Inorg. Chem. **2007**, *46*, 6230–6232

Inorganic Chemistry
Communication

Carbene- and Carbyne-like Behavior of the Mo–P Multiple Bond in a Dimolybdenum Complex Inducing Trigonal-Pyramidal Coordination of a Phosphinidene Ligand

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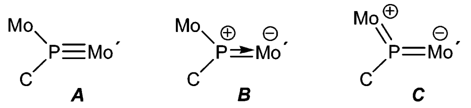
Received May 30, 2007

The phosphinidene complex $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}R^*H)]$ (**2**; Cp = η^5-C_5H_5; R* = 2,4,6-$C_6H_2{}^tBu_3$) has substantially different Mo–P bonds and displays a high reactivity located at the short Mo–P bond. Sideways cycloaddition or addition processes are observed toward RC≡CR, HCl, and $[Fe_2(CO)_9]$, to give respectively metallacyclobutene and arylphosphide-bridged and heterometallic phosphinidene-bridged derivatives, a behavior reminiscent of the nucleophilic mononuclear phosphinidene complexes (carbene-like behavior), which is in good agreement with the ground-state electronic structure of **2** derived from density functional theory calculations. However, the reaction of **2** with $[Co_2(CO)_8]$ implies the addition of two cobalt fragments to its short Mo–P bond and thus reveals a carbyne-like behavior of compound **2**. In most of the new products, the P atom displays an unprecedented trigonal-pyramidal-like environment, instead of the expected tetrahedral distribution of bonds.

Coordinatively unsaturated phosphorus species exhibit fascinating structural and electronic features and also provide for novel applications as synthetic reagents. As a result, they are currently under intense research at the frontier between inorganic and organic chemistry.[1] In this context, the chemistry of phosphinidenes (PR, with R = alkyl, aryl, etc.) and their metal complexes occupies a relevant position,[2] much stimulated by its analogy with carbene chemistry.[2a−d] The latter derives from the similarity between the M−C and M−P bonds in terminal carbene and bent-phosphinidene complexes, and this is why mononuclear PR complexes are remarkably versatile and have been extensively studied.[2] In contrast, the chemistry of phosphinidene-bridged binuclear complexes has been comparatively little explored even when the presence of multiple M−P bonding makes these molecules potentially reactive.[3,4] While studying the reactivity of the binuclear complex $[Mo_2Cp_2(\mu\text{-}PR^*)(CO)_4]$, we discovered its selective transformation into the asymmetric species $[Mo_2Cp_2(\mu\text{-}\kappa^1{:}\kappa^1,\eta^6\text{-}PR^*)(CO)_2]$ (**1**) and $[Mo_2Cp(\mu\text{-}\kappa^1{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}R^*H)]$ (**2**) (Cp = η^5-C_5H_5; R* = 2,4,6-$C_6H_2{}^tBu_3$), which exhibit unprecedented coordination modes of a phosphinidene ligand.[3,5] Both products have a PR group connecting 17- and 15-electron metal fragments, a circumstance rarely found previously.[6] In such a situation, several resonance forms can be used to describe the Mo−P bonds (three of them shown in Chart 1; Mo′ stands for the 15-electron fragment),[3] which suggests the attractive idea that the reactivity of these multiple Mo−P bonds might be related to that of the double M═C bonds (carbene complexes) or even to that of the triple M≡C bonds (carbyne complexes).

Chart 1



Although the data available for **1** suggest considerable multiplicity in the P−Mo′ bond, the reactivity of this bond is limited by the considerable steric crowding in its vicinity. We then turned to study complex **2**, with a more exposed P−Mo′

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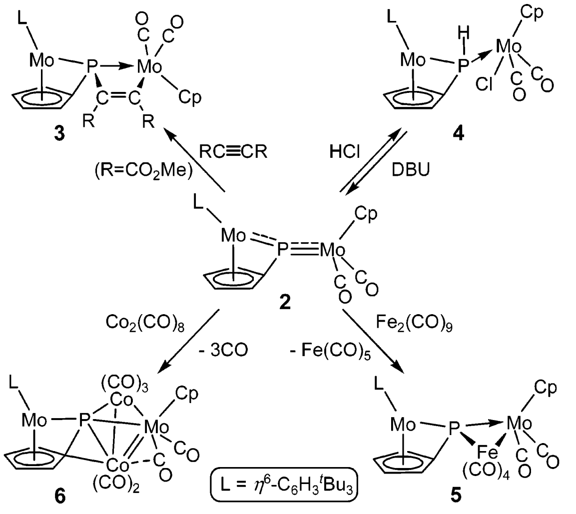
10.1021/ic701055y CCC: $37.00

Scheme 1



bond. As it will be discussed next, both the ground-state structure of **2** and part of its reactivity are more consistent with a description in terms of a P−Mo′ double bond, but other aspects of its reactivity are reminiscent of that expected for a triple bond. Thus, relationships with both the carbene and carbyne complexes can be established. In addition, most of the reaction products have been found to display an unusual geometry around the P atom, derived from a trigonal-pyramidal (TP) rather than tetrahedral distribution of bonds around (Scheme 1).

