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High Yield Synthesis and Reactivity of a Phosphinidene Bridged Dimolybdenum Complex

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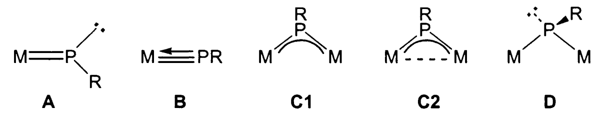
The chemistry of complexes having phosphinidene (PR) ligands is an active field within the current organometallic research.[1] The phosphinidene group is a very versatile ligand and can display several coordination modes (some shown in Chart 1).

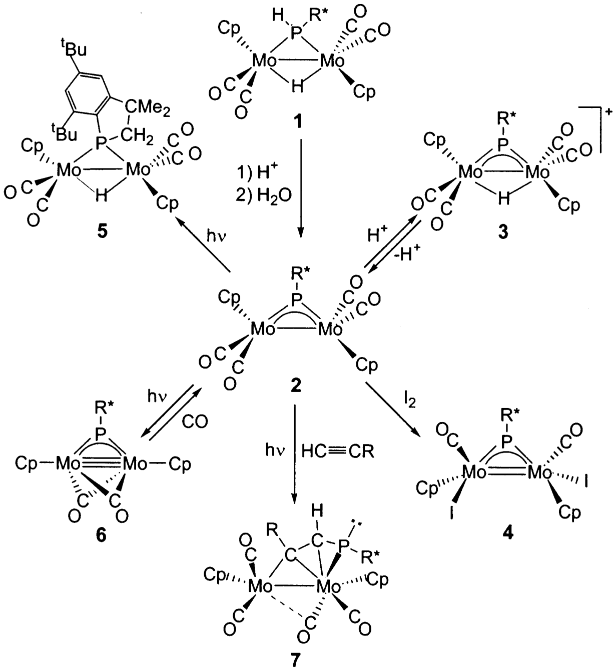
In the terminal mode (A or B), the metal−phosphorus bond has a considerable multiple character, and this confers a high reactivity to the corresponding complexes. This is especially true for the bent complexes A, which are comparable to carbene complexes and can be also classified as either electrophilic (with good π acceptor ligands around M) or nucleophilic (strong σ donors around M), this being supported by theoretical calculations.[2] These complexes have been shown to be very useful intermediates for making new P−E (E = C, O, N, S, etc.) or P−M bonds and are hence of great interest also in the field of organophosphorus or cluster chemistry. By contrast, M−P bonds in the μ_3 or μ_4 bridging modes are essentially single, and little reactivity is expected in this case. Indeed, phosphinidene groups behave usually as good supporting ligands in clusters, although some reactions involving the M−P bond can occur.[3,4]

The situation in the trigonal bridging mode C can be considered intermediate, as the M−P bond has still a considerable multiple character and should be reactive. However, while some chemistry of the open complexes (type C1) has been developed,[5] the chemical behavior of closed phosphinidene complexes (metal−metal bonded, type C2) remains largely unknown. In fact, the only reactions we can quote on these complexes are those carried out on the transient species $[Fe_2(\mu\text{-}PN^iPr_2)_2(CO)_6]$[6] or $[Fe_2(\mu\text{-}P^tBu)(CO)_6]$,[7] which can be generated in situ from suitable precursors. By contrast, no reactivity studies have been reported on the few stable compounds of type C2 previously known. This could be due in part to the lack of good synthetic routes to these compounds. In this paper, we report a new high yield synthesis for Cowley's complex $[Mo_2Cp_2(\mu\text{-}PR^*)(CO)_4]$ (**2**) (Cp = η^5-C_5H_5; R* = 2,4,6-$C_6H_2{}^tBu_3$).[8] This has allowed us to start a wide study on its reactivity. Our preliminary results, here presented, indicate that the phosphinidene ligand in **2** behaves in part as a robust supporting group, preserving the nuclearity of the dimetallic unit through a number of reactions such as protonation, halogenation, or decarbonylation. However, the Mo−P bond becomes chemically active under UV conditions, and intramolecular C−H oxidative addition or intermolecular insertion of alkynes is induced under these conditions (Scheme 1).

