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The Quest for Terminal Phosphinidene Complexes

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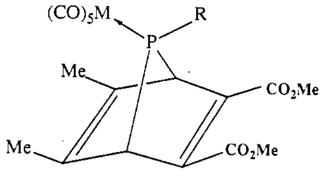
One of the seminal developments of organometallic chemistry has been the synthesis of transition-metal carbenes, $RR'CML_n$.[1] Analogous transition-metal imides, $RNML_n$, have also attracted significant attention.[2] Interestingly, the heavier congeneric terminal silylenes and phosphinidenes have so far eluded isolation, although in both instances[3,4] there is evidence for their intermediacy in chemical reactions. The purpose of this Account is to summarize the various attempts that have been made to isolate stable terminal phosphinidene complexes. Reactivity and bonding aspects are also discussed, and a comparison is made between terminal phosphinidene chemistry and that of 16-electron organometallic fragments.

Why study terminal phosphinidene complexes? Given that stable compounds featuring multiple bonding between the heavier main-group elements have now become available,[5] an obvious next step is to explore the consequences of binding these fragments to transition metals. Phosphinidene (RP) units seem ideally suited for this purpose, not only because of their isolobal relationship[6] to carbenes but also because of the ready availability of ^{31}P NMR spectroscopy as an investigative tool. As in the case of the corresponding carbene complexes,[1] intriguing questions arise regarding the nature of the bonding between the metallic and nonmetallic entities. Phosphinidenes, in fact, are anticipated to be particularly rich in bonding modes. Considerable interest is also associated with the reactivity patterns of terminal phosphinidene complexes. A potential benefit of such studies is the development of new phosphorus-containing synthons. A further practical potential for terminal phosphinidene complexes is the possibility that they might serve as precursors for the thermal or photochemical generation of metal phosphides.

Attempts To Prepare Terminal Phosphinidene Complexes



M = Cr, Mo, W

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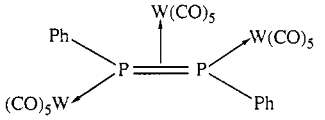
The earliest work in the area focused on the thermolysis of P-coordinated norbornadiene complexes, 1.[7] Mass spectrometric assay of the volatile thermolysis products revealed a peak corresponding to the composition $PhPM(CO)_5$ (2). However, in the absence of trapping agents, 2 dimerizes to the diphosphene complex 3 in ca. 20% yield.[8a] Interestingly, a rather similar derivative, 4, had been reported previously by Power et al.[8b] Although not mentioned explicitly in this paper, it is possible that 4 arose via dimerization of the terminal phosphinidene complex, $(Me_3Si)_2C(H)PFe(CO)_4$. Comparison of 3 and 4 indicates that one consequence of increasing substituent bulk is to cause one less organometallic moiety to coordinate to the diphosphene. We therefore decided to explore the effect of even larger



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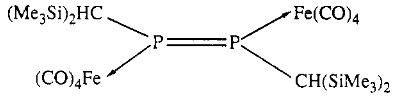

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Alan H. Cowley was born in Manchester, England, and received B.Sc., M.Sc., and Ph.D. degrees from the Victoria University of Manchester. Graduate study was conducted under the supervision of the late Professor F. Fairbrother. After postdoctoral study with Professor H. H. Sisler at the University of Florida and a brief sojourn in industry, he joined the faculty of The University of Texas at Austin, where he is presently the George W. Watt Centennial Professor of Chemistry.

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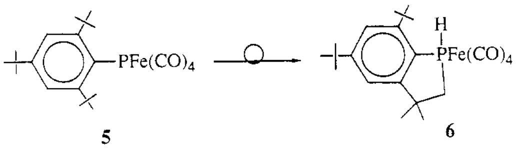
units. We turned our attention initially to attachment of a (2,4,6-*t*-$Bu_3C_6H_2$)P group to a transition-metal moiety. The reaction of ArP=C=O (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) with $Fe_2(CO)_9$ did, in fact, produce a compound of empirical formula $ArPFe(CO)_4$. However, it was evident from NMR spectroscopic data that the product was, in fact, the bicyclic secondary phosphine complex **6**.[9] The most likely precursor to **6** is the

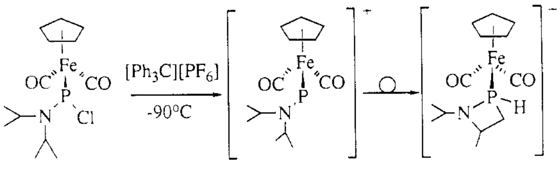


(1)

5 6

terminal phosphinidene complex **5**, which rearranges to **6** via insertion of phosphorus into a C–H bond of an *o*-*t*-Bu group. In principle, of course, a free-radical mechanism could be written to account for the production of **6**. However, this possibility is unlikely because no P–D bond formation was observed when the reaction was conducted in deuteriated solvents.

