Electrophilic “Fischer Type” Phosphinidene Complexes of Molybdenum, Tungsten, and Ruthenium

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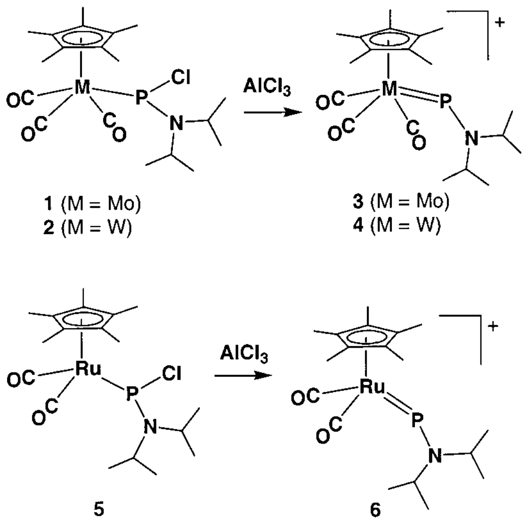
Summary: Chloride abstraction from chloroaminophosphido complexes of molybdenum, tungsten, and ruthenium leads to the terminal aminophosphinidene complexes [Cp(CO)$_3$Mo(=PN^{i}Pr$_2$)][AlCl$_4$] (**3**), [Cp*(CO)$_3$W(=PN^{i}Pr$_2$)][AlCl$_4$] (**4**), and [Cp*Ru(CO)$_2$(=PN^{i}Pr$_2$)][AlCl$_4$] (**6**). These are the first structurally characterized examples of heteroatom-substituted phosphinidene complexes, and **6** is the first example of a late transition metal phosphinidene complex.*

Despite increasing attention, well-characterized examples of terminal phosphinidene complexes remain relatively rare.[1] Most known examples contain an alkyl or aryl substituent and are formally derived from a free phosphinidene with triplet ground state and are thus analogous to nucleophilic or Schrock type carbenes.[2] Introduction of π-donor substituents onto phosphorus, however, should stabilize the singlet state of the free phosphinidene and result in electrophilic phosphinidene complexes that are analogous to electrophilic or Fischer type carbene complexes.[3] Phosphinidenes of this type have proven to be more elusive. A base-stabilized example of an aminophosphinidene complex of iron has been described,[4] and spectroscopic evidence for aminophosphinidenes has been reported by us[5] and others.[6] Transient electrophilic phosphinidene complexes generated in situ have also been reacted with a variety of organic substrates.[7] We report here the first structurally characterized heteroatom-substituted phosphinidene complexes.

The molybdenum and tungsten phosphinidene complexes **3** and **4** were formed by abstraction of chloride from the chloroaminophosphido complexes [Cp*M(CO)$_3$-{P(Cl)N^{i}Pr$_2$}] (**1**, M = Mo; **2**, M = W)[8] with AlCl$_3$, as shown in Scheme 1.[9] Complex **3** had been previously observed spectroscopically.[5] The phosphinidene complexes are thermally stable but very water sensitive.

Scheme 1



The unit cell and space group data[10] clearly show that crystals of the two complexes are isomorphous. The structures are nearly identical and will be described together. An ORTEP diagram of the cation of compound

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(8) Compounds **1** (ref 5), **2**, and **5** have been fully characterized by X-ray crystallography, spectroscopy, and elemental analysis. Crystallographic data for **2**: triclinic, $P\bar{1}$, $a = 8.4541(3)$ Å, $b = 9.0862(4)$ Å, $c = 15.1262(6)$ Å, $\alpha = 102.444(1)°$, $\beta = 98.438(1)°$, $\gamma = 96.770(1)°$, $V = 1108.82(8)$ Å^3, $Z = 2$, $D_{calc} = 1.706$, $T = 173(2)$ K, 5691 independent reflections [R(int) = 0.0311], $R = 0.217$, wR2 = 0.0591. Crystallographic data for **5**: monoclinic, $P2_1$, $a = 8.0741(9)$ Å, $b = 15.139(2)$ Å, $c = 9.031(1)$ Å, $V = 1068.2(2)$ Å^3, $Z = 2$, $D_{calc} = 1.427$, $T = 173(2)$ K, 5701 independent reflections [R(int) = 0.0726], $R = 0.0470$, wR2 = 0.1207.

