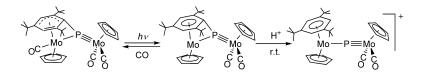Communication

Ten-Electron Coordination and Reactivity of an Arylphosphinidene Ligand

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Ten-Electron Coordination and Reactivity of an Arylphosphinidene Ligand

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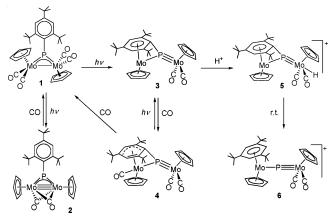John C. Jeffery,[†] and Thomas Riis-Johannessen[†]

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The chemistry of metal complexes having phosphinidene (PR, with R = alkyl, aryl, etc.) ligands is currently a very active research field in the frontier between inorganic and organic chemistry.[1] The phosphorus atom in the PR moiety has four valence electrons available for ligation and can bind from one to four metal atoms M in many different ways. In mononuclear complexes the M−P bonds have considerable multiple character, and this confers a high reactivity to the corresponding molecules. This inherent reactivity, added to the conceptual analogy established between the chemistry of multiple M−P and M−C bonds,[2] has meant that such complexes have became very useful synthetic reagents in organophosphorus and cluster chemistry.[1,2]

As we pointed out recently, the chemistry of metal−metal bonded complexes with trigonal phosphinidene bridges remains largely unexplored, and this prompted us to study the chemical behavior of the dimolybdenum complex [Mo₂Cp₂(μ-PR*)(CO)₄] (1) (R* = 2,4,6-C₆H₂tBu₃).[3] In our preliminary studies we found that UV irradiation of 1 led to the triply bonded derivative [Mo₂Cp₂(μ-PR*)-(μ-CO)₂] (2) and a minor unidentified product with a ³¹P NMR resonance at 509.7 ppm. Herein, we report an optimized synthesis of this compound, now characterized as [Mo₂Cp₂(μ-κ¹:κ¹,η⁶-PR*)-(CO)₂] (3) and describe its remarkable structure and reactivity (Scheme 1). The discovery of this 10-electron donor arylphosphin-

Scheme 1

idene ligand is relevant for different reasons apart from novelty: first, most of the PR complexes known to date have R = phenyl or 2,4,6-substituted phenyl, so that the new coordination mode now disclosed should be taken into account when analyzing the chemical transformations of any arylphosphinidene ligand at di- and poly-nuclear centers. Second, the simultaneous coordination of the bridging P and the aryl ring in a dinuclear complex is totally unexpected on geometrical grounds, as it implies a strong deviation
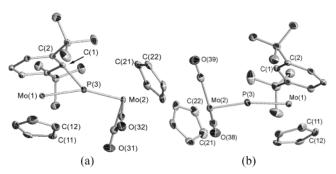
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Figure 1. View of the molecular structure of compounds 3 (a) and 6 (b). The tBu group on C(4) is omitted in both cases.

from planarity for the C atom bonded to phosphorus. Finally, the PR ligand in this new coordination environment is chemically active, and unexpected transformations, involving changes in the hapticity of the aryl ligand or the cleavage of the P−C bond, can occur under mild conditions.

Compound 3 is best prepared by UV irradiation of a concentrated tetrahydrofuran solution of 1, under a nitrogen purge. This leads to a mixture of the isomeric complexes 2 (41%) and 3 (19%).[4] In the crystal (Figure 1a),[5] the complex 3 has a PC₆H₂tBu₃ ligand which is η⁶-bound to Mo(1), while the P atom binds to both Mo centers. The constraints thus imposed lead to an unprecedented situation in which the P atom lies 1.58 Å out of the plane of the arene ring. This largely exceeds the small related distortions (less than 0.6 Å) usually found in PR*-bridged dimetal complexes. The carbon atom C(1) is therefore pyramidal, but rather than being displaced away from the metal, it is ca. 0.1 Å closer to Mo(1) [Mo(1)−C(1) = 2.202(2) Å] than are the remaining aryl ring carbons [2.315 ± 0.015 Å]. To achieve an electron count of 18 at each metal atom, the phosphorus atom should formally bind the metals via P(3)−Mo(1) single and P(3)≡Mo(2) triple bonds, respectively. The interatomic distances, however, suggest intermediate bond orders. Thus, the P(3)−Mo(2) length of 2.2480(6) Å is intermediate between the reference values found in 1 (formal P=Mo, ca. 2.30 Å)[6] and that in [WCl₂(PR*)(CO)(PMePh₂)₂] (formal P≡W, 2.169(1) Å).[7] Similarly, the P(3)−Mo(1) distance of 2.3630(6) Å is longer than a typical Mo=P bond, but much shorter than the values observed for comparable M−P single bonds [i.e. 2.550(3) Å for the single W−P length in [W₂Cp₂(μ-PR′)-(CO)₄(PH₂R′)] (R′ = 2,4,6-C₆H₂Me₃)].[8] These data suggest that the P−Mo bonds in 3 are best described by contributions from the following resonance structures: Mo−PR*≡Mo ↔ Mo⁺=PR*=Mo⁻.