A similar C–H insertion process has also been observed by Gladysz et al.[10] In this instance, chloride ion was abstracted from a precursor phosphide complex, **7**. A transient ^{31}P NMR signal at δ 954 was attributed to the cationic terminal phosphinidene complex, **8**. However, the isolated product was the metallophosphonium salt, **9**.



(2)

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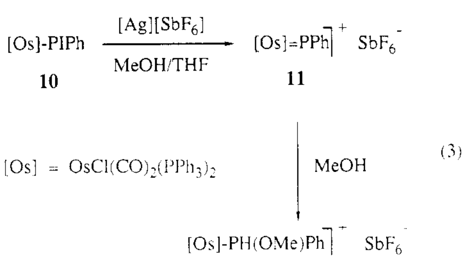
A cationic terminal phosphinidene complex has also been proposed in the reaction of the osmium(II) iodophosphide **10** with [Ag][SbF$_6$] in MeOH/THF.[11] If this



$$[\mathrm{Os}]\text{-PIPh} \xrightarrow[\text{MeOH/THF}]{[\mathrm{Ag}][\mathrm{SbF_6}]} \left[[\mathrm{Os}]\text{=PPh}\right]^+ \mathrm{SbF_6}^-$$

10 11

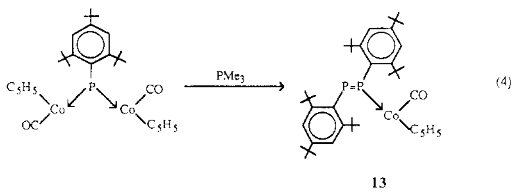
$[\mathrm{Os}] = \mathrm{OsCl(CO)_2(PPh_3)_2}$ MeOH (3)

$\left[[\mathrm{Os}]\text{-PH(OMe)Ph}\right]^+ \mathrm{SbF_6}^-$

12

reaction is conducted at ambient temperature, an unidentified mixture of products is formed. However, if the reaction mixture is allowed to warm slowly from −78 °C, the product is the metallophosphonium salt, **12**. Presumably **12** arises from insertion of the phosphinidene complex **11** into the O–H bond of MeOH.

In principle, terminal phosphinidenes should be obtainable by removal of one organometallic moiety from bridging bimetallic phosphinidenes of the general type $RP[ML_n]_2$. However, the only attempt at this approach resulted in the formation of a diphosphene complex, **13**,[12] which is akin to **3** and **4**.



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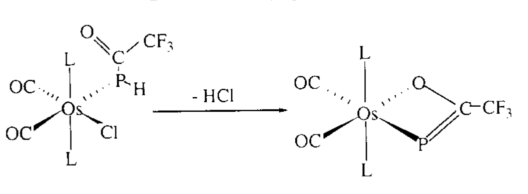
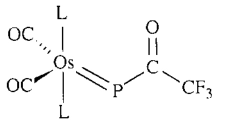
Attempts have been made to prepare neutral terminal phosphinidene complexes via intramolecular elimination of HCl or Me_3SiCl from precursor metal phosphides. For example, the acylphosphido complex **14** is



(5)

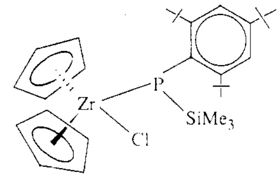
14 15



16

dehydrohalogenated by either DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or NaH in THF solution.[13] Although the product of this reaction is best described as the phosphaalkene complex **15**, it is interesting to note that X-ray crystallography revealed that the Os–O bond length [2.226 (11) Å] is 0.15–0.2 Å longer than usual. Moreover, the C–O bond length is somewhat short [1.246 (27) Å], thus suggesting a contribution to the bonding from **16**.

Lithium silylphosphines of the type RP($SiMe_3$)(Li) represent valuable synthons for the introduction of RP groups.[14] We have therefore investigated the reactivity of ArP($SiMe_3$)(Li) toward a variety of transition-metal dihalides. In the case of (η^5-C_5H_5)$_2$ZrCl$_2$, reaction stops at the LiCl elimination stage and the product was shown by X-ray crystallography to be the (three-electron donor) terminal phosphido complex **17**.[15] Unfortunately, **17** does not undergo loss of Me_3SiCl either thermally or photochemically. We attribute this to the halophilicity of Zr and possibly to the reluctance of a phosphinidene to function as a four-electron donor. Attention was therefore turned to more electron-rich organometallic fragments. The reaction of (η^5-



