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Unusual Reactivity of the Unsaturated Dimolybdenum Complex [$Mo_2(\eta^5$-$C_5H_5)_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_2$]

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Reaction of the doubly metal−metal bonded compound [$Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_2$] with [$Fe_2(CO)_9$] leads to the 46 e^- cluster [$FeMo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_5$]. By contrast, reaction of [$Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_2$] with $SnCl_2$ leads to the incorporation of two molecules of reagent: one molecule inserts into the Mo−O bond, and the other one adds to the Mo═Mo double bond to finally yield the tetranuclear compound [$Mo_2Cp_2\{\mu$-$(EtO)_2POSnCl_2\}\{\mu$-$P(OEt)_2\}(\mu$-$SnCl_2)(CO)_2$] as confirmed by an X-ray diffraction study. Complex [$Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_2$] reacts with HCC(p-C_6H_4Me) to give a mixture of the alkyne-bridged compound [$Mo_2Cp_2\{\mu$-η^2:η^2-HCC(p-C_6H_4Me)$\}\{\mu$-$(EtO)_2POP(OEt)_2\}(CO)_2$] and the alkenyl-bridged [$Mo_2Cp_2\{\mu$-η^1,κ^1:η^2-$OP(OEt)_2CH$═$C(p$-$C_6H_4Me)\}\{\mu$-$P(OEt)_2\}(CO)_2$] (structure confirmed through an X-ray diffraction study). This requires either P−O reductive elimination between phosphonate and phosphido ligands or insertion of the incoming alkyne into the Mo−P (phosphonate) bond, all these uncommon processes occurring at room temperature. The solution structure of the new compounds is analyzed on the basis of their IR and NMR data and X-ray diffraction studies, and the reaction pathways prevalent for the title compound are discussed on the basis of the data available.

Introduction

The reactivity of complexes having multiple metal−metal bonds has been a lively research area during the last years,[1] and much effort has been dedicated to the understanding of the many factors governing the chemical behavior of the dimetal center in these species. Some of the most important factors are the electronic and steric properties of the coordinated ligands, their influence being more critical when these ligands act as bridges between the metals involved in the multiple M−M bond. The unsaturated cyclopentadienyl carbonyls of general formula [$M_2Cp_2(CO)_x$] (M = transition metal, Cp = η^5-C_5H_5, x = 2−5) form an important class within the organometallic complexes having multiple intermetallic bonds, because of both their electronic structure and wide reactivity, which makes them useful synthetic reagents.[2] We have previously studied the decarbonylation reactions of the complexes [$M_2Cp_2(CO)_4(\mu$-$L_2)$] [M = Mo or W; L_2 = $Ph_2PCH_2PPh_2$, $Me_2PCH_2PMe_2$, $(EtO)_2POP(OEt)_2$][3] as a synthetic approach to diphosphine-stabilized unsaturated cyclopentadienyl compounds. From these studies we have concluded that the formation of multiple M−M bonds competes with several intramolecular oxidative additions such as those from the C−H (cyclopentadienyl) or backbone P−C and P−O bonds in the bridging phosphorus ligands. During these studies we found that the thermal cleavage of a backbone P−O bond in the molybdenum complex [$Mo_2Cp_2\{\mu$-$(EtO)_2POP(OEt)_2\}(CO)_4$] gave the unsaturated compound [$Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_2$] (**1**) in high yield.[3d] There were two points of interest in the chemical behavior of **1**. First, this compound was found to carbonylate readily to give either [$Mo_2Cp_2\{\mu$-$OP(OEt)_2\}\{\mu$-$P(OEt)_2\}(CO)_4$] or the starting complex [$Mo_2Cp_2\{\mu$-$(EtO)_2POP(OEt)_2\}(CO)_4$], depending on the reaction conditions (Scheme 1), thus providing the first example of reversibility of the P−O cleavage in this type of bridging diphosphite ligand. Second, compound **1** combines the presence of a double M═M bond with a bridging alkoxyphosphido group, itself a poorly studied ligand. We therefore decided to explore the reactivity of compound **1** in some more detail. By taking into account the significant differences in the bridging ligands, we could anticipate a chemical behavior quite different from that shown by the isoelectronic diphenylphosphido complex [$Mo_2Cp_2(\mu$-$CH_2PPh_2)(\mu$-$PPh_2)(CO)_2$].[3b,4] In this paper we report some reactions of

