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Terminal Phosphinidene and Heavier Congeneric Complexes. The Quest Is Over

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> "In framing an ideal we may assume what we wish, but should avoid impossibilities."
>
> Aristotle

Introduction

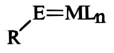
The chemistry of terminal phosphinidene (phosphanediyl) and heavier congeneric complexes is much less developed than that of the familiar metal imides.[1] The road to stable terminal phosphinidene complexes has not been straightforward, and several of the vicissitudes were described in a 1988 Account.[2] However, this state of affairs has changed rapidly and there has been sufficient recent progress to warrant an updated Account.

At the outset, it should be stressed that, while there are many interesting examples of bridging phosphinidene complexes,[3] such compounds are not discussed here. Likewise, even though transient metal phosphinidenes[4] continue to provide a wealth of information regarding reactivity patterns, they too fall outside the scope of the present article.

Thus far, the majority of the effort on stable terminal phosphinidene complexes has been devoted to cases in which a phosphinidene ligand is bonded to a d-block element. However, more recently the first structurally characterized f- and p-block examples have begun to emerge. Not unexpectedly, less emphasis has been placed on the heavier congeneric arsinidenes (arsanediyls). Furthermore, there are no examples of stable terminal stibinidene (stibanediyl) or bismuthinidene (bismuthanediyl) complexes. Generally speaking, synthetic and structural studies have occupied center stage and less effort has been expended in terms of exploration and exploitation of reactivity patterns. This situation is likely to change, however, with the advent of more reactive complexes.

d-Block Terminal Phosphinidenes and Arsinidenes

As in the case of carbene complexes, the bonding in terminal phosphinidenes and arsinidenes will depend inter alia on the electronic state of the main-group fragment. Theoretical studies indicate that a triplet ground state is favored for the parent phosphinidene, PH,[5] and a variety of substituted phosphinidenes including PCH_3,[6] PC_6H_5,[7] and PC(O)H.[8] Experimentally, P(2,4,6-$Me_3C_6H_2$) has been matrix isolated and shown to possess a triplet ground state on the basis of ESR evidence[9] and the triplet−singlet energy gap of PH has been measured in flowing afterglow experiments.[10] If the pnictinidene coordinates in a triplet state, formal double bonding to the organometallic fragment can take place (**1**). In the sense that higher oxidation states are favored for both the organometallic and main-group fragments, there is an obvious resemblance between **1** and Schrock-type carbene (alkylidene) complexes. An obvious difference, however, between the carbene and pnictinidene complexes is the presence of a lone pair on the latter. If, for example, a two-electron donor ligand, L, is removed from the metal, this would permit the formation of an ancilliary donor−acceptor linkage thus raising the metal−pnictinidene bond order to 3 (**2**). Note, however, that the angular (**1**) and linear (**2**) structures represent extreme canonical forms and that the potential energy well for M−P−C bending may be somewhat shallow.



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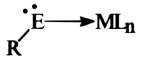
By analogy to Fischer-type carbene complexes, the bonding of singlet pnictinidenes to organometallic fragments is anticipated to be favored by low metal oxidation states and by the presence of a strong π-donor substituent at the main-group center. Although such complexes are written with a dative bond of order 1 (**3**), it should be borne in mind that molecular orbital calculations on Fischer-type carbene complexes[11] indicate a modicum of π-back-bonding from the organometallic to the main-group fragment.



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Alan H. Cowley was born in Manchester, U.K., and educated at the University of Manchester. Following a postdoctoral sojourn at the University of Florida, he served as a Technical Officer with Imperial Chemical Industries (Billingham Division). He has taught at the University of Texas for over 30 years, where he currently holds the Robert A. Welch Chair in Chemistry. He has broad interests in the domain of main group chemistry and has been the recipient of the Royal Society of Chemistry Award for Main Group Chemistry (1980), the RSC Centenary Medal and Lectureship (1986), the Southwest Regional ACS Award (1986), and the Chemical Pioneer Award of the American Institute of Chemists (1994). He was elected a Fellow of the Royal Society in 1988.

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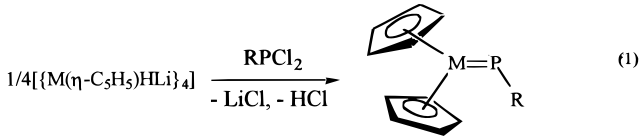
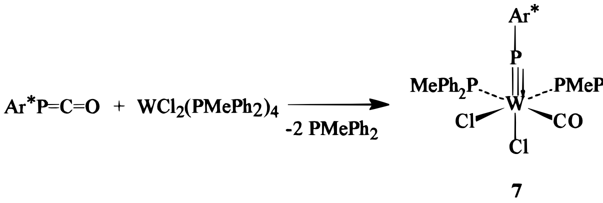
The first examples of terminal phosphinidene complexes were reported by Lappert et al.[12] The molybdenum and tungsten derivatives **4**−**6** were formed by treatment