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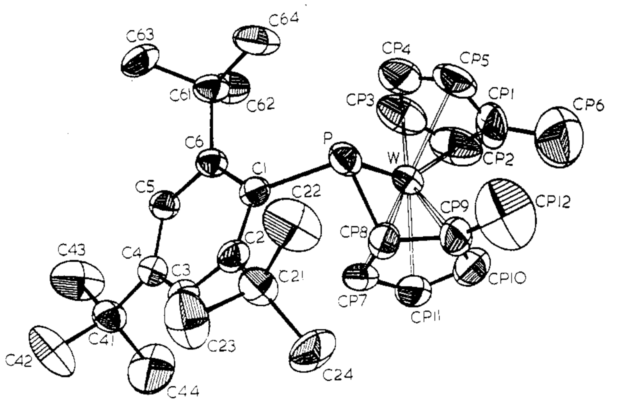
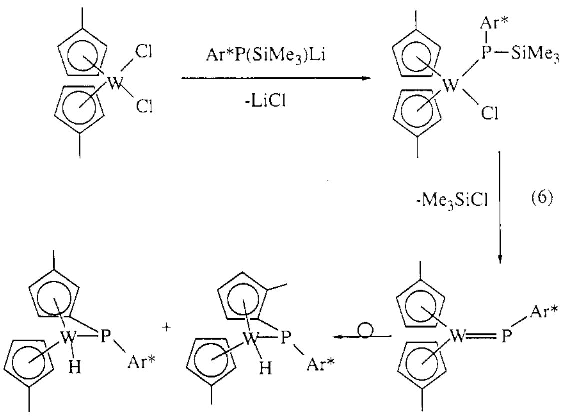


Figure 1. View of $(\eta^5\text{-}C_5H_4Me)\overline{WH[\eta^5\text{-}C_5H_3Me(P}Ar)]$ (Ar = 2,4,6-t-$Bu_3C_6H_2$) showing the atom numbering scheme. Important parameters: P–W = 2.583 (4), P–C(1) = 1.877 (12), P–CP(8) = 1.780 (15) Å.

$C_5H_4Me)_2WCl_2$ with $ArP(SiMe_3)(Li)$ afforded two isomers, **18** and **19**, in relative yields of 10% and 90%, respectively, both of which were identified by X-ray crystallography (Figure 1).[15] The isolation of **17** suggests initial loss of LiCl. In the case of tungsten this seems to be followed by Me_3SiCl elimination, to afford the terminal phosphinidene complex, **20**. In turn, the electrophilic phosphorus center presumably undergoes reaction with cyclopentadienyl C–H bonds to produce **18** and **19**.



(6)

18 19 20

Synthesis of Base-Stabilized Terminal Phosphinidene Complexes

Taken collectively, the foregoing attempted syntheses imply that terminal phosphinidene complexes are quite electrophilic. It therefore occurred to us that such complexes might be stabilized by Lewis base incorporation. Initial experiments were made by generating phosphinidene complexes in the presence of monodentate Lewis bases. However, this approach was not successful, and attention was therefore turned to the possibility of stabilization by means of the chelate effect. The pyrazolylborate ligand system seemed ideally suited for this purpose. In passing, we note that while many pyrazolylborato-substituted transition-metal compounds are known,[16] very little use of this ligand has been made in the context of main-group chemistry. The choice of the hydridotris(3,5-dimethyl-1-pyrazolyl)borato ligand, $[HB(pz^*)_3]^-$, was based on its desirable solubility characteristics. The halophosphine $[HB(pz^*)_3]PCl_2$, which is apparently the first tris(pyrazolyl)borato-substituted phosphorus compound, was synthesized by a metathetical reaction between PCl_3 and $[HB(pz^*)_3]K$.[17] The reaction of equimolar quantities of $[HB(pz^*)_3]PCl_2$ and $Na_2[Fe(CO)_4]$ afforded the intramolecularly base-stabilized phosphinidene complex $[HB(pz^*)_3]PFe(CO)_4$. By means of X-ray crystallography (Figure 2) it was shown that the phosphinidene unit occupies an axial site of a locally trigonal-bipyramidal geometry at iron.[17] Only two of the three (pyrazolyl)borato nitrogens are coordinated to phosphorus, the overall geometry at this center being approximately tetrahedral. Within experimental error the two P–N bond lengths are identical (av 1.770 (7) Å) and fall in the range anticipated for single bonds.[18] In principle, the iron–phosphorus bonding can be described by canonical forms **21** and **22**. In **21** the phosphorus and iron oxidation states are +3 and −2, respectively, and a double bond exists between phosphorus and iron. By contrast, the P–Fe bond order is unity in **22** and the oxidation states of P and Fe are +1 and 0, respectively. Canonical forms **21** and **22** can, in principle, be differentiated on the basis of the P–Fe bond length. The observed distance of 2.274 (4) Å falls in the range expected for a single bond,[18] thus implying