Chart 1



Scheme 1. (R* = 2,4,6-$C_6H_2{}^tBu_3$)



The hydrido-phosphido precursor $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PHR^*)(CO)_4]$ (**1**) can be conveniently prepared (93%) by reaction of $[Li(THF)_3][PHR^*]$ and $[Mo_2Cp_2(CO)_4]$, followed by protonation of the resulting green phosphido anion with 85% H_3PO_4.[9] Protonation of **1** with $HBF_4 \cdot OEt_2$ occurs instantaneously to give a dark green intermediate which, treated with water, yields the phosphinidene complex **2** in 95% yield. The above intermediate can be selectively and reversibly formed from **2** and $HBF_4 \cdot OEt_2$ and has been identified as the hydrido-phosphinidene complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR^*)(CO)_4]BF_4$ (**3**).[10] The Mo−P in **2** is stable toward I_2 addition, which occurs at the dimetal center instead, giving $[Mo_2Cp_2I_2(\mu\text{-}PR^*)(CO)_2]$ (**4**).[11] In the crystal (Figure 1),[12] compound **4** displays a structure closely related to that of **2**.[8] The Mo−P lengths are also short (2.294(2) Å) and therefore indicative of multiple bond character. However, the intermetallic length in **4** (2.960(2) Å) is much shorter than that in **2** (3.220(3) Å), in agreement with the double Mo−Mo bond resulting from the application of the EAN formalism to **4**. To our knowledge, compound **4** represents the first

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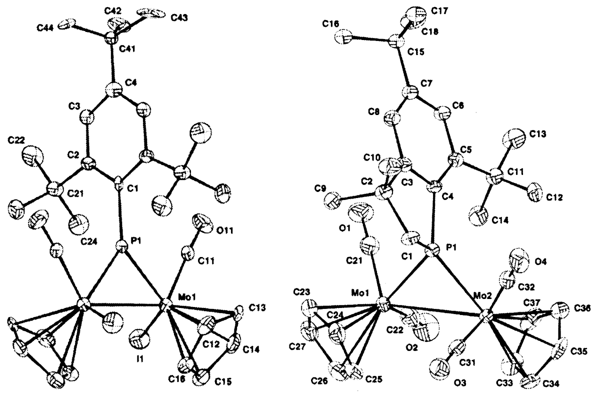

Figure 1. Molecular structure of compounds **4** (left) and **5** (right, hydride ligand not located).

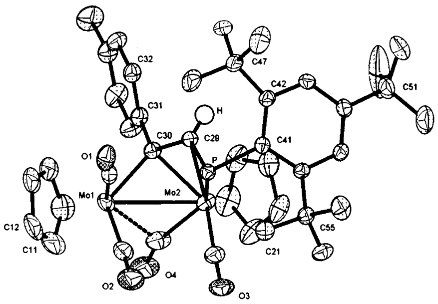

Figure 2. Molecular structure of compound **7**.

example of a complex exhibiting a phosphinidene ligand bridging a formally double metal−metal bond.

The stability of the Mo−P bonds in **2** is high, as further illustrated by the absence of changes even in refluxing xylenes. However, the situation changes dramatically under UV irradiation, which leads to a mixture of the hydridophosphido $[Mo_2Cp_2(\mu\text{-}H)\{\mu\text{-}P(CH_2CMe_2)C_6H_2{}^tBu_2\}(CO)_4]$ (**5**) (major), phosphinidene $[Mo_2Cp_2(\mu\text{-}PR^*)(\mu\text{-}CO)_2]$ (**6**), and a third product yet unidentified (δ_P = 509.7 ppm). Spectroscopic[13] and X-ray data for **5** (Figure 1)[14] have allowed us to identify this product as a result of the oxidative addition of a C−H(^{t}Bu) bond to a formally double P═Mo bond in **2**. This is in contrast with some related C−H cleavages induced by bent phosphinidenes, which invariably lead to the oxidative addition at the P atom (then forming a secondary phosphine ligand).[1a,15,16] This could be an indication that closed phosphinidene bridges might display reactivity patterns different from those of bent PR complexes.

Complex **6** can be selectively formed upon photolysis of THF solutions of **2** and a small amount of MeCN. This compound bears just two carbonyls and a PR* bridge[17] and would thus represent the first example of a complex having a phosphinidene ligand bridging a formally triple metal−metal bond. A rich chemistry can be anticipated from the concurrence of both M−P and M−M multiple bonds within the same molecule, and studies in that direction are being currently carried out in our laboratory.

The formation of **5** suggests the presence of a reactive, but not dissociative, photoexcited state for **2**. Indeed, photolysis of **2** in the presence of HC≡C(*p*-tol) gives also a tetracarbonylic species, this being the metallaphosphaallyl complex $[Mo_2Cp_2\{\mu\text{-}\eta^1:\eta^2,\kappa\text{-}C(p\text{-tol})CHPR^*\}(CO)_4]$ (**7**).[18] The structure of **7** (Figure 2)[19] reveals that an alkyne insertion into a Mo−P has occurred, but the piramidal environment around the P atom is unexpected. The proposal of a 32 e$^-$ bent structure for the nondissociative photoexcited state of **2** (type D in Chart 1) is then quite attractive. In any case, the synthetic potential of compound **2** under photochemical conditions can be anticipated to be high.