4: M = Mo, R = 2,4,6-t-$Bu_3C_6H_2$
5: M = W, R = 2,4,6-t-$Bu_3C_6H_2$
6: M = W, R = $(Me_3Si)_2CH$

of the tetramers $[M(\eta\text{-}C_5H_5)_2HLi]_4$ with appropriately bulky phosphorus dichlorides, $RPCl_2$. Two of the compounds, **4** and **5**, have been characterized by X-ray crystallography and found to be isomorphous. Both molecular structures are in conformity with canonical form **1**. Thus, the metal−phosphorus bond distances (2.370(2) Å in **4**; 2.349(5) Å in **5**) are appropriate for a bond order of 2; moreover, the M−P−C bond angles of 115.8(2)° in **4** and 114.8(5)° in **5** are in accord with the presence of a stereochemically active lone pair. Further support for the double-bond description stemmed from the nonequivalence of the cyclopentadienyl groups in the ambient-temperature ^1H NMR spectra of **4** and **5** and from the unusually deshielded ^{31}P NMR chemical shifts of +799.5, +661.1, and +679.6 ppm for **4**, **5**, and **6**, respectively. The observation of such low-field ^{31}P chemical shifts finds a parallel in ^{13}C NMR spectroscopy where, due to the importance of the paramagnetic contribution to the chemical shift, olefinic carbons resonate at lower fields than aliphatic carbons. In the cases of **4**−**6**, the major contributors to the paramagnetic term are low-lying n → π* and π → π* transitions.

In developing an alternative synthetic approach to terminal phosphinidenes, our attention was drawn to elegant work of Mayer et al.[13] which established that heterocumulenes such as carbon dioxide and isocyanates undergo cleavage reactions with tungsten(II) phosphine complexes. Accordingly, it was decided to attempt the reaction of the isolobal phosphaketene Ar*P=C=O (Ar* = 2,4,6-t-$Bu_3C_6H_2$)[14] with $WCl_2(PMePh_2)_4$. The reaction was successful and resulted in the first example of a linear terminal phosphinidene complex, **7**.[15] Consistent with canonical form **2**, the W−P−C angle is close to linearity (168.2(2)°) and the W−P bond distance (2.169(1) Å) is 0.17 Å shorter than that ascribed to the tungsten−phosphorus double bond in **5** (Figure 1). The triple-bond description also explains the dramatic difference between the ^{31}P chemical shifts of **7** (+193.0 ppm) and those of **4**−**6**, which span the range +661.1 to +799.5 ppm. Once again, a parallel with ^{13}C NMR spectroscopy is apparent in the sense that the chemical shifts of alkynes are more shielded than those of alkenes. It is also noteworthy that the one-bond $^{183}W-^{13}P$ coupling constant for **7** (649 Hz) is considerably larger than that for **5** (153.5 Hz) and **6** (144.1 Hz) since the percentages of s-character in the phosphorus bonding orbitals are approximately 33.3 and 50.0% in **5** or **6** and **7**, respectively.



(2)

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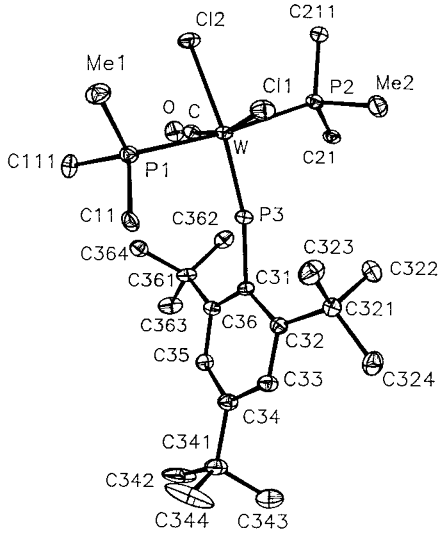
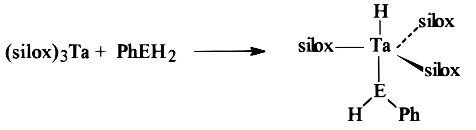


FIGURE 1. Molecular views of $(Ph_2MeP)_2(CO)(Cl)_2W{\equiv}PAr^*$ (7; Ar* = 2,4,6-t-$Bu_3C_6H_2$).

It is also possible to effect the requisite kinetic stabilization of terminal pnictinidenes (i.e., to inhibit dimerization) by employing bulky ligands at the metal rather than the main-group center. Thus, Wolczanski et al.[16] have used the $(silox)_3Ta$ moiety (silox = t-Bu_3SiO) to support terminal PPh and AsPh groups, the latter compound representing the first example of a stable terminal arsinidene complex. Both derivatives were prepared via a two-step process, the first of which was an oxidative addition reaction of $(silox)_3Ta$ with $PhEH_2$ (E = P, As) to afford the corresponding pnictide hydrides **8** (eq 3). In turn, the pnictide hydrides underwent loss of dihydrogen