A DFT calculation[9] on 3 gave minimized structural parameters in good agreement with those obtained from the X-ray diffraction study. The four frontier HOMOs for 3 are close in energy and are largely metal d-orbital in character. The latter orbital (Figure 2a) has a significant antibonding interaction between the pyramidal carbon C(1) and its adjacent ring carbons, which is consistent with
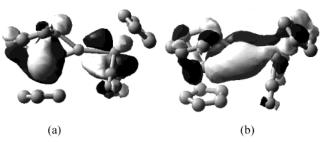
Figure 2. The HOMO-3 (a) and HOMO-4 (b) orbitals of compound **3**, from the DFT calculation, with ^{t}Bu groups omitted for clarity.

the lengthening of ca. 0.04 Å that is found for the C(1)−C(*n*) bonds (*n* = 2,6) in the crystal. The presence of a π-bonding interaction between Mo(1) and P, inferred from the X-ray interatomic distances, is supported by the nature of the HOMO-4 orbital, which shows a major contribution from a phosphorus p-orbital overlapping with d orbitals on both metals (Figure 2b).

The decarbonylation of **1** which affords **3** is reversible, and CO addition to **3** proceeds stepwise through the tricarbonyl complex [Mo$_2$Cp$_2$(μ-κ^1:κ^1,η^4-PR*)(CO)$_3$] (**4**) which then adds a further CO ligand to give **1**. Spectroscopic data for **4** reveal that a CO ligand has been added to the Mo(1) atom with a concomitant change in the hapticity of the aryl ligand, which is now π-bonded to the metal through just four of the ring C-atoms (η^4-mode).[10] This is readily deduced from the ^{13}C{^{1}H} NMR spectrum, which exhibits just four strongly shielded ring resonances.

The coordination mode of the phosphinidene in complex **4** makes this ligand act as an 8-electron donor, which has no precedent in the literature. Moreover, its formation from **3** suggests that a 6-electron coordination mode (μ-κ^1:κ^1,η^2-PR*) might occur in the next intermediate likely to be formed in the carbonylation pathway leading to **1**.

Protonation of **3** also leads to unexpected results. Reaction with [H(OEt$_2$)$_2$][BAr′$_4$], [Ar′ = 3,5-C$_6$H$_3$(CF$_3$)$_2$], occurs rapidly at 233 K to give initially the hydride complex [Mo$_2$Cp$_2$(H)(μ-κ^1:κ^1,η^6-PR*)(CO)$_2$][BAr′$_4$] (**5**).[11] Compound **5** exists in solution as an equilibrium mixture of cis and trans isomers, and at room temperature it rearranges to give the phosphido-bridged complex [Mo$_2$Cp$_2$(μ-P)(CO)$_2$(η^6-HR*)][BAr′$_4$] (**6**) in high yield.[12] An X-ray study of this product (Figure 1b)[13] confirmed the P−C cleavage in the phosphinidene ligand and formation of a new C−H bond, resulting in a π-bound arene HR* and a phosphido ligand bridging the Mo atoms in an almost linear fashion [Mo(1)−P(3)−Mo(2) 169.31(4)°]. Formal Mo−P bond orders should again be one and three, respectively. In agreement with this, the Mo(2)−P(3) length is very short, 2.1685(9) Å. However, the Mo(1)−P(3) distance of 2.3573(9) Å is at least 0.1 Å shorter than expected for a single Mo−P bond (for example, the single and triple W−P lengths in the phosphido complex [{N$_3$N}W≡P]$_2$W(CO)$_4$] [N$_3$N=(Me$_3$-SiNCH$_2$CH$_2$)$_3$N] were ca. 2.46 and 2.20 Å, respectively).[14]

Although a few dimetallic, linearly bridged phosphido complexes related to **6** are known,[15] the H$^+$ induced P−C cleavage responsible for the formation of **6** is largely unprecedented in phosphinidene chemistry. We note, however, that the phosphinidene complex [W$_2$-(μ-PCp*)(CO)$_{10}$] (Cp* = C$_5$Me$_5$) is believed to transform into the transient phosphido complex [W$_2$Cp*(μ-P)CO)$_8$] in refluxing toluene.[16a] Moreover, a sterically induced P−C bond cleavage is thought to be responsible for the formation of [Zr$_2$Cp*$_4$(μ-P)] from [ZrCp*$_2$Cl(PR*H)].[16b] DFT calculations correctly predict that the energy of **6** is some 104 kJ mol^{-1} below that of **5**, and further studies are now in progress to attempt to identify the path by which **5** rearranges to the final complex **6**.

