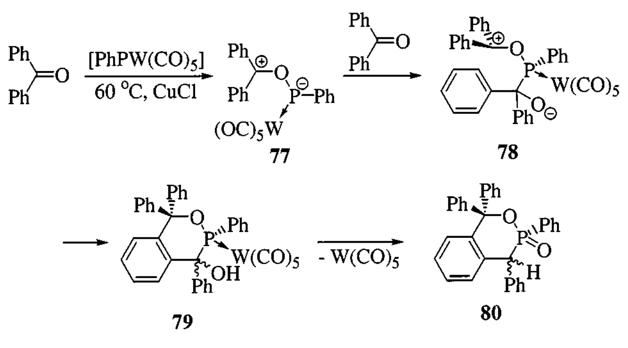
Reactions with C=O bonds must be divided into those with enolizable and those with non-enolizable ketones. Mathey and co-workers[74] showed that PhPW(CO)$_5$ reacts with enolizable ketones such as $PhCH_2C(O)Ph$, to give O−H insertion of the enol tautomer (such as **71**). No addition either to the C=C bond or to the C=O bond is observed. In contrast, the corresponding reaction with β-diketone **72** results in C−C insertion product **74**, presumably by rearrangement of the transient 1,2 adduct **73**, with no insertion into the O−H bond being observed.[74] Acetone and acetophenone instead undergo methyl C−H insertion to give **76**, which has been explained as occurring through a rearrangement of transient phosphirane **75**.

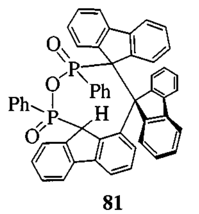






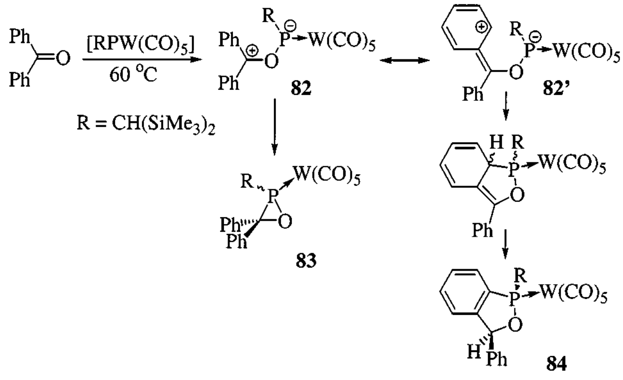
Reactions with non-enolizable ketones follow a different pathway. For example, $PhPW(CO)_5$ reacts with benzophenone at 60 °C, with CuCl as catalyst, to give bicyclic **80**. Its formation was explained as the result of initial coordination of the phosphinidene to the benzophenone oxygen atom. This P,O-ylide **77** reacts with another equivalent of benzophenone to give **78**, which, after cyclization to **79** and decomplexation, yields the final product.[75] Similarly, treatment with three equivalents of fluorenone yields the eight-membered ring structure **81**.[75]

