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Formation of P−H, P−C, and C−H Bonds by Hydride Attack on a Electrophilic Phosphide-Bridged Dimolybdenum Complex. Trapping the Phosphinidene Ligand with Borane

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*Summary: The phosphide-bridged complex $[Mo_2Cp_2(\mu\text{-}P)(CO)_2(\eta^6\text{-}HR^*)][BAr'_4]$ (**1**) [$Cp = \eta^5\text{-}C_5H_5$; $R^* = 2,4,6\text{-}C_6H_2{}^tBu_3$, $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$] is deprotonated by KH in THF at 293 K to give the (cyclopentadienylidene)phosphinidene derivative $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HR^*)(CO)_2]$. In contrast, reaction with $K[BH^sBu_3]$ at 213 K gives the cyclopentadiene complex $[Mo_2Cp(\mu\text{-}P)(CO)_2(\eta^6\text{-}HR^*)(\eta^4\text{-}C_5H_6)]$, resulting from hydride attack at a carbon atom. This compound undergoes spontaneous C−H bond cleavage above 253 K to give the phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PH)(CO)_2(\eta^6\text{-}HR^*)]$, which turns out to be the direct product of the reaction of **1** with $Li[BHEt_3]$ in THF at 213 K. This thermally unstable species can be stabilized through reaction with $BH_3{\cdot}THF$, to give $[Mo_2Cp_2\{\mu\text{-}\kappa^1{:}\kappa^1,\eta^2\text{-}HPBH_3\}(CO)_2(\eta^6\text{-}HR^*)]$, the first complex reported to have the phosphinidene−borane ($HPBH_3$) ligand.*

Since the appearance some 10 years ago of the first reports of stable complexes having a metal−phosphorus triple bond [species with terminal (M≡P)[1] or asymmetrically bridging (M≡P→M′)[2] phosphide ligands], substantial development in the synthesis and reactivity of these molecules has followed.[3] In the case of the P-bridged complexes, however, all the work has been carried out so far on neutral species, which are dominated by the nucleophilicity of their M≡P triple bonds. No information is yet available on the chemical properties of cationic complexes, which should exhibit an electrophilic behavior. Further interest in the reactivity of complexes displaying bonds between transition-metal elements and bare P atoms stems from the potentially useful information these studies can provide concerning the activity at the P sites of binary and ternary transition-metal phosphides (M_xP, $M_xM'_yP$), yet not fully understood. Indeed, these materials have been found recently to display high catalytic activities in hydrodesulfurization (HDS),[4] hydrodenitrogenation (HDN),[4] and other reactions relevant to the production of clean fuels,[5] and are serious candidates to replace the commercial catalysts currently used in these industrial processes.

Recently, we reported the synthesis of $[Mo_2Cp_2(\mu\text{-}P)(CO)_2(\eta^6\text{-}HR^*)][BAr'_4]$ (**1**), [$Cp = \eta^5\text{-}C_5H_5$; $R^* = 2,4,6\text{-}C_6H_2{}^tBu_3$, $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$], the first example of a stable cation with an asymmetrically bridged P ligand.[6] This gave us a unique opportunity for exploring its chemistry, likely to depict an electrophilic behavior. In adddition, we wanted to clarify our recent observation that compound **1** reacts with KOH in THF solution to give the (cyclopentadienylidene)phosphinidene derivative $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HR^*)(CO)_2]$ (**2**) (Chart 1).[7] The apparent acidity of the Cp protons in **1** seemed quite unusual and worth further analysis. We thus decided to study with some detail the reactions of **1** with distinct types of bases. In this paper we report our preliminary results on the reactions with different hydride sources, which have revealed an unexpected multisite reactivity, with the acidic positions located not only at the P atom but also at the H and C atoms of the Cp ligands. This in turn allows for the formation of several unusual complexes (Scheme 1).