(9) Data for **3**: Anal. Calcd for $C_{19}H_{29}O_3AlCl_4MoNP$: C, 37.10; H, 4.75; N, 2.28. Found: C, 37.04; H 4.90; N 2.35. IR νCO (CH_2Cl_2): 2041 s, 1986 s, 1959 s. ^{1}H NMR: δ 5.11 (septet, 1H, $^3J_{HH} = 6.6$, CH(CH$_3$)$_2$), 4.96 (doublet of septets, 1H, $^3J_{HH} = 6.7$, $^3J_{HP} = 5.9$, CH(CH$_3$)$_2$), 2.24 (singlet, 15H, C$_5$(CH_3)$_5$), 1.64 (doublet, 6H, $^3J_{HH} = 6.6$, CH_3), 1.50 (doublet, 6H, $^3J_{HH} = 6.7$, CH_3), ^{31}P NMR: δ 1007.5. Data for **4**: Anal. Calcd for $C_{19}H_{29}NO_3WPCl_4Al$: C, 32.46; H 4.16; N 1.99. Found: C, 32.93; H, 4.79; N, 2.23. IR (νCO): 2051 m, 1970 s, 1951 s. ^{1}H NMR: δ 5.10 (septet, ^{1}H, $^3J_{HH} = 6.7$, CH(CH$_3$)$_2$), 4.94 (doublet of septets, 1H, $^3J_{HH} = 7$, $^3J_{HP} = 5.5$, CH(CH$_3$)$_2$), 2.24 (singlet, 15H, C$_5$(CH_3)$_5$), 1.61 (bm, 6H, $^3J_{HH} = 7.0$, CH_3), 1.50 (doublet, 6H, $^3J_{HH} = 6.7$, CH_3). ^{31}P NMR: δ 939.4. FAB-MS (m/z): 703 [M]$^+$.

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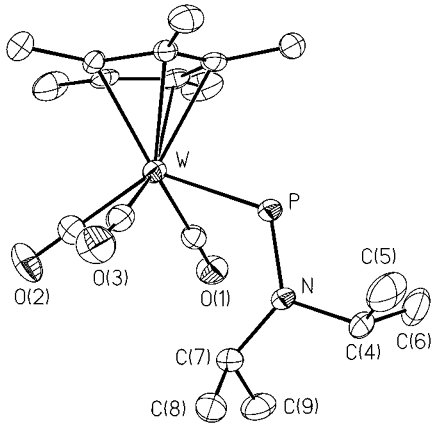

Figure 1. ORTEP diagram of the cation of complex **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been eliminated for clarity. Selected distances (Å) and angles (deg): W−P = 2.4503(6); W−C(1) = 2.005(3); W−C(2) = 2.010(3); W−C(3) = 2.008(3); P−N = 1.629(2); W−P−N = 118.69(8). Distances (Å) and angles (deg) for $[Cp^*Mo(CO)_3\{=PN^iPr_2\}][AlCl_4]$ (**3**): Mo−P = 2.4506(4); Mo−C(1) = 2.0216(17); Mo−C(2) = 2.0077(17); Mo−C(3) = 2.0074(18); P−N = 1.6309(12); Mo−P−N = 118.79(5).

4 is shown in Figure 1. The geometry at the metal is that of a square-based pyramid with three carbonyl groups and the phosphinidene ligand forming the base and with the center of the Cp* ligand occupying the apical position. All parameters involving the Cp* and carbonyl ligands are normal.

The Mo−P bond distance of 2.4506(4) Å in **3** is longer than is typical for Mo−P double bonds. In particular, it is considerably longer than the Mo−P distance of 2.370(2) Å observed in the only other structurally characterized terminal phosphinidene complex of molybdenum, namely, $[Cp_2Mo{=}P(2,4,6\text{-}^tBu_3C_6H_2)]$.[2] In fact, the Mo−P bond distance is comparable to those observed in molybdenum complexes with strongly donating phosphine ligands (for example, the average Mo−P distance in $Mo-PMe_3$ complexes is 2.462(46) Å[11]). The Mo−P bond length thus suggests that the aminophosphinidene ligand has similar σ-donor/π-acceptor capabilities as phosphines. The W−P distance of 2.4503(6) Å in **4** is identical within experimental error to the Mo−P distance and is also significantly longer than the 2.349(5) Å distance observed in $[Cp_2W{=}P(2,4,6\text{-}^tBu_3C_6H_2)]$.[12]