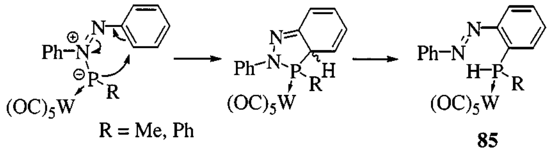




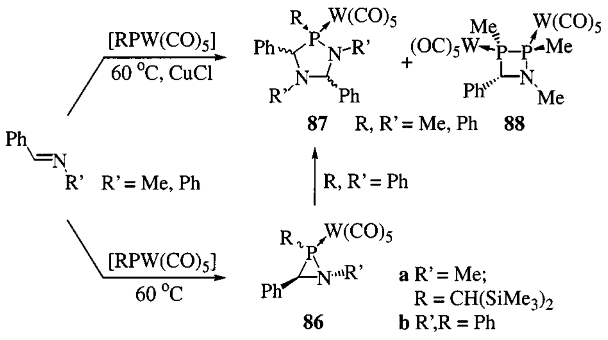
81

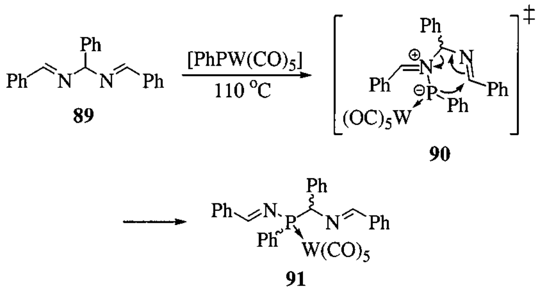
Streubel and co-workers treated benzophenone with phosphinidene **14**, bearing the bulkier $(Me_3Si)_2HC$ substituent. In this case a mixture of oxaphosphirane **83** and oxaphospholane **84** was obtained.[76] Only the 1,2 adduct was obtained with benzaldehyde.[77] Their formation was explained by initial addition of the complexed phosphinidene to the benzophenone oxygen atom. The 1,2 adduct resulted from simple ring-closure of this P,O-ylide **82**, while bond formation between the negatively charged phosphorus atom and the electropositive phenyl ring with a subsequent H-shift gave the bicyclic structure. A related process has been reported for azobenzene, but the H-shift in this case is toward the phosphorus atom, thereby giving a formal phosphinidene insertion into an aromatic *ortho*-C−H bond to furnish **85**.[78]

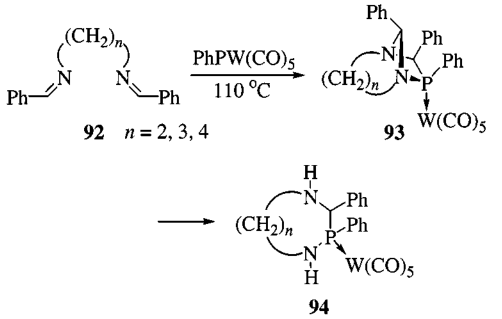




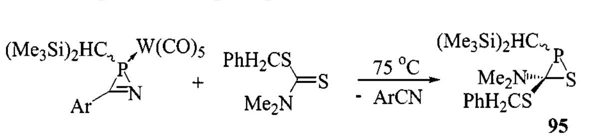
Rather different products result from reactions with C=N bonds. For example, addition of $RPM(CO)_5$ (R = Me, Ph) to simple imines results in the formal [2+2+1] cycloadduct **87**,[79] which is likely to have been generated via an azaphosphirane intermediate, as has been demonstrated for **86b**.[80] The reaction resembles the formation of phospholanes **34** from electron-rich olefins. Azaphosphirane **86a** was synthesized with the bulkier phosphinidene **14** (R = $CH(SiMe_3)_2$).[76] With $MePW(CO)_5$, a four-membered structure **88** was obtained in addition to **87**, presumably through a C−N insertion of the intermediate azaphosphirane, for which there is precedence.[81] Treatment of $PhPW(CO)_5$ with bis(imine) **89** yielded the formal C−N insertion product **91** through a 2,3-sigmatropic shift of the intermediate P,N-ylide **90**.[82] With a larger carbon spacer between the two imine groups, as in **92**, a 1,3-dipolar cycloaddition of the intermediate P,N-ylide took place to give **93**, which on hydrolysis yielded large-ring heterocycles **94**.[80]