Compound **1** is deprotonated rapidly by KH in THF at 293 K to give complex **2**, a process similar (but much faster) to that observed with KOH.[7] In contrast, very different results are obtained when using borohydride reagents as soluble sources of the hydride anion. Thus, reaction of **1** with $Li[BHEt_3]$ in THF at 213 K gives instantaneously the red-purple phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PH)(CO)_2(\eta^6\text{-}HR^*)]$ (**3**),[8] which is unstable at 293 K but could be characterized by NMR in tol-d_8 solutions at 233 K. The presence of a trigonal PH bridge is denoted by the appearance of quite deshielded ^{31}P (512.5 ppm) and ^1H (12.44 ppm) NMR resonances, with a large (one-bond) P−H coupling ($J_{HP} = 179$ Hz). Although PH ligands are well documented as bridging groups in metal clusters (μ_3 or μ_4 coordination modes),[9] the binuclear species reported so far are reduced to the symmetrically bridged $[M_2L_2(CO)_4(\mu\text{-}PH)]$ ($M = Mn$, $L = C_5Me_5$;[10a] $M = Re$, $L = C_5Me_5$, $C_5{}^iPr_5$)[9a] and the recently reported mixed-valence (asymmetrically bridged) $[Nb_2(OR)_6(\mu\text{-}PH)]$,[10b] and none of these compounds were formed

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(8) Selected data for **3**: $\nu(CO)$ (THF) 1890 (vs), 1811 (s). $^{31}P\{^1H\}$ NMR (161.97 MHz, 233 K, tol-d_8): δ 512.5 (s, μ-PH). ^1H NMR (400.13 MHz, 233 K, tol-d_8): δ 12.44 (d, $J_{HP} = 179$, 1H, PH), 4.65 (s, 3H, C_6H_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, 233 K, tol-d_8): δ 247.8 (s, br, 2 × CO).

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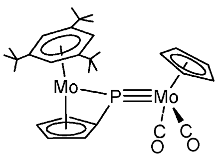
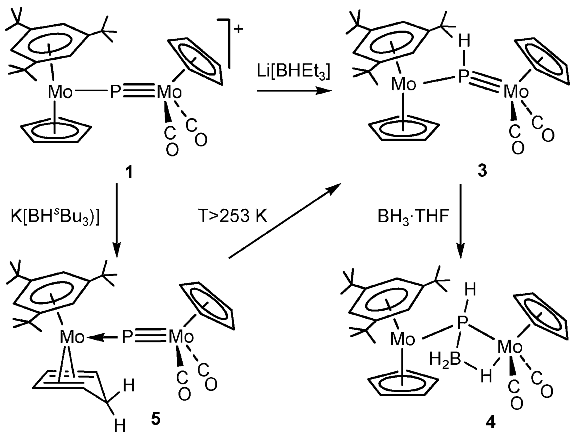
10.1021/om061097m CCC: $37.00

Chart 1



2

Scheme 1



by hydride attack on a phosphide ligand. Complete NMR data are available only for the rhenium compounds,[9a] and these are comparable to those of **3**.

To explain the above results we carried out a DFT analysis of the cation in **1**.[11] The minimized geometry reproduces well the X-ray data,[6] as it displays a quite linear and asymmetrically bound phosphide atom (Mo−P = 2.199 and 2.381 Å). These values are consistent with the presence of two orthogonal π-bonding orbitals (HOMO−3 and HOMO−5, Figure 1) mostly centered on the *short* P−Mo bond, while the partial delocalization of the latter orbital over the *long* Mo−P bond explains its somewhat short value (for a single bond). The LUMO is centered on phosphorus (Figure 1), an atom that also bears a relatively high positive charge [+0.12*e* (Mulliken) or +0.45*e* (natural population analysis)], almost comparable to those of the C(carbonyl) atoms. This explains the preferential attack of H^- at the P site, and hence the formation of **3**. Deprotonation of the cyclopentadienyl hydrogen atoms (as required to yield **2**) is unexpected because the atomic charges at the H atoms are similar in both the Cp and the HR* rings [ca. +0.20*e* (Mulliken) or ca. +0.28*e* (NPA)] and not higher than the positive charge at phosphorus. A possible interpretation is that the surface hydrides at the solid KH particles might react with the cyclopentadienyl H atoms just because the P-site is less accessible, rather than being less acidic. To check the relevance of steric effects in the chemistry of **1**, we examined its reactions with $[PPN][BH_4]$ and $K[BH^sBu_3]$.