In the crystal, compound **2** has a PC$_5$H$_4$ ligand that is η^5-bound to Mo(2) while the P atom binds to both Mo centers (Figure 1).[7] Thus, the PR ligand in **2** acts as a 9-electron donor, which itself is unprecedented. The carbon atom C(8) is pyramidal (sum of the angles = 327.6°), but it is still strongly bound to the both P [1.807(6) Å] and Mo [2.208(5) Å] atoms, and the Mo−P distances suggest intermediate orders for these bonds. Thus, the P(1)−Mo(1) length of 2.252(2) Å is somewhat longer than the reference values of 2.13−2.20 Å expected for triple Mo≡P bonds and similar to those found for 3-electron donor PR$_2$ and related terminal ligands.[3] On the other hand, the P(1)−Mo(2) distance of 2.403(1) Å is substantially shorter than the values observed for comparable M−P single bonds [i.e., 2.550(3) Å for the single W−P length in the asymmetrically bridged [W$_2$Cp$_2$(μ-PR′)(CO)$_4$(PH$_2$R′)] (R′ = 2,4,6-C$_6$H$_2$Me$_3$)].[6a]

A density functional theory (DFT) calculation on **2** revealed that the π-bonding interaction between Mo and P atoms is mainly described by highest occupied molecular orbital (HOMO)−1, localized on the short Mo−P bond, and HOMO−4, delocalized over the Mo−P−Mo skeleton (Figure 2).[8] The lowest unoccupied molecular orbital (LUMO) has π-antibonding Mo−P character, and then the HOMO−1/LUMO pair resembles the characteristic frontier orbitals of double bonds. All of this suggests that at least the forms **B** and **C** in Chart 1 are needed to describe the bonding in **2**, while **A** possibly has only a minor contribution to the ground-state structure. In any case, the chemistry observed so far for **2** is derived from the multiplicity of the P−Mo′ bond (Scheme 1).

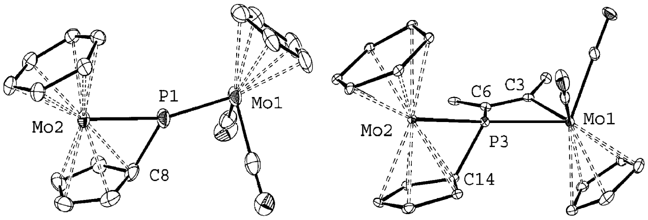


Figure 1. Molecular structures of compounds **2** (left) and **3** (right), with H atoms and ^{t}Bu groups omitted for clarity.

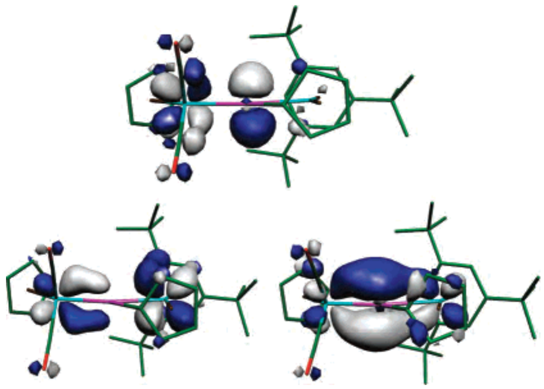


Figure 2. LUMO (up), HOMO−1 (left), and HOMO−4 (right) orbitals of compound **2** viewed from the Mo$_2$P plane, according to DFT calculations.

The treatment of **2** with C$_2$R$_2$ in toluene at 95 °C leads to [Mo$_2$Cp{μ-κ^1,η^1:κ^1,η^5-P(C$_5$H$_4$)RC═CR}(CO)$_2$(η^6-R*H)] (**3**; R = CO$_2$Me).[9] This rare [2 + 2] cycloaddition of the alkyne along the multiple P−Mo′ bond is reminiscent of the cycloaddition reactivity observed for nucleophilic zirconium[2e] and titanium phosphinidene complexes.[10] The almost planar phosphametallacycle in **3** (Figure 1)[11] displays a C(3)−C(6) length of 1.352(4) Å, consistent with a double C═C bond and a Mo(1)−P bond length of 2.4810(8) Å, comparable to the values of dative single P → Mo bonds (cf. PR$_3$ complexes), while the Mo(2)−P length of 2.5136(9) Å is now closer to the reference values for single Mo−P bonds. The environment of the P atom is most unusual, with a TP-like rather than tetrahedral distribution of bonds around because the Mo, P, and C(6) atoms are almost in the same plane, while the carbon atom C(14) binds the P atom from below that plane.