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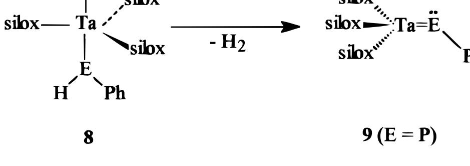

(4)

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9 (E = P)

10 (E = As)

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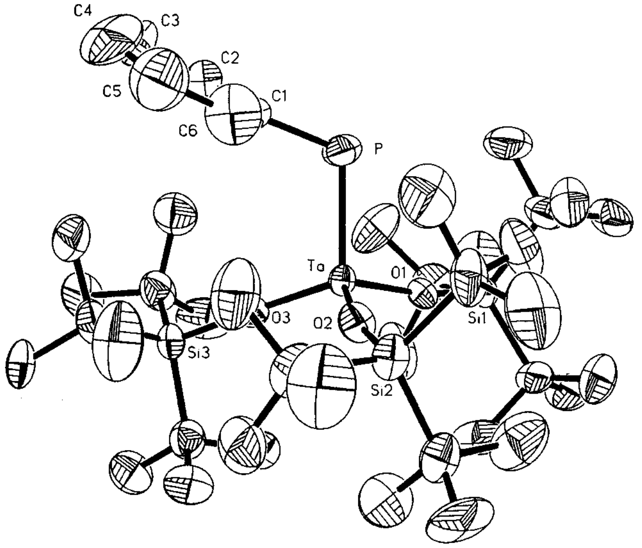
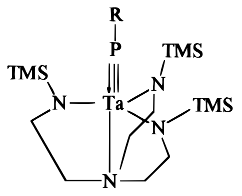


FIGURE 2. Molecular views of (silox)$_3$Ta=AsPh (10; silox = *t*-Bu$_3$SiO).

in benzene solution to afford the terminal phosphinidene (**9**) and arsinidene (**10**) complexes. The reactions shown in eq 2 were found to be first-order in **8** and zeroth-order in added PhEH$_2$, thus implying a straightforward 1,2-H$_2$ elimination processes. X-ray diffraction experiments revealed that **9** and **10** are isomorphous and that individual molecules adopt the bent-type structure **1** (Figure 2). The observation that the Ta–As–C bond angle in **10** (107.2(4)°) is smaller than the Ta–P–C bond angle in **9** (110.2(4)°) follows the normal group 15 trend and is also evident in, for example, the structural chemistry of diphosphenes (RP=PR) and diarsenes (RAs=AsR).[17] The sum of covalent radii for tantalum and phosphorus is 2.44 Å;[18] hence, the Ta–P bond distance of 2.317(4) Å is appropriately shortened for a bond order of 2, as is the Ta–As bond distance of 2.428(2) Å in **10** when the ~0.11 Å difference in phosphorus and arsenic covalent radii is factored in. The adoption of bent (**1**) rather than linear (**2**) structures by **9** and **10** conforms to expectation in the sense that there is strong competition for back-bonding into vacant Ta(dπ) orbitals from filled O(pπ) orbitals on the silox groups. Preliminary EHMO calculations[16] reveal that the HOMO's of **9** and **10** correspond to pnictinidene lone pairs, and this is probably the case for the other angular derivatives, **4**–**6**. It is interesting to note, however, that the ^{31}P chemical shift of **9** (+334.6 ppm) is considerably more shielded than those of **4**–**6**, possibly suggesting a stronger double bond in the case of the tantalum compound although, as pointed out by Wolczanski et al.,[16] the possibility of electrostatic interactions between the electrophilic metal fragments and the more electronegative main-group moieties should not be overlooked.

The foregoing examples of pnictinidene complexes each involve the presence of bulky substituents at either the metal or main-group center. This creates somewhat of a "Catch-22" situation in the sense that the steric blockade that is needed for kinetic stabilization of the desired compounds is likely to inhibit reactivity at the metal–pnictogen multiple bond. An elegant escape from this dilemma was realized by Schrock and Cummins et al.,[19] who developed tetradentate triamidoamine ligands[20] of the type [(Me$_3$SiNCH$_2$CH$_2$)$_3$N)$^{3-}$ which feature a sterically protective periphery of Me$_3$Si groups, thus permitting the passage of reagents through the clefts. Treatment of the trilithium salt of the above [N$_3$N]$^{3-}$ ligand with TaCl$_5$ resulted in [(N$_3$N)TaCl$_2$] which, in turn, reacted with 2 equiv of LiPHR to afford the corresponding terminal phosphinidene complexes **11**–**14** (eq 5).[19,21] The mechanism of formation of **11**–**14** is not clear at present. The second equivalent of LiPHR might be used as a base for dehydrohalogenation; alternatively, phosphinidene formation could take place via RPH$_2$ elimination from a bis(phosphido) species.[22] The phenylphosphinidene complex **11** is a useful synthon for the preparation of further examples of terminal phosphinidene complexes. Thus, **11** undergoes phosphorus–phenyl cleavage with excess lithium in THF and subsequent treatment with alkyl or silyl halides afforded **14**–**17** (eq 6).[21] On the basis of ^{31}P NMR evidence, it was proposed that the intermediate in the above reaction is [N$_3$N]Ta=PLi.[21] However, attempts to convert this intermediate into the parent phosphinidene complex, [N$_3$N]Ta=PH, have not been successful thus far. The ^{31}P NMR chemical shifts for **11**–**17** span the range +157 to +227 ppm, and in concert with the observation of ligand equivalence on the NMR time scale, these data implied the adoption of a linear coordination mode for the terminal phosphinidene. Confirmation by X-ray analysis was obtained in the case of **12**. The Ta–P bond distance (2.145(7) Å) in the essentially linear Ta–P–C fragment is considerably shorter than the Ta–P bond distance in the angular complex **9** (2.317(4) Å)[16] and thus