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Scheme 1. Carbonylation/Decarbonylation Reactions of Compound 1[3d]

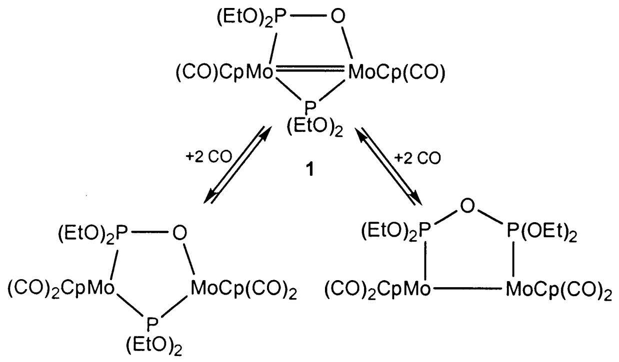
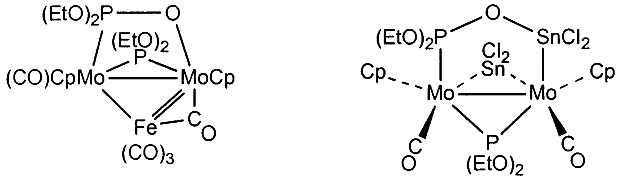


Chart 1



2 **3**

compound **1** aimed at the formation of new Mo−C or Mo−metal bonds. As it will be shown, the reactivity of **1** is quite unusual, because it involves not only the expected additions to the Mo=Mo bond but also some easy insertion reactions into Mo−P or Mo−O bonds as well as reductive elimination of P−O bonds, all occurring under very mild conditions.

Results and Discussion

Synthesis and Characterization of $[\mathrm{FeMo_2Cp_2}\{\mu\text{-OP(OEt)}_2\}\{\mu\text{-P(OEt)}_2\}(\mathrm{CO})_5]$ (2). Compound **1** is a highly reactive molecule due to its unsaturated nature, this being both electronic (it is a 32 e^- complex) and coordinative ($\mathrm{CpML_3}$ environment around Mo) in origin. In the first place we studied the reactions of **1** with some 16 e^- metal fragments in order to obtain heterometallic clusters (the metallic cyclopropanation reaction, by following the isolobal relationship).[5] Indeed, compound **1** reacts slowly with $[\mathrm{Fe_2(CO)_9}]$ in toluene to give the 46 e^- cluster $[\mathrm{FeMo_2Cp_2}\{\mu\text{-OP(OEt)}_2\}\{\mu\text{-P(OEt)}_2\}(\mathrm{CO})_5]$ (**2**) (Chart 1), along with small amounts of the trinuclear cluster $[\mathrm{Fe_3(CO)_{12}}]$. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits two signals (Table 1). That at high chemical shift (356.0 ppm) is assigned to the phosphorus atom of the alkoxyphosphido ligand, while the other one (129.0 ppm) is assigned to the phosphorus atom of the phosphonate ligand. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows five signals of equal intensity in the carbonyl region, and it does not experience appreciable changes with temperature, which indicates that the molecule behaves as rigid on the NMR time scale. Three of these signals (δ = 214.9, 213.2, and 202.7 ppm) appear within the chemical shift region characteristic of CO ligands coordinated to iron atoms in Fe−group 6 mixed metal clusters,[6,7] while CO ligands bonded to molybdenum atoms give rise to resonances at higher chemical shifts and exhibit informative PC couplings [243.8 ppm (d, J_{CP} = 12 Hz) and 238.1 ppm (dd, J_{CP} = 24, 17 Hz)]. From the multiplicity of the latter we conclude that the 238.1 ppm resonance corresponds to the carbonyl bonded to the molybdenum atom bearing both phosphorus atoms, its chemical shift and PC couplings being similar to the corresponding values for compound **1** [239.3 ppm (dd, J_{CP} = 24, 17 Hz)].[3d] By contrast, the resonance at 243.8 ppm has shifted 12.3 ppm downfield with respect to the corresponding one in compound **1** (231.5 ppm).[3d] This is taken as an indication of a coordination change of a CO ligand from terminal to bridging (or semibridging) between the iron and molybdenum nuclei bonded to a single phosphorus atom. The IR spectrum of **2** (Table 1) shows five signals in the CO stretching region. The first three bands (2026, 1964, and 1948 cm^{-1}) have the typical pattern of compounds having $[\mathrm{Fe(CO)_3}]$ fragments.[6−8] The other two bands correspond essentially to the carbonyls bonded to the molybdenum atoms (1880 and 1804 cm^{-1}). By comparing these two frequencies with those in the starting compound **1** (1882 and 1839 cm^{-1}) we can appreciate a substantial red-shift in the low-frequency band. This could be indicative of bridging or semibridging coordination of one of the CO ligands in compound **2**, in agreement with the $^{13}C\{^1H\}$ NMR data. This coordinative behavior of CO is not unusual, and it has been observed in other 46 e^- clusters such as $[\mathrm{FeM_2Cp_2}\{\mu^3\text{-}\mathrm{C_2(C_6H_4Me\text{-}4)_2}\}(\mathrm{CO})_6]$[7] and $[\mathrm{M_2RhCp_3}(\mu\text{-CO})_2(\mathrm{CO})_3]$[9] (M = Mo, W). In these molecules, the bridging CO ligands seem to contribute to a more equitative distribution of the electronic deficiency (2 e^-) of the trimetal cores. We must remark, however, that even when compound **2** is formally unsaturated, it does not react with simple Lewis bases such as CO or $\mathrm{PPh_3}$ under ordinary conditions. This thermodynamic preference for unsaturated (46 e^-) rather than saturated (48 e^-) structures was also observed for the above-mentioned cluster $[\mathrm{FeMo_2Cp_2}\{\mu^3\text{-}\mathrm{C_2(C_6H_4Me\text{-}4)_2}\}(\mathrm{CO})_6]$[7] and might be both steric and electronic in origin.