Apart from the metal fragment, the phosphorus atom is bound only to nitrogen with bond distances of 1.631(1) and 1.629(2) Å respectively for M = Mo and M = W. These values are intermediate between typical bond distances for P−N single bonds (e.g., 1.678(26) Å average in aminophosphines) and double bonds (e.g., 1.540(22) Å average in iminophosphines).[11] The bond angles at phosphorus (118.79(5)° and 118.69(8)°) are very close to the 120° angle expected for trigonal geometry, and the amino substituent is directed away from the Cp* ring. The geometry at nitrogen is exactly planar within experimental error. The bond angles between the three nitrogen substituents deviate from 120 Å, with the P−N−C(7) angle opened to 128.1(10)° and the other two angles compressed to compensate. This deviation is attributed to steric interaction between the C(7) isopropyl group and the carbonyl ligands. The dihedral angles M−P−N−C(7) (1.6(1)° and 2.0(3)°) and M−P−N−C(4) (178.4(1)° and 178.0(2)°) show that the entire $M-P-N-C_2$ unit is coplanar. This orientation maximizes the overlap of the nitrogen lone pair with the empty phosphorus p-orbital. Together with the planarity at nitrogen and the short P−N bond, this indicates substantial P−N multiple bond character, which is analogous to the carbon−heteroatom multiple bonding observed in Fischer type carbene complexes. The $AlCl_4$ counterion is well behaved, and packing diagrams show that there are no interactions of the anion with the phosphinidene cation.

Spectroscopically, these terminal phosphinidene complexes are characterized by extremely low-field phosphorus NMR chemical shifts, which appear at δ 1007 for the Mo complex and δ 939 for tungsten. The ^1H NMR spectra of compounds **3** and **4** show resonances for two inequivalent isopropyl groups. This inequivalence results from a barrier to rotation about the P−N bond, and there is no evidence of exchange between the two isopropyl groups at room temperature or at temperatures up to 60 °C. The infrared spectra show three bands at 2041, 1986, and 1959 cm^{-1} (M = Mo) and 2051, 1970, and 1951 cm^{-1} (M = W). A direct comparison with the carbonyl frequencies of the known phosphine complex $[Cp^*Mo(CO)_3PPh_3]^+$ (ν(CO) = 2050, 1990, 1960 cm^{-1})[13] confirms the similarity between the phosphinidene and phosphine ligands.

The clear analogy between the aminophosphinidene complexes and Fischer carbene complexes, which are well known for late transition metals, led us to consider the possibility of forming late transition metal aminophosphinidene complexes. Thus the chloroaminophosphido complex $[Cp^*Ru(CO)_2\{P(Cl)N^iPr_2\}]$ (**5**) was synthesized and reacted with $AlCl_3$. Chloride abstraction occurs as in the Mo and W complexes, leading to $[Cp^*Ru(CO)_2\{=PN^iPr_2\}][AlCl_4]$ (**6**).[14]

An ORTEP diagram of the cation of complex **6** is shown in Figure 2.[15] The molecule lies on a crystallographic mirror plane, with Ru, P, N, C(2), C(4), C(6), and C(9), as well as Al and two Cl atoms of the counterion lying in the plane. The other atoms are symmetry pairs. The geometry at Ru is that of a three-legged piano stool. The Ru−P distance of 2.2654(5) Å is slightly shorter than typical Ru−P phosphine distances in strongly donating phosphines (the average Ru−P

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(10) Crystallographic data for **3**: orthorhombic, $P2_12_12_1$, $a = 10.8686(12)$ Å, $b = 15.0956(14)$ Å, $c = 16.7128(19)$ Å, $V = 2742.0(5)$ Å^3, $Z = 4$, $D_{calc} = 1.490$, $T = 173(2)$ K, 7063 independent reflections [R(int) = 0.0226], $R = 0.0185$, wR2 = 0.0454. Crystallographic data for **4**: orthorhombic, $P2_12_12_1$, $a = 10.88712(5)$ Å, $b = 15.0794(7)$ Å, $c = 16.6946(8)$ Å, $V = 2736.8(2)$ Å^3, $Z = 4$, $D_{calc} = 1.706$, $T = 173(2)$ K, 7086 independent reflections [R(int) = 0.0365], $R = 0.0178$, wR2 = 0.0501.