In summary, we have shown that the phosphinidene ligand in compound **2** is robust enough so as to preserve the dimetal center from disruption in a number of reactions. It can span not only single, but also double or triple metal−metal bonds. In contrast, the phosphinidene bridge becomes quite reactive under UV excitation, and a rich chemistry centered at the Mo−P bond can be thus anticipated under the right experimental conditions. This might follow patterns distinct from those well established for mononuclear bent phosphinidene complexes.

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Supporting Information Available: Experimental procedures and microanalytical data for new complexes (PDF), and crystallographic data for compounds **4**, **5**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Selected spectroscopic data for **1**: ν(CO) (CH_2Cl_2) 1965 (w, sh), 1940 (vs), 1865 (s) cm^{-1}. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 243 K): δ 7.94 (d, J_{HP} = 355, 1H, HP), 5.52, 5.19 (2 × s, 2 × 5H, Cp), −12.99 (d, J_{HP} = 36.5, 1H, μ-H). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 243 K): δ 80.5 (s, μ-PHR*).

(10) Selected spectroscopic data for **3**: ν(CO) (CH_2Cl_2) 2025 (w), 1997 (vs), 1966 (s), 1952 (s, sh) cm^{-1}. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 5.76 (s, 10H, Cp), −9.15 (d, J_{HP} = 51, 1H, μ-H). $^{31}P\{^1H\}$ NMR (81.08 MHz, CD_2Cl_2): δ 724.9 (s, μ-PR*).

(11) Selected spectroscopic data for **4**: ν(CO) (CH_2Cl_2) 1942 (s, sh), 1925 (vs) cm^{-1}. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 5.24 (d, J_{HP} = 0.5, 10H, Cp). $^{31}P\{^1H\}$ NMR (81.07 MHz, CD_2Cl_2): δ 596.4 (s, μ-PR*).

(12) X-ray data for **4**: black crystals, monoclinic (*C*2/*c*), $a = 14.673(5)$ Å, $b = 14.438(6)$ Å, $c = 16.653(16)$ Å, $\beta = 113.13(5)°$, $V = 3244(4)$ Å^3, $T = 295$ K, $Z = 4$, $R = 0.042$, GOF = 1.13.

(13) Selected spectroscopic data for **5**: ν(CO) (CD_2Cl_2) 1959 (w, sh), 1936 (vs), 1862 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.49, 5.33 (2 × s, 2 × 5H, Cp), 3.07 (t, $J_{HP} = J_{HH}$ = 14, 1H, CH_2), 1.51 (s, 6H, CMe_2), 1.40, 1.18 (2 × s, 2 × 9H, ^{t}Bu), 1.36 (m, 1H, CH_2), −12.55 (d, J_{HP} = 37, 1H, μ-H). $^{31}P\{^1H\}$ NMR (121.51 MHz): δ 166.8 (s, μ-P).

(14) X-ray data for **5**: red crystals, monoclinic ($P2_1/c$), $a = 13.630(2)$ Å, $b = 13.612(3)$ Å, $c = 16.664(6)$ Å, $\beta = 98.05(2)°$, $V = 3061(1)$ Å^3, $T = 295$ K, $Z = 4$, $R = 0.0599$, GOF = 0.99.

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(17) Selected spectroscopic data for **6**: ν(CO) (CH_2Cl_2) 1741 (m), 1709 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (121.57 MHz, CD_2Cl_2): δ 532.1 (s, μ-PR*). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 223 K): δ 296.0 (d, J_{CP} = 14, μ-CO), 98.0 (s, Cp).

(18) Selected spectroscopic data for **7**: ν(CO) (CH_2Cl_2) 1959 (vs), 1915 (s), 1948 (m), 1806 (w) cm^{-1}. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 5.80 (s, 1H, CH), 4.77, 4.39 (2 × s, 2 × 5H, Cp). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 18.1 (s, κ-P). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 179.1 (d, J_{CP} = 39, μ-C), 114.4 (d, J_{CP} = 64, HCP).

(19) X-ray data for **7**. 1/2 C_6H_{12}: green crystals, monoclinic ($P2_1/c$), $a = 10.1070(12)$ Å, $b = 24.320(3)$ Å, $c = 16.839(2)$ Å, $\beta = 98.224(17)°$, $V = 4096.3(8)$ Å^3, $T = 173(2)$ K, $Z = 4$, $R = 0.0368$, GOF = 0.955.

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