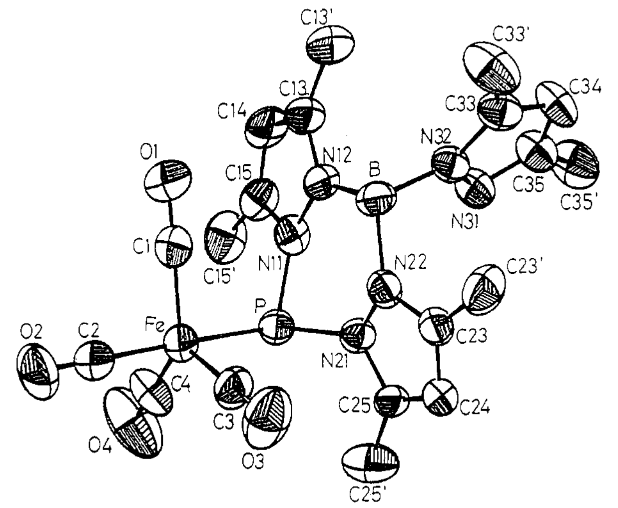
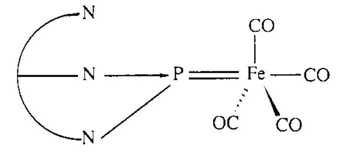


Figure 2. View of $[HB(pz^*)_3]PFe(CO)_4$ showing the atom numbering scheme. Important parameters: P–Fe = 2.274 (2), P–N(11) = 1.777 (7), P–N(21) = 1.764 (7) Å; Fe–P–N(11) = 109.7 (2), Fe–P–N(21) = 110.1 (2), N(11)–P–N(21) = 91.5 (3)°.



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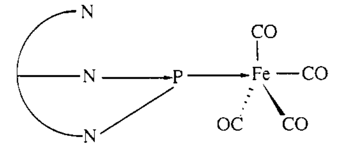

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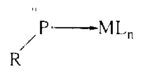
(16) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. Shaver, A. *J. Organomet. Chem. Library* **1977**, *3*, 157.

(17) Cowley, A. H.; Geerts, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 6523.

that **22** is the preferred structure.

Bonding Considerations

Phosphinidenes are potentially rich in bonding modes. If the phosphinidene coordinates to an organometallic fragment in the singlet state, either two- or four-electron donation is possible, thus giving rise to bent and linear complexes, **23** and **24**, respectively.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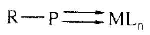
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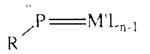
Theoretical studies, however, indicate that the parent phosphinidene, HP, adopts a triplet ground state.[19] Triplet ground states may also be assumed for substituted phosphinidenes.[20] In turn, the coordination of a triplet phosphinidene results in two additional bonding modes, **25** and **26**. It is important to stress the difference in these classes of terminal phosphinidene complex. Structures **23** and **24** are favored when the metal M is in a low oxidation state; i.e., ML_n is typically a metal(0) fragment such as $W(CO)_5$ or $Fe(CO)_4$. On the other hand, structures **25** and **26** require a high oxidation state metal. A similar dichotomy exists in the context of metal carbene chemistry. Carbene complexes represented by **27**, the so-called Fischer-type carbenes,[1a,b] require low oxidation state metals while the Schrock-type complexes, **28**, are found for metals in higher oxidation states.[1c] In passing, we note that some confusion exists in the literature regarding the choice of bonding description for the heavier congeneric silylene, germylene, stannylene, and plumbylene complexes. Interestingly, several of these compounds were designated correctly with structures analogous to **27** in the original publications.[21] However, in a recent review article[22] the same compounds were depicted with formal double bonds (i.e., structure **28**).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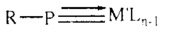
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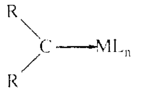
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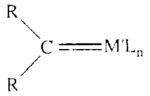
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Attention should also be drawn to the requisite changes of oxidation state of the main-group element in the foregoing discussion. In the specific case of terminal phosphinidene complexes, structures **23** and **24** imply a phosphorus oxidation state of 1, while in **25** and **26** the formal oxidation state is 3.