The multiple P−Mo′ bond in **2** experiences the instantaneous addition of ethereal HCl to give the chloro complex

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(7) X-ray data for **2**: dark-red crystals, monoclinic ($P2_1/n$), a = 9.9404(3) Å, b = 20.2853(7) Å, c = 14.4831(5) Å, β = 96.217(2)°, V = 2903.25(17) Å^3, T = 120 K, Z = 4, R = 0.0194, GOF = 1.083.

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

(9) Selected data for **3**. IR [ν(CO), CH$_2$Cl$_2$]: 1944 (vs), 1864 (s), 1743 (w), 1696 (m) cm^{-1}. ^{31}P{^{1}H} NMR (toluene-d_8): δ −24.0 (s, μ-PC$_5$H$_4$). ^{13}C{^{1}H} NMR: δ 199.2 [d, J_{PC} = 25 Hz, C═C], 176.2 [d, J_{PC} = 27 Hz, C═C].

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(11) X-ray data for **3**: dark-green crystals, monoclinic ($P2_1/c$), a = 12.4010(2) Å, b = 14.8569(3) Å, c = 20.2993(5) Å, β = 116.633(2)°, V = 3441.0(14) Å^3, T = 100 K, Z = 4, R = 0.0305, GOF = 1.057.

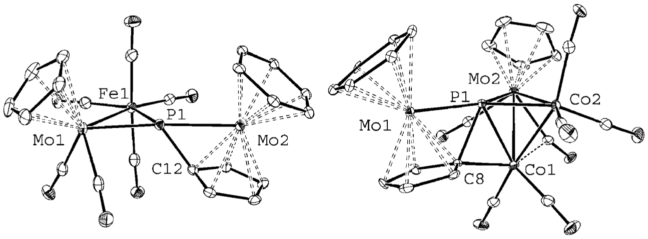

Figure 3. Molecular structures of compounds **5** (left) and **6** (right), with H atoms and ^{t}Bu groups omitted for clarity.

[$Mo_2Cp\{\mu$-κ^1:κ^1,η^5-$P(H)C_5H_4\}(Cl)(CO)_2(\eta^6$-R*H)] (**4**),[12] which is obtained as an inseparable mixture of two diastereoisomers. This reaction can be fully reversed by the addition of a strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene. The observed regioselectivity, with only the proton binding the P atom (δ_P ca. -14 ppm, $J_{PH} = 290$ Hz), is again reminiscent of the chemistry of nucleophilic PR complexes.[2d,e]

The multiple P−Mo′ bond in **2** is basic enough to add unsaturated metal fragments of the type $M(CO)_x$, thus providing a rational route to heterometallic species bridged by PR ligands. In the reaction with $[Fe_2(CO)_9]$, one $Fe(CO)_4$ fragment adds to the P−Mo′ bond sideways to give the trimetal complex [$FeMo_2Cp(\mu$-κ^1:κ^1:κ^1,η^5-$PC_5H_4)(CO)_6(\eta^6$-R*H)] (**5**),[13] a process comparable to a cyclopropanation reaction if we consider the pertinent isolobal relationships. There is just one precedent of a similar reaction, this involving the asymmetric phosphinidene complex [FeMn(μ-PR)(C_5Me_5)$(CO)_6$], although the corresponding product was not characterized at the time.[6c] In the crystal (Figure 3),[14] the P atom displays again an unusual TP geometry, being trigonally bound to the metal atoms (sum of the M−P−M angles = 359.6°) and to the carbon atom C(12) below that plane. To our knowledge, this geometry is unprecedented for a PR ligand, and perhaps it is behind the anomalous ^{31}P NMR chemical shift of **5** (205.5 ppm), more than 200 ppm lower than that expected for a μ_3-PR ligand.[3,15] The interatomic distances in the Fe−P−Mo(1) ring of **5** are similar to those in the PCy_2-bridged complex [FeMoCp(μ-PCy_2)$(CO)_6$],[16] and the P−Mo(2) distance [2.5953(7) Å] is now much longer than the P−Mo(1) distance in that ring [2.4390(7) Å], thus supporting the description of these bonds as essentially single Mo−P and dative Mo → P bonds, respectively.