$$[(\text{N}_3\text{N})\text{TaCl}_2] + 2\ \text{LiPHR} \xrightarrow[\text{-2 LiCl, -2 RPH}_2]{} (\text{N}_3\text{N})\text{Ta}{\equiv}\text{PR} \tag{5}$$



TMS = Me$_3$Si

11, R = Ph (δ_p +175.1)

12, R = Cy (δ_p +209.8)

13, R = *t*-Bu (δ_p +227.3)

14, R = *n*-Bu (δ_p +186)

$$[\text{N}_3\text{N}]\text{Ta}{\equiv}\text{PPh} \xrightarrow{\text{Li, RX}} [\text{N}_3\text{N}]\text{Ta}{\equiv}\text{PR} + \text{PhR} + 2\ \text{LiX} \tag{6}$$

14, R = *n*-Bu (δ_p +186)

15, R = Me (δ_p +157)

16, R = Me$_3$Si (δ_p +212)

17, R = PhMe$_2$Si (δ_p +203)

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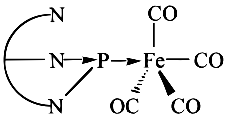
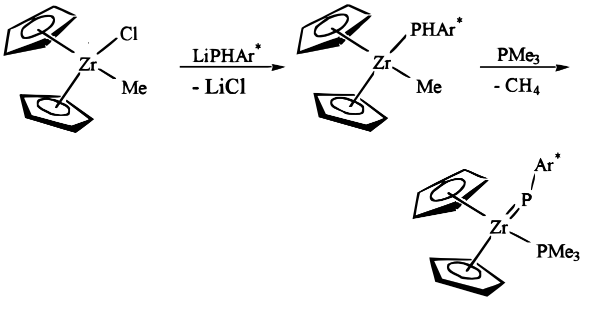
consistent with the presence of a pseudo triple bond. The orbital arrangement of the $[N_3N]^{3-}$ ligand is, in fact, well-suited to triple- or pseudo-triple-bond formation because of the presence of a ligand-centered nonbonding MO constructed from N(2p) AO's.

Supplemental Lewis base coordination also represents a viable approach to the stabilization of terminal pnictinidene complexes. Clearly, such base stabilization can be intra- or intermolecular and the donor–acceptor site can be the metal or the group 15 element. An early example of intramolecular base stabilization involved the use of the hydridotris(3,5-dimethyl-1-pyrazolyl)borato ligand, $[HB(pz^*)_3]^-$, at the phosphorus center.[23] X-ray analysis of $[HB(pz^*)_3]PFe(CO)_4$ (**18**), the product of the reaction of $[HB(pz^*_3)]PCl_2$ with $Na_2Fe(CO)_4$, revealed that only two of the three ligand nitrogen atoms are coordinated; hence, this system can be regarded as an amine-coordinated amidophosphinidene complex, the preferred canonical form for which is shown above. Theoretical investigations[6] have shown that the placement of π-donor ligands such as NH_2 on a phosphinidene leads to a singlet ground-state; hence, it is not surprising that the bonding in **18** is of the donor–acceptor (Fischer) type and that the P–Fe bond order is unity.



18

Stephan et al. have employed intramolecular base stabilization very effectively for the preparation of the first zirconium phosphinidene complex. Earlier work from the Stephan group[22] demonstrated that transient phosphinidenes of the type $(\eta\text{-}Me_5C_5)_2Zr{=}PR$ were formed by primary phosphine elimination from bis(phosphide) complexes. However, to render compounds of this type isolable, it was necessary to modify the steric demands of the zirconium and phosphorus substituents and to coordinate a molecule of Me_3P to the metal center.[24] Although H_2 and Ar^*PH_2 elimination routes to **19** have been described,[25] superior yields are obtained by the CH_4 elimination procedure summarized in eq 7.[26] The low-field chemical shift for **19** (+792.4 ppm) was indicative of a bent phosphinidene geometry, and this was confirmed by X-ray diffraction. The Zr–P–C bond angle in **19** (116.1(4)°)[24] is very similar to that in $(\eta\text{-}C_5H_5)_2Mo{=}PAr^*$ (115.8(2)°);[12] hence, the addition of a Me_3P ligand in the case of **19** seems to have little effect on the metal–P–C angle. While the Zr–P(phosphinidene) bond distance in **19** (2.505(4) Å) is shorter than the Zr–P(phosphine) distance (2.741(5) Å), it is not much shorter than those in zirconium phosphide complexes bearing similar substituents such as $Cp_2ZrCl(P(SiMe_3)Ar^*)$, (2.541(4) Å)[25] and $Cp_2ZrCl(PHAr^*)$ (2.543(3) Å).[27] A bent-type structure is, in fact, anticipated for **19** because in this arrangement the $[PAr^*]^{2-}$ ligand is a four-electron donor, and consequently, an 18-electron configuration is achieved at the Zr(IV) center. Using a similar argument, a linear geometry might be expected for the phosphine-free transient phosphinidene $Cp_2Zr{=}PAr$.* However, MO calculations on the model compounds Cp_2ZrPH and Cp_2ZrPPh showed minimum energy structures at Zr–P–X angles of 109.3 and 120.9°, respectively.[25] The preference for the bent geometry may arise because of poor overlap between a P(3p) orbital and the b_1 frontier orbital of the Cp_2Zr fragment.