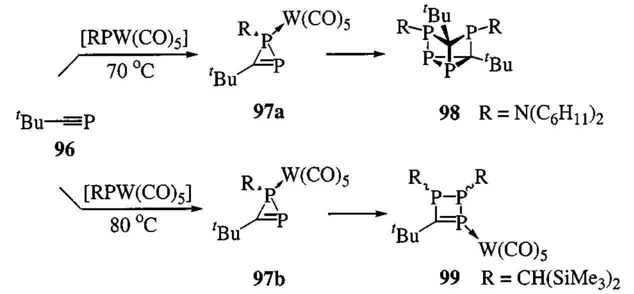




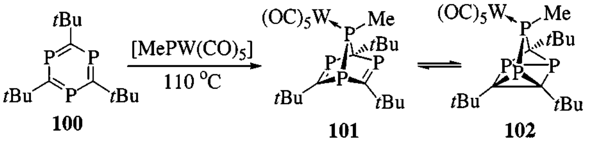
Streubel et al. reported 1,2-addition to a C=S bond to yield decomplexed thiaphosphirane **95**.[83]



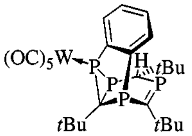
Treatment of PhPW(CO)$_5$ with a phosphaalkene (P=C) at 110 °C gives the expected 1,2-addition product, but in this case the coordinating W(CO)$_5$ group is also eliminated during the reaction.[84] Aminophosphinidene complex (C$_6$H$_{11}$)$_2$NPW(CO)$_5$ likewise adds to phosphaalkyne **96** in a 1,2-fashion, although the resulting diphosphirene **97a** could not be isolated since it slowly dimerized to form tricyclic **98**.[35] Streubel et al.[85] reported that the 1,2-dihydro-1,2,3-triphosphete complex **99** was formed from the insertion of (Me$_3$Si)$_2$CHPW(CO)$_5$ into the transient diphosphirene **97b**. They also described the formation of a stable diphosphirene complex in the case of the bulky N(SiMe$_3$)*i*Pr-substituted compound.



Treatment of MePW(CO)$_5$ with triphosphabenzene **100** resulted in a mixture of tetraphosphanorbornadiene **101**, a formal 1,4 adduct, and its corresponding quadricyclane **102** in a 1:8 mixture.[86] The two products were in thermal and photochemical equilibrium.



Use of the phenyl-substituted phosphinidene complex gives instead **103** and quadricyclane **104**.[87] The formation of **103** is remarkable and suggests an initial 1,2-addition to a C=P bond of the triphosphabenezene, followed by an intramolecular electrophilic addition of a ring phosphorus atom on the *P*-phenyl ring. Ab initio calculations indicated that the tetraphosphaquadricyclanes **102** and **104** resulted from [2+2] cycloaddition of the corresponding norbornadienes (e.g., **101**), and that these were formed through 1,3-sigmatropic shifts in the initial 1,2 adducts.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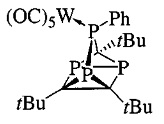
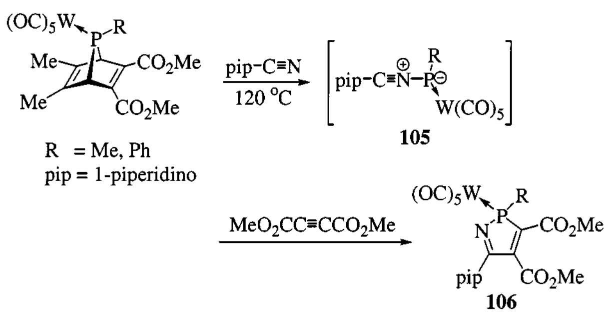
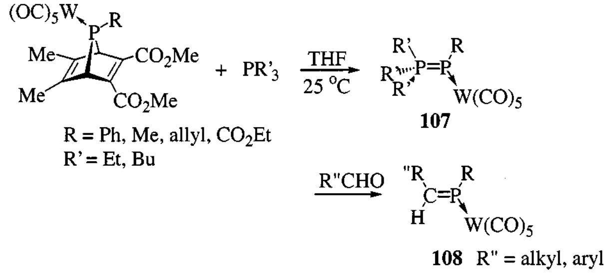
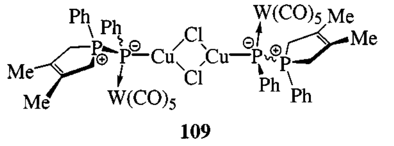