The majority of terminal phosphinidene complexes proposed as intermediates involve zero oxidation state metals and should, in our opinion, be described by structure **23** rather than **24**. To the best of our knowledge only two of the proposed terminal phosphinidene complexes, **16** and **20**, exhibit a reactivity consistent with the presence of a formal double bond implied by structure **25** (vide infra). In contrast, terminal imido complexes are known only with higher oxidation state metals[2] and are thus best described by structures **25** and **26**.

Unfortunately, the presently available theoretical studies[20,23] are not in agreement regarding the ground states of the coordinated phosphinidenes or the metal–phosphorus bond lengths. However, these calculations are in agreement regarding the prediction of an appreciable positive charge at phosphorus. More extensive theoretical work is clearly desirable and such studies are currently in progress in our laboratory.

Reactivity Considerations

At the present time there is no compelling evidence for the intermediacy of four-electron-donor terminal phosphinidene complexes.[24] Attention is therefore focused on the two-electron-donor cases. The reactivity patterns should depend on whether the phosphinidene is bonded to a metal in a low or high oxidation state. Structure **23** features a single bond to the metal and the presence of a vacant orbital and a lone pair of electrons at the phosphorus atom. As a consequence the phosphorus atom is anticipated to be the principal site of reactivity. In contrast, structure **25** implies both a metal–phosphorus double bond and a phosphorus lone pair. Evidence for the reactivity of the M=P functionality is therefore expected.

Marinetti and Mathey[25] have studied the reactions of transient terminal phosphinidene complexes with water, alcohols, and amines. In each instance oxidative addition occurred exclusively at phosphorus to afford **29**. In turn, these results suggest that the transient species of the type $PhPM(CO)_5$ (M = Cr, Mo, W) are best represented by the phosphorus(1)/metal(0) description, **23**. If the double-bonded form, **25**, were prevalent, HX addition would result in phosphido complexes, **30**.[13] In principle, of course, **30** could rearrange to **29** via a 1,2 hydride shift and concomitant two-electron reduction at the metal. Comparable 1,2 hydride shifts have, in fact, been postulated, e.g., in the


(7)

29

X = OH, OR, NH_2, NHR, NR_2


(8)

30

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(18) (a) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974. (b) Brown, I. D.; Brown, M. C.; Hawthorne, F. C. *Bond Index to the Determinations of Inorganic Crystal Structures*; Institute for Material Research, McMaster University, Hamilton, Ontario, Canada, 1969–1977.

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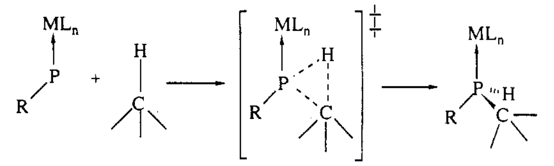
(24) It is conceivable that the interesting Fe_2P_2 ring compound $[\{Fe(CO)_3P(4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2C_6H_2O)\}_2]$ is formed via dimerization of the corresponding four-electron donor terminal phosphinidene complex. See: Flynn, K. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813. Note, however, that the tetrahedrane analogue $[\{(OC)_3FeP\text{-}t\text{-}Bu\}_2]$ is not produced by phosphinidene dimerization. See: Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.

(25) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

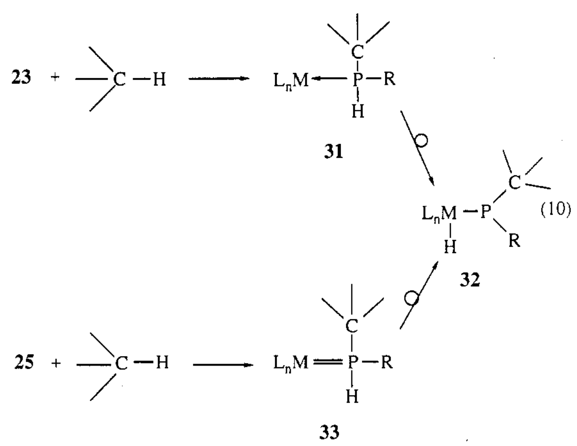
formation of formyl complexes.[26] However, convincing evidence for such processes is lacking.

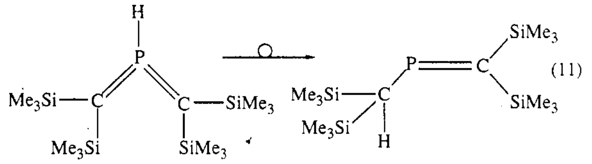
The coordinative unsaturation at the phosphorus center implied by structure **23** is also manifested by the observation that terminal phosphinidene complexes with bulky organic substituents undergo intramolecular C–H activation reactions (eq 1 and 2).[9,10] As in the case of the activation of C–H bonds by transition metals,[27] this is most likely a concerted process (eq 9).