(7)

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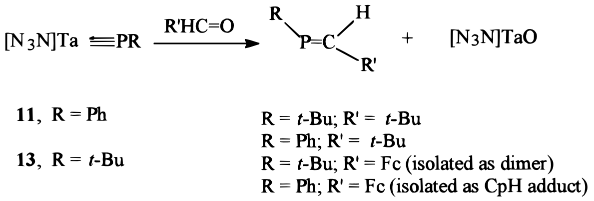
The study of the reactivities of stable terminal pnictinidene complexes promises to be a fertile and rewarding area. So far, the reactivities of only three of the terminal phosphinidenes described above (**11**, **13**, and **19**) have been described. The reactivities of **11** and **13** are high because the phosphorus substituents are of modest size and the steric shield encompassing the $Ta\equiv P$ moiety permits the passage of reagents through the clefts in the $[N_3N]$ ligand.[19,21] In the case of **19**, the enhanced reactivity stems from the relatively facile removal of the stabilizing base Me_3P.[26] Given the pronounced oxophilicity of tantalum[28] and zirconium, it is not surprising that **11,**[19] **13,**[19] and **19**[26] undergo reactions with, for example, aldehydes or ketones to produce phosphaalkenes and oxotantalum or oxozirconium species (eqs 8 and 9). The transformations shown above are facile and represent more convenient phosphaalkene syntheses than those effected by conventional methodologies. Moreover, these hetero-



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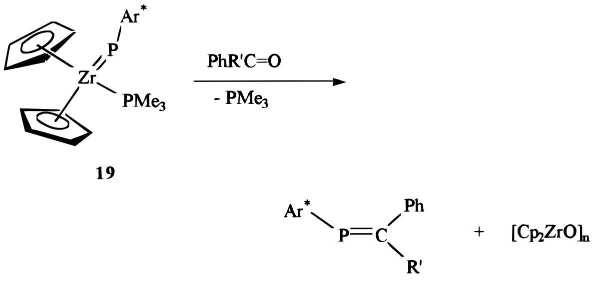

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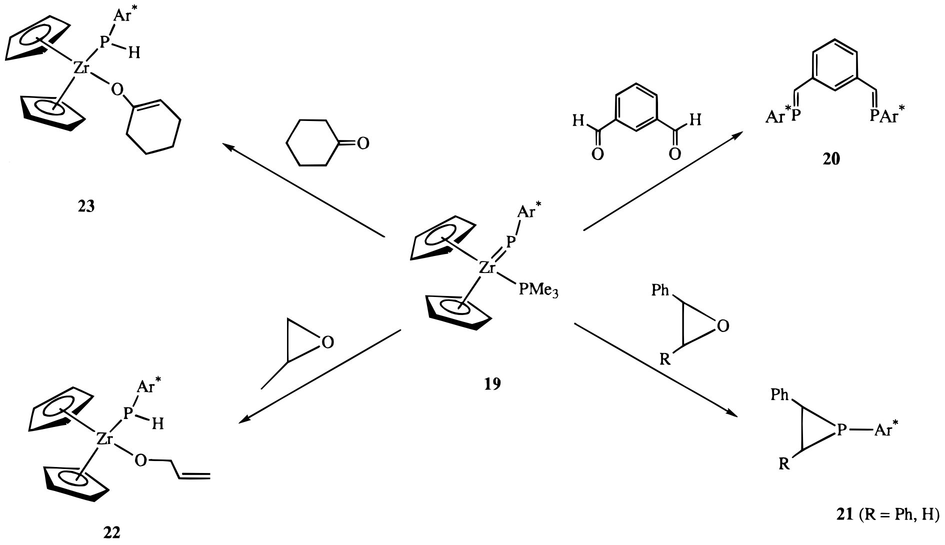
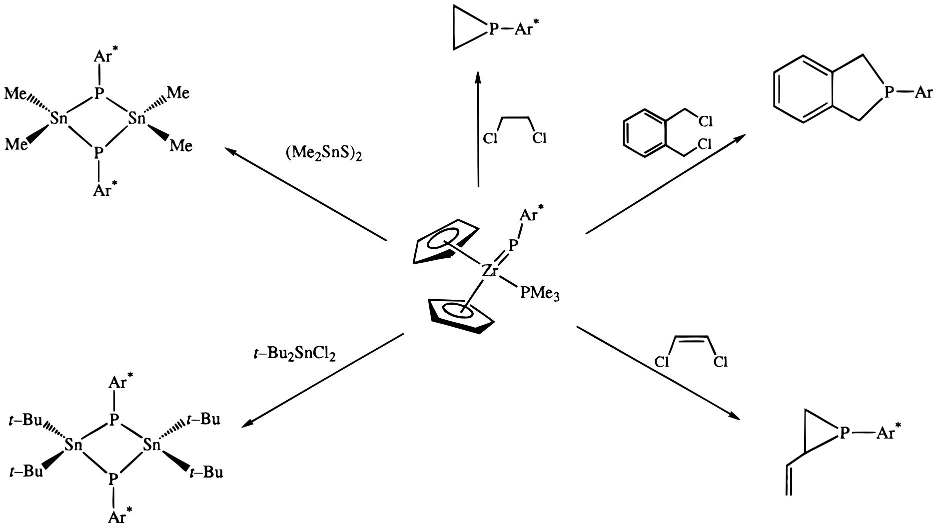
[28] It has been estimated[19] that the Ta=O bond strength exceeds that of the Ta=P bond by at least 63 kcal/mol.