104

Insertion of complexed phosphinidenes into the O−H and N−H bonds of alcohols and amines may well proceed through initial formation of P−O or P−N ylides, respectively.[88] Theoretical calculations have shown that singlet PH does indeed coordinate to the lone pair of the heteroatom prior to insertion.[89] Treatment of complexed phosphinidenes with a mixture of 1-piperidinonitrile and dimethyl acetylenedicarboxylate (DMAD) provided indirect evidence of these Lewis acid/base adducts. Specifically, the five-membered ring structure **106** is probably formed from a [3+2] cycloaddition between the transient nitrilium phosphane ylide **105** and DMAD.[90]

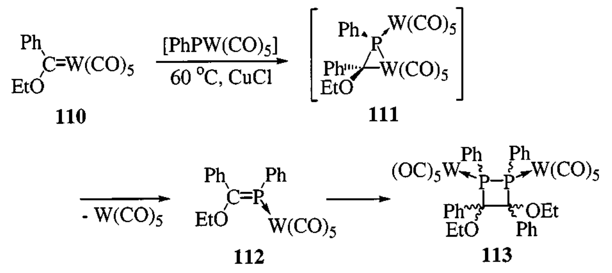


While the complexed P−N and P−O ylides remain elusive, the related P−P ylides are well known. The phosphoranylidenephosphane complex **107**, for example, formed in the reaction between a complexed phosphinidene and a phosphane, has even been characterized by an X-ray crystal structure analysis of the CO_2Et derivative. The less stable derivatives of **107** convert aldehydes into the phosphaalkenes **108** by a phospha-Wittig reaction.[91] Related P,P-ylides of phospholes and phospholenes are known. An X-ray structure has been reported for the double CuCl-bridged dimer **109**.[92]



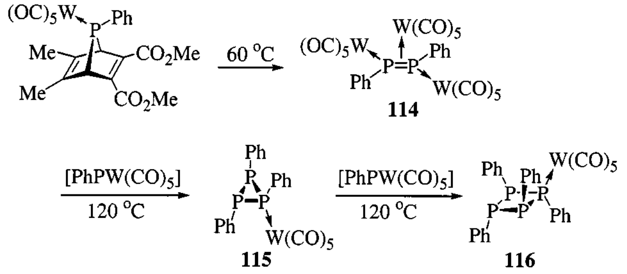


Treatment of $PhPW(CO)_5$ with carbene complex **110** yields 1,2-diphosphetane **113**, probably through a [2+2] cycloaddition between two initially formed phosphaalkenes **112**.[93,94] The P=C bond is believed to be formed by elimination of $W(CO)_5$ from the transient 1,2 adduct **111**. A three-membered PCW ring has also been obtained from the reaction with the carbyne complex $PhC{\equiv}W(CO)_2Cp$.[95]