The new coordination modes and transformations of the arylphosphinidene ligand here described may be of relevance in the field of transition-metal phosphides. These materials are currently under intense research both because of their electric properties[17] and catalytic activity in processes such as hydrodesulfurization (HDS) or dehydrodenitrogenation (HDN) of fuels.[18] It is conceivable that intermediate species having phosphorus environments similar to those found in complexes **3** to **6** might be involved in the synthesis of metal phosphides by chemical vapor deposition (CVD) techniques (for instance, MoP from MoCl$_5$ and PCyH$_2$)[19] or as chemisorbed species in the metal phosphide-catalyzed HDS or HDN of fuels.

Supporting Information Available: Experimental procedures, spectroscopic and microanalytical data for new complexes (PDF), and crystallographic data for compounds **3** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Selected spectroscopic data for **3**: *ν*(CO) (CH$_2$Cl$_2$) 1891 (vs), 1816 (s) cm^{-1}. ^{31}P{^{1}H} NMR (121.57 MHz) δ 509.9 (s, μ-PR*). ^{13}C{^{1}H} NMR (100.63 MHz) δ 242.2 (d, J_{CP} = 7, 2 × CO), 112.1 [s, ^{2,6}C(C$_6$H$_2$)], 99.3 [s, ^{4}C(C$_6$H$_2$)], 92.5, 88.0 (2 × s, Cp), 84.2 [d, J_{CP} = 74, ^{1}C(C$_6$H$_2$)], 80.2 [s, ^{3,5}C(C$_6$H$_2$)].

(5) X-ray data for **3**: Black crystals, monoclinic (*P*2$_1$/*n*), *a* = 9.952(2) Å, *b* = 19.642(4) Å, *c* = 14.316(3) Å, β = 90.39(3)°, *V* = 2798.3(10) Å^3, *T* = 100 K, *Z* = 4, *R* = 1.94, GOF = 1.052.

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(9) The structures were optimized using unrestricted B3LYP theory, together with standard 6-31G* on all atoms except Mo, for which the Jaguar triple-ζ form of the standard Los Alamos ECP basis set (LACV3P) was used. Calculations were performed with the Jaguar 4.1 program package (Schrödinger, Inc., Portland, OR, 1995−2002).

(10) Selected spectroscopic data for **4**: *ν*(CO) (CH$_2$Cl$_2$) 1961 (s), 1899 (vs), 1823 (s) cm^{-1}. ^{31}P{^{1}H} NMR (121.53 MHz) δ 476.1 (s, μ-PR*). ^{13}C{^{1}H} NMR (75.47 MHz) δ 243.9 (d, J_{CP} = 16, CO), 238.9 (d, J_{CP} = 17, CO), 234.5 (d, J_{CP} = 13, CO), 158.5 [s, ^{6}C(C$_6$H$_2$)], 126.3 [s, ^{5}C(C$_6$H$_2$)], 109.8, 108.9 [2 × s, ^{2}C and ^{4}C(C$_6$H$_2$)], 91.7, 91.4 (2 × s, 2 × Cp), 87.2 [s, ^{3}C(C$_6$H$_2$)], 78.8 [d, J_{CP} = 65, ^{1}C(C$_6$H$_2$)].

(11) Selected spectroscopic data for **5**: *ν*(CO) (CH$_2$Cl$_2$) 1986 (s), 1932 (vs) cm^{-1}. Data for *trans*-**5**: ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, 213 K) δ 5.99 (s, 2H, C$_6$H$_2$), 5.65, 5.52 (2 × s, 2 × 5H, Cp), −3.91 (d, J_{HP} = 20, 1H, Mo−H). ^{31}P{^{1}H} NMR (162.09 MHz, 213 K) δ 644.6 (s, μ-PR*).

(12) Selected spectroscopic data for **6**: *ν*(CO) (CH$_2$Cl$_2$) 1987 (vs), 1927 (s) cm^{-1}. ^{31}P{^{1}H} NMR (121.55 MHz) δ 908.5 (s, μ-P). ^{13}C{^{1}H} NMR (75.47 MHz) δ 230.2 (s, br, 2 × CO), 118.7 [s, ^{2,4,6}C(C$_6$H$_3$^{t}Bu$_3$)], 92.1, 86.1 (2 × s, 2 × Cp), 84.4 [s, ^{1,3,5}C(C$_6$H$_3$^{t}Bu$_3$)].

(13) X-ray data for **6**: Black crystals, monoclinic (*P*2$_1$/*c*), *a* = 15.1853(3) Å, *b* = 21.1676(5) Å, *c* = 19.4760(4) Å, β = 98.6950(10)°, *V* = 6188.3(2) Å^3, *T* = 100 K, *Z* = 4, *R* = 3.29, GOF = 0.910.

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