Scheme 1



Scheme 2



olefin processes are reminiscent of the Wittig reaction and can be dubbed phospha-Wittig reactions. Coined originally by Mathey,[4] this term was applied to metathesis reactions of transient phosphinidenes, RP→M(CO)$_5$ (M = Mo, W). However, the reactions summarized in eqs 8 and 9 are distinct from, but complementary to, those of the transient phosphinidenes in the sense that the latter, being analogous to Fischer-type carbene complexes, are electrophilic at phosphorus. A consequence of this electrophilicity is that the M(CO)$_5$ fragment remains coordinated to the phosphaalkene product. The most plausible mechanism for the phospha-Wittig reactions involves a four-centered metallacycle, $\overline{\mathrm{M{-}P{-}C{-}O}}$ (M = Ta, Zr),[19,26] and the observation of exclusive *E*-isomer formation in the aldehyde reactions presumably results from the minimization of steric effects in this transition state.

The reactivity of **19** toward several additional substrates is illustrated in Scheme 1.[26] Straightforward phosphinidene-for-oxygen interchanges take place to afford the *E,E*-isomer of the benzodiphosphaalkene **20** and the phosphiranes **21** along with [Cp$_2$ZrO]$_n$ and PMe$_3$. Note, however, that complications can arise when acidic protons are present (**22** and **23**).

The thio- and halophilicity of zirconium are also appreciable, and as a consequence, **19** is reactive toward a variety of sulfur- and chlorine-containing substrates. For example, the reaction of **19** with PhNCS produces the heteroallene PhN=C=PAr* along with the byproducts [Cp$_2$ZrS]$_2$ and Me$_3$P, and phosphinidene transfer to tin centers occurs when [Me$_2$SnS]$_2$ is treated with **19**.[26] Phosphaalkene formation was observed when the *gem*-dihalides were treated with **19**;[26] here the primary driving force of the reaction is the formation of Cp$_2$ZrCl$_2$. This type of metathesis reaction is also effective for the synthesis of a wide range of organophosphorus and main group heterocycles (Scheme 2).[26]

Analogously to the [2 + 2] cycloaddition reactions of alkynes with metal carbene complexes,[29] the terminal phosphinidene **19** undergoes reaction with alkynes to form the first examples of phosphametallacyclobutenes, **24** and **25** (eq 10).[30] As expected, the rate-determining step is the elimination of Me$_3$P to form the base-free

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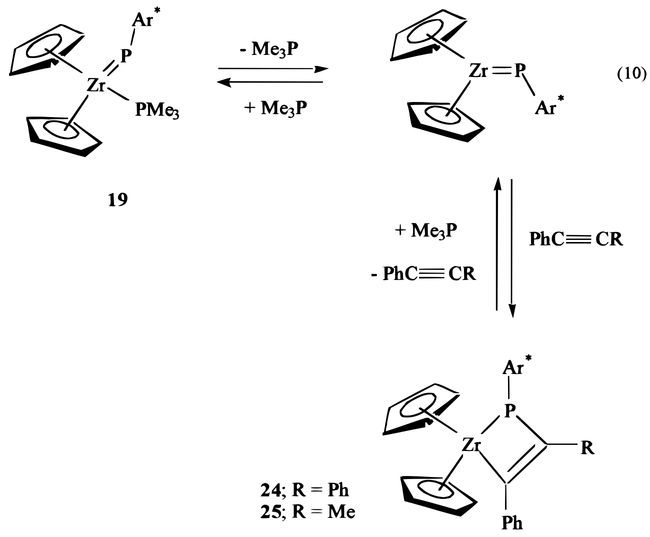
(29) See, for example, ref 1b and the following: *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; Jai Press Inc: Greenwich, CT, 1994; Vol. 3.