Not unexpectedly the small-sized $[BH_4]^-$ reacts instantaneously with **1** in THF at 243 K to give **3** as the major product, but a minor species was also present. The latter could be formed quantitatively by adding BH_3·THF to the reaction mixture, and it has been identified as $[Mo_2Cp_2\{\mu\text{-}\kappa^1:\kappa^1,\eta^2\text{-}HPBH_3\}(CO)_2(\eta^6\text{-}HR^*)]$ (**4**), which is the first complex reported to have the phosphinidene−borane ($HPBH_3$) ligand.[12] In the crystal (Figure 2),[13] this ligand bridges the metal atoms through single Mo−P bonds (ca. 2.51 and 2.57 Å), while one B−H bond coordinates to the $MoCp(CO)_2$ fragment in a side-on fashion (Mo−H ca. 1.9 Å, Mo−B ca. 2.62 Å). Thus compound **4** can be viewed as an intermediate in the addition of a B−H bond of borane to the multiple Mo−P bond present in **3**, resembling the behavior of the amidophenylphosphide complex $[MoCp\{PPh(NR_2)\}(CO)_2]$ (R = $SiMe_3$) to give $[MoCp\{\eta^2,\kappa^1\text{-}H_3BPPh(NR_2)\}(CO)_2]$.[14] We note, however, that no previous reaction of borane with a trigonal PR bridge seems to have been reported, although we can quote one precedent involving a pyramidal arylphosphinidene bridge (formation of $[Pt(dppe)\{\mu\text{-}\kappa^1:\kappa^1\text{-}P(BH_3)Mes\}]_2)$,[15] in which case the BH_3 moiety does not interact with the dimetal center. Overall, the formation of **4** destroys the Mo−P multiple bond present in **3**, thus explaining the dramatic shielding of the P (630 ppm) and H (10 ppm) nuclei upon borane addition. It is conceivable that **4** could be used as a thermally stable precursor for the unstable phosphinidene complex **3**, a matter under current investigation.

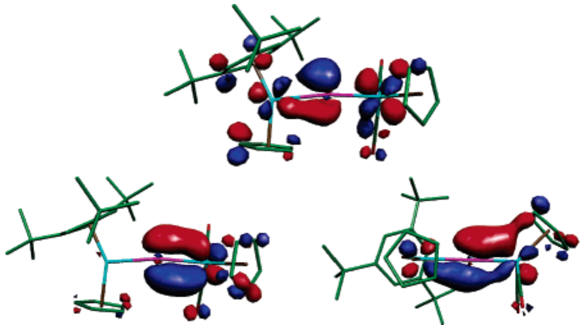


Figure 1. LUMO (up), HOMO−3 (left), and HOMO−5 (right) of the cation in **1**, from DFT calculations.

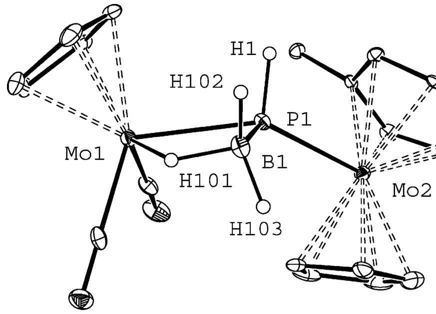


Figure 2. ORTEP diagram (30% probability) of compound **4**, with Me groups and most of the H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−P(1) 2.510(1), Mo(1)−H(101) 1.87(5), Mo(1)−B(1) 2.617(5), Mo(2)−P(1) 2.573(1), P(1)−B(1) 1.907(7), P(1)−H(1) 1.28(5), B(1)−H(101) 1.24(5), B(1)−H(102) 1.12(6), B(1)−H(103) 1.15(5); Mo(1)−P(1)−Mo(2) 138.7(1), Mo(1)−P(1)−H(1) 102(2), Mo(2)−P(1)−H(1) 110(2), Mo(1)−P(1)−B(1) 71.2(2), Mo(2)−P(1)−B(1) 124.4(2).