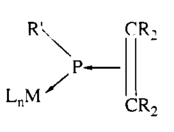
(9)

The putative W(IV) phosphinidene **20** behaves in a fundamentally different fashion to the corresponding metal(0) complexes in the sense that C–H insertion results in the metal hydrides **18** and **19** (eq 6).[15] As summarized below, the observed products could arise via two distinct routes (eq 10). The isomerization **31** → **32** implies the conversion of a coordinated secondary phosphine to the corresponding phosphide. To the best of our knowledge, an isomerization of this type is unknown. By contrast, the transformation **33** → **32** via a 1,2 reductive hydride shift (at phosphorus) finds a precedent in organophosphorus chemistry (eq 11).[28]

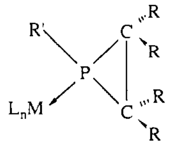




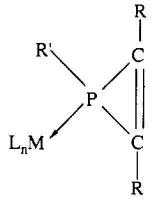
The addition of transient terminal phosphinidene complexes to olefins has been studied by Marinetti and Mathey.[29] As in the case of the interaction of coordinatively and electronically unsaturated organometallic fragments,[30] two limiting structures, **34** and **35**, should be considered for the reaction products. Comparable structures can be written for the corresponding alkyne reactions.[31] In **34** the alkene is π-bonded to phosphorus, which therefore remains in oxidation state 1. (As an aside, we note that **34** can also be regarded as a base-stabilized terminal phosphinidene complex akin to **22**.[17]) Structure **35**, on the other hand, represents an insertion or oxidative addition of the phosphinidene moiety into the π-bond of the alkene, thus affording a coordinated phosphirane. On the basis of ^{31}P NMR data it was concluded that the phosphirane structure **35** is preferred. In the case of the corresponding alkyne reactions, a phosphirene structure, **36**, was established on the basis of X-ray analysis.[31] Similar considerations to the foregoing apply to the reactions of transient terminal phosphinidene complexes with 1,3-dienes. Initial complexation is believed to afford **37**, which in turn undergoes ring expansion to the corresponding 3-phospholene derivatives, **38**.[29]



34



35



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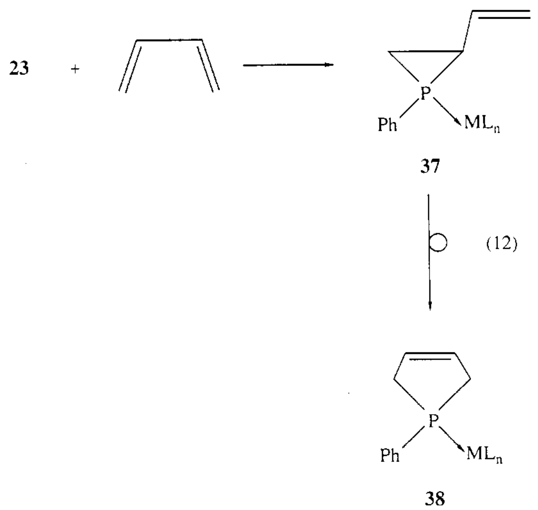
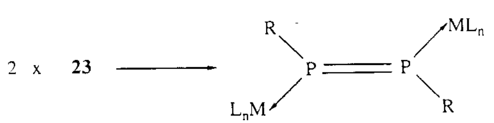


A final argument in favor of the predominance of **23** and **25** for low oxidation state metals stems from the fact that the dimerization products of **23** are diphosphene complexes such as **39**.[8] If **25** were the dominant form [2 + 2] dimerization would be anticipated. Significantly, the only clear evidence for simultaneous reactions at both metal and phosphorus centers comes from reaction of the higher oxidation state metal phosphinidene intermediate **16**.[13]



39

Compound **15** ↔ **16** is, in fact, closely related to the phosphavinylidenes, **42**, in the sense that they feature both a two-coordinate phosphorus and a degree of

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[26] Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.

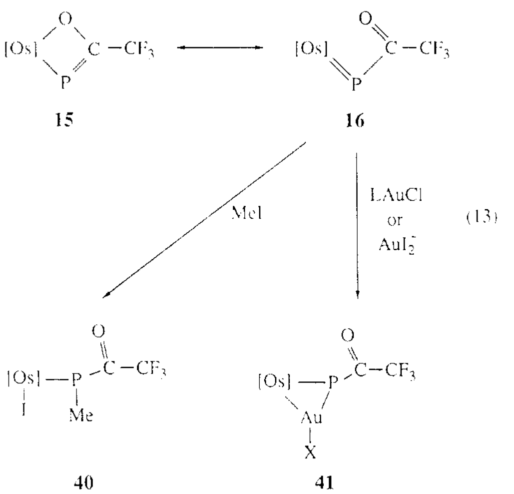
[27] Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

[28] Barron, A. R.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1092.