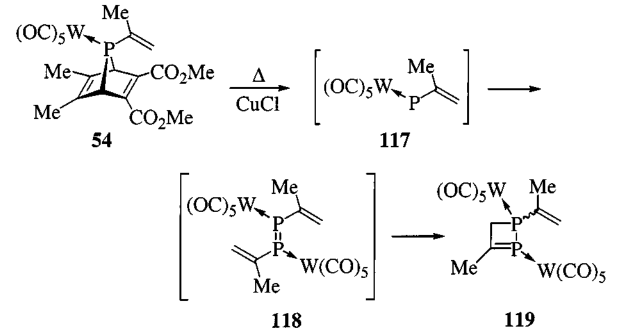


6. Self-Condensation

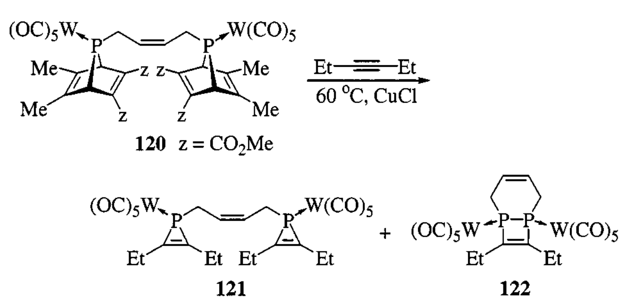
In the absence of trapping reagents, $PhPW(CO)_5$ dimerizes to **114**,[28] which reacts further at elevated temperatures to give triphosphirane **115**, with liberation of $W(CO)_5$ groups similar to that seen in the reaction of phosphaalkenes.[96] The ultimate product is tetraphosphetane **116**, with loss of yet another $W(CO)_5$ group.



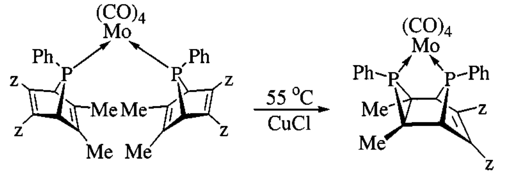
Vinylphosphinidene **117**, generated from precursor **54**, undergoes self-condensation to give 2,3-dihydro-1,2-diphosphete **119** rather than undergoing ring-closure to afford a phosphirene.[97] The formation of **119** suggests an intramolecular [2+2] cycloaddition by the transient dimer **118**.



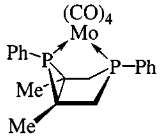
Attempts to dimerize phosphinidenes intramolecularly, starting from, for example, a *cis*-2-butene-bridged bis(7-phosphanorbornadiene) complex **120**, were not successful, with bicyclic products resulting instead on trapping with acetylenes, dienes, and carbene complexes.[98] Illustrative is the formation of **121** and **122** on trapping with 3-hexyne. Bicyclic **122** is believed to result from insertion of the "second" phosphinidene in the initially formed monophosphirene.



The reaction of bis(7-phosphanorbornadiene) complex **123** follows a different course, in that the phosphinidene $PhPMo(CO)_4L$, generated in situ, adds to the remaining 7-phosphanorbornadiene ligand to give diphos **124**.[99] When this second ligand is a phospholene instead, the more condensed diphos **125** results, but with a phosphole only monodentate products **126** are obtained, due to excessively high strain in the bidentate intermediate.[99]



123 z = CO_2Me **124**



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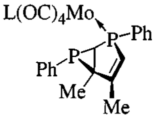
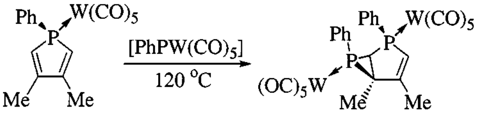


126 L = CO, phosphole

The related and rather congested biphos compound **128** is produced on addition of $PhPW(CO)_5$ to phospholene complex **127**.[99]



127 **128**

7. Conclusion

These presented reactions of electrophilic phosphinidene complexes illustrate the versatile chemistry of these reactive species. Their carbene-like reactivity and the observed rearrangements of their adducts underline the diagonal relationship between low-valent phosphorus and carbon compounds.[2] The complexed phosphinidenes are particularly useful as synthons for strained three-membered ring systems through 1,2-addition reactions. However, larger ring systems and also acyclic compounds can readily be obtained from rearrangements or subsequent reactions of initially formed 1,2 adducts or P-ylides. Hence, complexed phosphinidenes can be employed for the synthesis of a great variety of organophosphorus compounds that are not otherwise easily accessible.

Acknowledgments

Financial support of this research by the Netherlands Organization for Scientific Research (NWO/CW) and the National Science Foundation (NSF) for work performed at the University of Alabama at Birmingham is gratefully acknowledged. K. L. wishes heartily to thank his previous students and postdocs for their commitment in developing the chemistry of phosphinidene complexes.

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