(30) Green, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 4204. Breen, T. L.; Stephan, D. W. *Organometallics* **1996**, *15*, 5729.

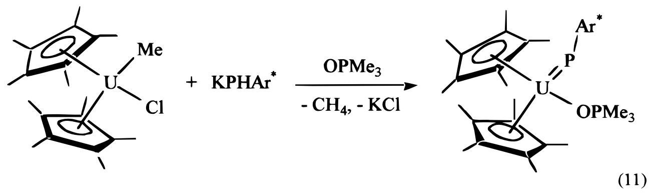


(10)

transient phosphinidene which, in turn, reacts with alkynes. Interestingly, the formation of the phosphametallacycles is reversible since the addition of Me_3P to **24** or **25** results in quantitative reversion to **19** and the alkyne. The reaction of **19** with C−N multiple bonds takes a different course and results in phosphinidene transfer to carbon.[30] Protic reagents such as PhEH (E = O, S) and $PhEH_2$ (E = N, P) react with **19** via E−H addition across the Zr=P bond.[31]

f-Block Terminal Phosphinidenes

At the present time, only one f-block terminal phosphinidene complex has been reported. Compound **26** was formed via the methane/salt elimination reaction summarized in eq 11.[32] Note that, as in the case of the zirconium phosphinidene complex **19**,[24] it was necessary to append a molecule of base to effect stabilization of the product. Characterization of the phosphine oxide adduct by X-ray crystallography revealed an essentially tetrahedral geometry around the U(IV) center and an angular phosphinidene moiety (Figure 3). The U−P−C bond angle in **26** (143.7(3)°) is more obtuse than those in the angular d-block phosphinidene complexes (~110−116°), possibly implying a shallow potential energy well for angular deformation. The U−P bond distance of 2.562(3) Å is considerably shorter than, for example, the single-bond distance in the bridging phosphinidene complex $[\eta^5\text{-}C_5Me_5)_2U(OMe)]_2(\mu\text{-}PH)$ (2.743(1) Å).[33]



(11)

26

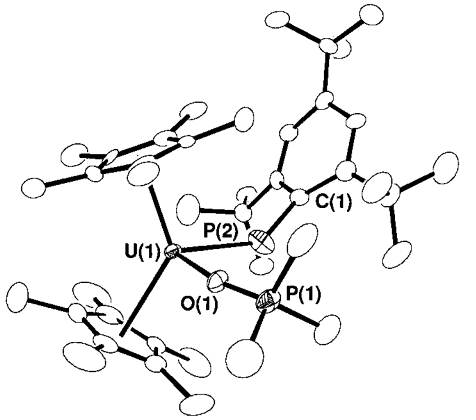
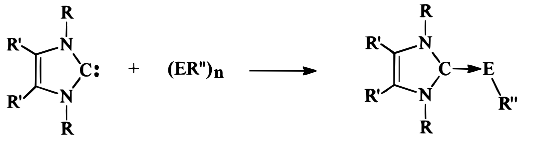


FIGURE 3. Molecular view of $(\eta^5\text{-}C_5Me_5)_2(OPMe_3)U{=}PAr^*$ (26; Ar* = 2,4,6-*t*-$Bu_3C_6H_2$).

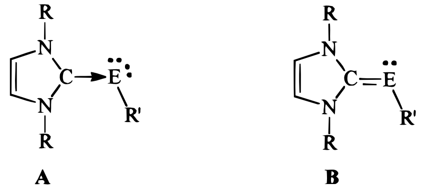
p-Block Terminal Phosphinidenes and Arsinidenes

Over 35 years ago,[34] it was reported that the reaction of trimethylphosphine with the cyclotetraphosphine $(CF_3P)_4$ affords the phosphine−phosphinidene complex, $Me_3P{\rightarrow}PCF_3$. More recently, it has been demonstrated[35,36] that stabilized carbenes are also sufficiently nucleophilic to depolymerize cyclopolyphosphines and cyclopolyarsines to produce **27**−**31** (eq 12). Two extreme canonical forms can be written for these compounds. Structure **A** is that of a terminal pnictinidene, while **B** corresponds to a conventional pnictaalkene. An interesting parallel exists between these two forms and metal carbene complexes if it is recognized that the roles of metal and carbene are played by carbene and pnictinidene, respectively, in **A** and **B**. Thus the single-bonded structure **A** resembles a Fischer-type complex and the double-bonded form **B** is akin to a Schrock-type alkylidene complex. Apart from the bond orders and oxidation states, a further conspicuous difference between structures **A** and **B** relates to the fact that they feature two and one lone pairs, respectively, at the group 15 element center. The observation that treatment of **28** with BH_3·THF resulted in exclusive forma-



(12)

27, R = R' = Me; E = P; R" = Ph; n = 5
28, R = Mes; R' = H; E = P; R" = Ph; n = 5
29, R = Mes; R' = H; E = P; R" = CF_3; n = 4
30, R = Mes; R' = H; E = As; R" = Ph; n = 6
31, R = Mes; R' = H; E = P; R" = C_6F_5; n = 4



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(32) Arney, D. S. J.; Schnabel, R. C.; Scott, B. C.; Burns, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 6780.
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(36) Arduengo, A. J., III; Calabrese, J. C.; Cowley, A. H.; Rasika Dias, H. V.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151.