[29] Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

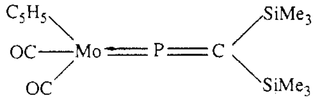
[30] (a) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335. (b) Hartley, F. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 596.

[31] Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

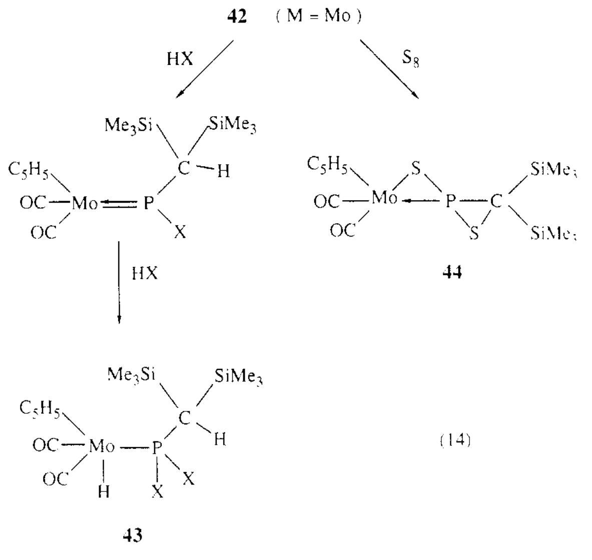


[Os] = OsCl(CO)$_2$(PPh$_3$)$_2$

metal–phosphorus multiple bonding.[32,33] Reactivity studies[34] (eq 14) of the molybdenum compound have established that initial attack occurs at the P=C functionality. However, with an excess of reagent, e.g., MeOH, addition across the molybdenum–phosphorus double bond occurs to afford the molybdenum hydride **43**. The reaction of **42** with elemental sulfur results in the novel spiro compound **44**.[35]



42 (M = Mo, W)



The foregoing results are consistent with an X-ray crystallographic study of **42** (Figure 3).[32] The Mo–P–C skeleton is essentially linear and the molybdenum–phosphorus bond length [2.174 (1) Å] is considerably shorter than the range of 2.40–2.57 Å, which has been established for phosphine complexes of molybdenum.[18]

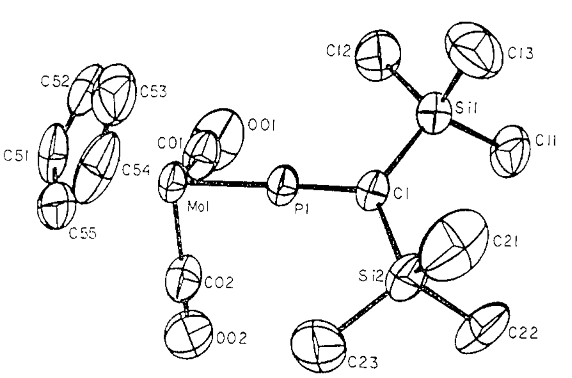
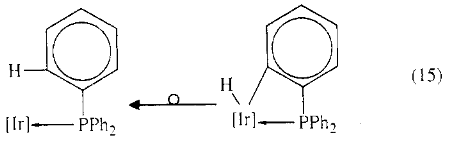


Figure 3. View of [Mo(CO)$_2$(η^1-P=C(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] showing the atom numbering scheme. Important parameters: Mo(1)–P(1) = 2.174 (1), P(1)–C(1) = 1.649 (4) Å; Mo(1)–P(1)–C(1) = 178.3 (2)°.

To What Extent Does the Chemistry of Terminal Phosphinidenes Resemble That of 16-Electron Organometallic Fragments?

Terminal phosphinidenes are isolobal[6] with 16-electron organometallic species such as (Ph$_3$P)$_3$RhCl and (Ph$_3$P)$_3$Pt. It is interesting therefore to note that both RP and 16-electron ML$_n$ fragments undergo oxidative addition reactions. The transition-metal compounds undergo oxidative addition reactions with both polar and nonpolar reagents to afford the corresponding 18-electron derivatives.[36] In the case of terminal phosphinidene complexes, oxidative addition reactions have been confined to polar reagents (eq 7). It might therefore be interesting to explore the reactivity of such complexes toward nonpolar reagents.

The intramolecular C–H activation reactions of metal phosphinidenes, which were summarized in eq 1 and 2, also find parallels in transition-metal chemistry. An example of an intramolecular C–H insertion by an Ir(I) moiety is shown in eq 15.[37] For both the phosphinidenes and the corresponding transition-metal complexes it is necessary that the center of reactivity be both electropositive and coordinatively unsaturated.