Up to two $M(CO)_x$ units can be added to the multiple P−Mo′ bond in **2**, as found in the reaction with $[Co_2(CO)_8]$, to give the unsaturated cluster [$Co_2Mo_2Cp(\mu$-κ^1:κ^1:κ^1:κ^1,η^5-$PC_5H_4)(CO)_7(\eta^6$-R*H)] (**6**).[17] The PR ligand in **6** exhibits also a quite shielded ^{31}P NMR resonance at 256.5 ppm. Indeed, its crystal structure discloses again an unprecedented geometry around the P atom (Figure 3).[18] As found for **5**, the P atom is trigonally bound to three metal atoms in a plane [Mo(1), Mo(2), and Co(2)], while the apical position of the TP is now occupied by incipiently bonded Co(1) and C(8) atoms, with the latter at an intermediate point of migration from P(1) to the Co(1) atom. Accordingly, the distances C(8)−P [1.962(6) Å] and C(8)−Co(1) [2.112(6) Å] are some 0.15 Å longer than the corresponding single-bond values. The Mo−P lengths [2.464(2) and 2.399(2) Å] are shorter than those in **5** or **3**, perhaps indicating that some multiplicity is retained in these bonds (see below). All other interatomic distances are normal except for the short Co(1)−Mo(2) distance [2.660(1) Å], obviously related to the electronic unsaturation in the $MoCo_2$ triangle (46 electrons). The formation of **6** is reminiscent of the reactions of the carbyne complexes [ML(CR)$(CO)_2$] (M = Cr, Mo, W; L = Cp or related ligand) with $[Co_2(CO)_8]$ to give the metallatetrahedrane clusters [$MCo_2(\mu_3$-CR)L$(CO)_8$][19] and thus reveals a carbyne-like behavior of compound **2**.

In summary, we have shown that the phosphinidene complex **2** contains an unsaturated Mo−P−Mo skeleton highly reactive on its short P−Mo′ bond. The latter is possibly best described as a double bond, thus explaining the analogies with the nucleophilic mononuclear phosphinidene complexes (carbene-like behavior), but similarities to the behavior of metal carbyne complexes can be also established. The TP-like environment of the P atom in compounds **3**, **5**, and **6** appears to have no precedent in the chemistry of PR_x ligands ($x = 1-3$). It is conceivable that some residual π interaction in the Mo−P−Mo framework is responsible for this unusual geometry, a matter under current study.

Acknowledgment. We thank the MEC of Spain for a grant (to D.G.-V.) and financial support (Grant CTQ2006-01207/BQU).

Supporting Information Available: Preparative and spectroscopic data for new complexes and details of DFT calculations (PDF) and crystallographic data for **2**, **3**, **5**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Selected data for **4**. IR [ν(CO), petroleum ether]: 1969 (vs), 1885 (d), 1874 (m) cm^{-1}. ^{31}P NMR (CD_2Cl_2): δ −14.5 (d, $J_{PH} = 290$ Hz, μ-PHC_5H_4, major isomer), −13.8 (d, $J_{PH} = 290$ Hz, μ-PHC_5H_4, minor isomer).

(13) Selected data for **5**. IR [ν(CO), petroleum ether]: 2056 (vs), 2002 (m), 1985 (s), 1976 (vs), 1927 (vs), 1860 (m) cm^{-1}. ^{31}P{^{1}H} NMR: δ 205.5 (s, μ-PC_5H_4).

(14) X-ray data for **5**: brown crystals, monoclinic ($P2_1/c$), $a = 12.4010(2)$ Å, $b = 14.8569(3)$ Å, $c = 20.2993(5)$ Å, $\beta = 116.633(2)°$, $V = 3343.13(12)$ Å^3, $T = 150$ K, $Z = 4$, $R = 0.0331$, GOF = 1.062.

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(17) Selected data for **6**. IR [ν(CO), CH_2Cl_2]: 2039 (vs), 1997 (vs, br), 1976 (m, sh), 1942 (w), 1918 (w, sh), 1765 (w, br) cm^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 K): δ 256.5 (br, μ-PC_5H_4).

(18) X-ray data for **6**: brown crystals, monoclinic ($P2_1/c$), $a = 9.7590(1)$ Å, $b = 17.3399(2)$ Å, $c = 22.6713(2)$ Å, $\beta = 97.326(1)°$, $V = 3805.12(7)$ Å^3, $T = 100$ K, $Z = 4$, $R = 0.0524$, GOF = 1.089.

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