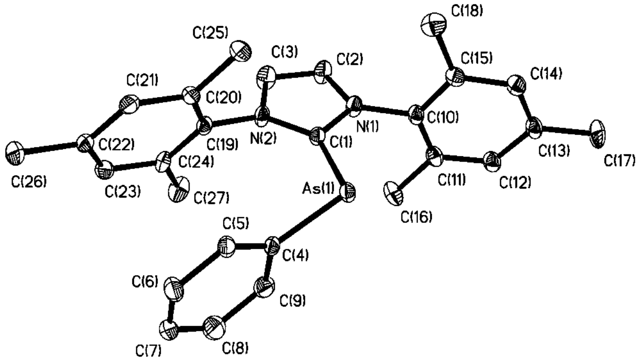
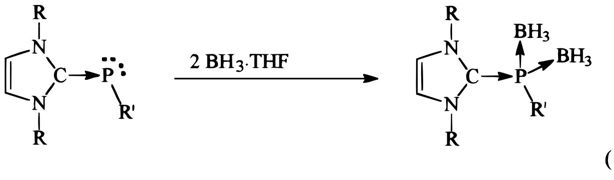


FIGURE 4. Molecular view of (1,3-dimesitylimidazol-2-ylidene)AsPh (30).

tion of the bis(borane) adduct **32** (eq 13) is consistent with



(13)

28 **32**

the predominace of structure **A**.[37] The ^{31}P NMR chemical shifts of **27** (−53.5 ppm), **28** (−28.0 ppm), and **29** (−23.63 ppm) are all upfield for two-coordinate phosphorus and thus indicative of high electron density at this center. Moreover, a preliminary bascity assessment of **28** indicates a pK_a in excess of 11.2 and cyclic voltammetry experiments reveal that the (irreversible) one-electron oxidation occurs at −0.08 V (vs SCE). Such a low oxidation potential is consistent with the transfer of negative charge to phosphorus since those of phosphaalkenes span the range +1.07 to +2.94 V (vs SCE). Further support for the pnictinidene model **A** can be garnered from X-ray structural data for **27**−**31**.[35,36] The P−C bond distances in **27** (1.794(3) Å), **28** (1.763(6) Å), and **29** (1.784(2) Å) are merely ~4% shorter than those of typical P−C bonds and considerably longer than those of phosphaalkenes. Similar comments apply to the bond distances in the arsinidene complexes **30** (1.899(3) Å) and **31** (1.902(7) Å). Another indicator of the single-bonded nature of **27**−**31** is that the angle of twist between the plane of the imidazole ring and the E−R′ bond ranges from 26.2 to 46°; moreover, the imidazole ring retains its carbene-like structure (Figure 4).

At the present time, there is a paucity of information on the reactivity of carbene−pnictinidene complexes. However, the reaction of **28** with BPh_3 results in phosphinidene extrusion and cyclopolyphosphine formation,[37] thus boding well for the possibility that carbene−pnictinidene complexes might serve as pnictinidene transfer reagents.

Concluding Remarks and Future Outlook

Despite the progress that has been made in the past few years, many exciting challenges lie ahead for this area of chemistry. From the standpoint of synthesis, abundant opportunities exist for the isolation of heavier congeneric stibinidene and bismuthinidene complexes of the d-block elements. Moreover, all the current examples of stable d-block phosphinidenes and arsinidines are of the higher oxidation state (Schrock) type. Although a substantial body of elegant work has accumulated on low-oxidation-state (Fischer-type) phosphinidenes, it would be of significant interest to isolate stabilized examples of this genre of complex. Likewise, it is important to augment the few examples of f- and p-block pnictinidene complexes. Exciting opportunities also exist for gaining a more profound understanding of the bonding in and spectroscopic properties of both the known compounds and those that the future will hold. Although synthetic and structural studies have tended to dominate the area so far, the most enduring impact of this field of chemistry is likely to be in the realm of reactivity. It is already evident that terminal phosphinidenes and arsinidenes of the d-block elements are highly reactive providing the steric bulk of the ligands is not excessive. Clearly, reactivity studies need to be extended to include the f- and p-block analogues and a further challenge exists for the development of catalytic processes involving the gamut of pnictinidene complexes. More facile, higher selectivity syntheses of known derivatives can be anticipated in addition to a cornucopia of new rings, cages, and polymers that feature group 15 elements.

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