[Ir] = Ir(PPh$_3$)$_2$Cl

As discussed earlier, two canonical forms, **34** and **35**, can be written for the bonding of alkenes or alkynes to terminal phosphinidene complexes. As is widely recognized,[30] similar structures, **45** and **46**, can be written for transition-metal fragments. However, in contrast to the terminal phosphinidene complexes, the predominant structure for transition metals in **45**. It is only when electron-withdrawing groups are present that **46**

45 46

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[32] Cowley, A. H.; Norman, N. C.; Quashie, S. *J. Am. Chem. Soc.* **1984**, *106*, 5007.

[33] Gudat, D.; Niecke, E.; Malisch, W.; Hofmockel, U.; Quashie, S.; Cowley, A. H.; Arif, A. M.; Krebs, B.; Dartmann, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1687.

[34] Arif, A. M.; Cowley, A. H.; Quashie, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1437.

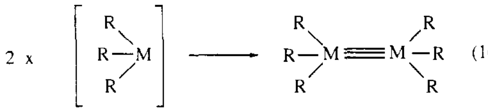
[35] Quashie, S. Ph.D. Dissertation, The University of Texas at Austin, 1987.

[36] Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 387.

[37] Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

becomes the preferred structure.[38]

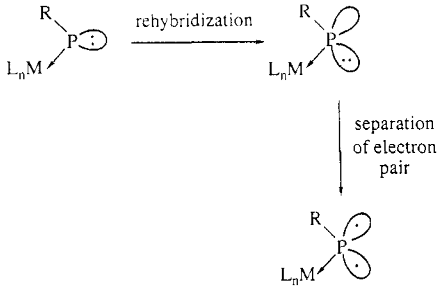
The formation of unsupported dimers containing metal–metal bonds has been studied extensively.[39] The dimerization of transition-metal fragments represented in eq 16[40] is strikingly similar to the dimerization of terminal phosphinidene complexes (eq 13). It is significant to note that in both cases no change of oxidation state of the central atom (M or P) occurs upon dimerization.



(16)

M = Mo, W R = CH_2SiMe_3

Finally, attention is drawn to the generally accepted view[41] that rehybridization and electron pair separation are prerequisites for the oxidative addition reactions of 16-electron transition-metal fragments. The same concept is encountered in organic chemistry, specifically for the oxidative addition reactions of singlet carbenes. As already noted, terminal phosphinidene complexes exhibit similar patterns of reactivity to both singlet carbenes and 16-electron ML_n fragments. Given these parallels, we suggest that the oxidative addition reactions of terminal phosphinidenes proceed via the sequence of events illustrated in eq 17.



(17)

Concluding Remarks

A summary has been made of the various attempts to synthesize stable terminal phosphinidene complexes. The bonding in and reactions of these species are also discussed. As a result of this summary it has become clear that, as is the case for transition-metal carbenes, terminal phosphinidene complexes should be classified on the basis of metal oxidation state. In the context of 16-electron metal fragments it is argued that the phosphorus–metal bond order is close to unity if the metal is in a low oxidation state. Phosphorus–metal double bonding only becomes significant when the metal adopts a higher oxidation state. The available reactivity data are supportive of these views. Thus, low oxidation state complexes react exclusively at the phosphorus center while the higher oxidation state complexes exhibit reactivity consistent with presence of a P=M functionality.

So far much of the experimental effort has been directed toward the attachment of phosphinidenes to low oxidation state transition-metal fragments. It is likely that future studies will focus on higher oxidation state derivatives. Once base-free 16-electron terminal phosphinidene complexes have been isolated, attention will probably turn to the synthesis of 14-electron complexes. In principle, there seems to be no particular reason why the chemistry of terminal phosphinidene complexes should not prove to be as extensive as that of transition-metal imides.

Note Added in Proof: Lappert et al. (Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* 1987, 1282) have reported the preparation of terminal phosphinidene complexes, $[M(\eta\text{-}C_5H_5)_2(=PAr)]$ (M = Mo, W; Ar = 2,4,6-t-$Bu_3C_6H_2$). The metric parameters for the Mo complex are consistent with the presence of a Mo=P double bond and a stereochemically active lone pair at phosphorus. Two base-stabilized terminal silylenes have also been reported. See: Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669.

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[38] (a) Clemens, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 375. (b) Beck, W.; Schlodder, R.; Lechler, K. H. *J. Organomet. Chem.* **1973**, *54*, 303.

[39] Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

[40] Chisholm, M. H.; Cotton, F. A.; Extine, M.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2252.

[41] Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Co.: Belmont, CA, 1985; p 275.