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(14) Data for **6**: IR νCO (CH_2Cl_2): 2051, 2007 cm^{-1}. ^1H NMR: δ 5.06 (septet, 1H, $^3J_{HH} = 6.6$, $CH(CH_3)_2$), 4.69 (doublet of septets, 1H, $^3J_{HH} = 6.8$, $^3J_{HP} = 2$, $CH(CH_3)_2$), 2.15 (singlet, 15H, $C_5(CH_3)_5$), 1.60 (doublet, 6H, $^3J_{HH} = 6.6$, CH_3), 1.51 (doublet, 6H, $^3J_{HH} = 6.8$, CH_3). ^{31}P NMR: δ 932. FAB-MS (m/z): 593 $[M + H]^+$.

(15) Crystallographic data for **6**: orthorhombic, $Pmn2_1$, $a = 10.6688(6)$ Å, $b = 10.2497(6)$ Å, $c = 12.1164(7)$ Å, $V = 1324.95(13)$ Å^3, $Z = 2$, $D_{calc} = 1.484$ Mg/m^3, $T = 173(2)$ K, 3588 independent reflections [R(int) = 0.0225], $R = 0.0167$, wR2 = 0.0435.

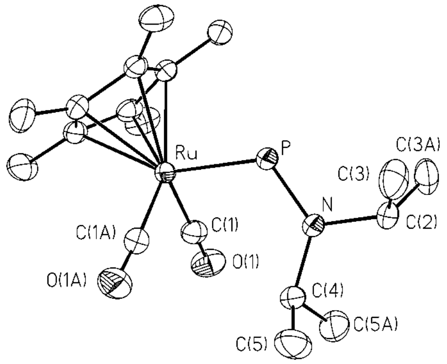


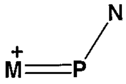
Figure 2. ORTEP diagram of the cation of complex **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been eliminated for clarity. Selected distances (Å) and angles (deg): Ru−C(1) = 1.9057(15); Ru−P = 2.2654(5); P−N = 1.6273(16); C(1)−O(1) = 1.1337(18); Ru−P−N = 119.58(6).

distance in $Ru-PMe_3$ complexes is 2.307(50) Å).[11] The P−N distance of 1.6273(16) Å does not differ significantly from the P−N distances in the Mo and W structures (1.631(1) and 1.629(2) Å), showing that there is a similar amount of π-donation from the nitrogen.

The bond angle at phosphorus is 119.58(6)°, close to the ideal trigonal bond angle of 120°. As in the Mo and W structures, the $Ru-P-N-C_2$ unit is exactly planar, although in this case, the planarity is required by the crystallographic symmetry.

As in the Mo and W complexes, the $^{31}P\{^1H\}$ resonance for the ruthenium phosphinidene complex exhibits an extreme downfield shift at δ 932, while the ^1H NMR spectrum shows two inequivalent isopropyl groups. The IR spectrum of **6** shows two bands at 2051 and 2007 cm^{-1}. A direct comparison of the IR carbonyl stretching frequencies with the known compound $[(\eta^5\text{-}C_5Me_4CH_2\text{-}OEt)Ru(CO)_2(PPh_3)]^+$ ($\nu CO = 2054, 2005\ cm^{-1}$)[16] again reveals the similar donor/acceptor properties of the phosphinidene ligand to phosphines.

Valence bond limiting structures for the phosphinidene complex are shown below. The structural parameters show that structure II, in which π-donation occurs from nitrogen to phosphorus, is important, while structure I, with π-bonding to the metal, is less significant. Density functional studies of transition metal phosphinidene complexes by Ehlers et al.[17] and Creve et al.[18] suggest that π-donation from the substituent on phosphorus plays an important role and effectively competes with back-donation from the transition metal. The structures of these phosphinidene complexes confirm that the amino group is an effective π-donor to phosphorus and that, as a result, metal−phosphorus multiple bonding is less important than in alkyl or aryl phosphinidene complexes.



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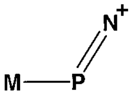

II

Compounds **3**, **4**, and **6** are the first structurally characterized examples of a new class of phosphinidene complexes, electrophilic or "Fischer type" phosphinidenes. Preliminary reactivity results show that the phosphinidene complexes indeed act as electrophiles, reacting with nucleophiles such as phosphines, acetonitrile, and THF at the phosphorus atom of the phosphinidene. A systematic study of the reactivities of these compounds is currently underway to explore their utility in synthetic phosphorus chemistry.

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Supporting Information Available: Synthetic procedures and analytical, spectroscopic, and crystallographic data for compounds **2**−**6**.

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