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(11) Density functional calculations were performed with the GAUSSIAN03 program package using the hybrid method B3LYP, together with the standard 6-31G* basis on all atoms except Mo, for which a valence double-ζ quality basis set and LANL2DZ effective core potentials were used. See Supporting Information for further details.

(12) Selected data for **4**: ν(CO) (CH_2Cl_2) 1930 (vs), 1847 (s). $^{31}P\{^1H\}$ NMR (161.95 MHz, 233 K, CD_2Cl_2): δ −120.8 (s, μ-$HPBH_3$)]. ^1H NMR (400.13 MHz, 188 K, CD_2Cl_2): δ 2.33 (d, J_{HP} = 278, 1H, PH), −0.46, −0.73 (2 × s, br, 2 × 1H, BH_2), −9.62 (br, 1H, B-H-Mo). $^{11}B\{^1H\}$ NMR (128.38 MHz, 298 K, CD_2Cl_2): δ −62.8 (s, br, $HPBH_3$).

(13) X-ray data for **4**: orange crystals, orthorhombic ($P2_12_12_1$), a = 11.3514(5) Å, b = 17.7124(8) Å, c = 29.7652(14) Å, V = 5984.6(5) Å^3, T = 100 K, Z = 8 (two independent molecules), Flack param = −0.022(9), R = 0.0342 (observed data with $I > 2\sigma(I)$), GOF = 0.983.

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The reaction of **1** with the sterically more demanding borohydride $[BH^sBu_3]^-$ revealed the presence of a third electrophilic site in the cation. Indeed, this reaction proceeds instantaneously at 213 K to give an orange solution containing as major species the cyclopentadiene complex $[Mo_2Cp(\mu\text{-}P)(CO)_2(\eta^6\text{-}HR^*)(\eta^4\text{-}C_5H_6)]$ (**5**),[16] resulting from H^- attack at a cyclopentadienyl C atom. This is highly unusual, since the Cp ligand is usually quite inert to all sorts of nucleophilic reagents. Actually, we are aware of only one precedent for this reaction, reported to occur for the cation $[FeCp(Ph_2PCH_2CH_2PPh_2)(CO)]^+$ at 344 K.[17] Since the calculated charges at the Cp carbon atoms are slightly negative, we interpret this reaction as being orbital driven, but resulting in hydride attack at the more accessible C atom rather than the P site (note the moderate contribution of a C orbital to the LUMO). Unexpectedly, **5** is stable only below ca. 253 K; otherwise it transforms into the phosphinidene **3**, a remarkable rearrangement involving the cleavage of a $C(sp^3)-H$ bond and denoting the presence of a very reactive Mo−P center. The retention of the bare P atom in **5** is readily apparent from its very strong deshielding (δ_P 1053.3 ppm, the highest one reported for a linear P bridge), and the synthetic potential of its reactive Mo−P center is under current investigation.

In summary we have shown that the phosphide compound **1** displays an unexpected multisite electrophilicity quite sensitive to the steric requirements of the reagent used, which might result in hydride attack at the phosphide, cyclopentadienyl carbon, or hydrogen atoms, to give very unusual and reactive derivatives having phosphinidene (PH), cyclopentadiene, or (cyclopentadienylidene)phosphinidene ligands, respectively. The PH complex is stabilized by coordination to borane, thus providing the first phosphinidene−borane metal complex. Further work to expand the synthetic potential of the neutral complexes here reported is now in progress.

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Supporting Information Available: Experimental procedures and spectroscopic data for new compounds and details of DFT calculations (PDF); crystallographic data for compound **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Selected data for **5**: ν(CO) (THF) 1920 (vs), 1857 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162.14 MHz, THF-d_8, 243 K): δ 1053.3 (s, μ-P) ppm. ^1H NMR (400.13 MHz, THF-d_8, 243 K): δ 5.46 (br, 2H, C_5H_4), 5.15 (br, 3H, C_6H_3), 4.22 (br, 2H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (100.63 MHz, THF-d_8, 243 K): δ 236.9 (s, 2 × CO), 87.1 [s, 2 × $CH(C_5H_6)$], 79.5, 78.2 [2 × s, 2 × $CH(C_5H_6)$], 47.9 [s, $CH_2(C_5H_6)$].

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