Synthesis and Structure of $[\mathrm{Mo_2Cp_2}\{\mu\text{-(EtO)}_2\mathrm{POSnCl_2}\}\{\mu\text{-P(OEt)}_2\}(\mathrm{CO})_2(\mu\text{-SnCl}_2)]$ (3). When a solution of **1** is transferred over 3 equiv of $\mathrm{SnCl_2}$, a color change is progressively observed and compound $[\mathrm{Mo_2Cp_2}\{\mu\text{-(EtO)}_2\mathrm{POSnCl_2}\}\{\mu\text{-P(OEt)}_2\}(\mathrm{CO})_2(\mu\text{-SnCl}_2)]$ (**3**) (Chart 1) is obtained as the major product after 1 h. The formation of **3** requires the incorporation of 2 equiv of $\mathrm{SnCl_2}$ to the molecule, one being inserted at the Mo−O bond and the other being added to the double Mo=Mo bond. Although some intermediate species are likely to be involved in the slow formation of **3**, reaction of compound **1** with just 1 equiv of $\mathrm{SnCl_2}$ failed to detect any of them, but led instead to **3** and unspecific decomposition of the starting compound. Thus, there seems to be a strong preference for the addition of two rather than single tin atoms to the unsaturated **1**.

The structure of **3** has been solved through an X-ray study, and it is depicted in Figure 1, while Table 2 lists

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Table 1. IR and NMR Data for Compounds 1–5

compound	ν_{st}(CO)/cm^{-1}	δ P/ppm	J_{PP}/Hz
[$Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2$] (**1**)[a]	1882(m), 1839(vs)[b]	347.0, 139.9[c]	9
[$FeMo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_5$] (**2**)	2026(vs), 1964(s), 1948(s) 1880(s), 1804(m)[b]	356.0, 129.0[d]	3
[$Mo_2Cp_2\{\mu\text{-}(EtO)_2POSnCl_2\}\{\mu\text{-}P(OEt)_2\}(\mu\text{-}SnCl_2)(CO)_2$] (**3**)	1978(vs), 1933(w)[e]	357.5[f,g] 139.9[f,h]	22 22
[$Mo_2Cp_2\{\mu\text{-}HCC(p\text{-}tol)\}\{\mu\text{-}(EtO)_2POP(OEt)_2\}(CO)_2$] (**4**)	1929(s), 1857(vs)[I]	175.7[f]	
[$Mo_2Cp_2\{\mu\text{-}OP(OEt)_2CH{=}C(p\text{-}tol)\}\{\mu\text{-}P(OEt)_2\}(CO)_2$] (**5**)	1899(w), 1886(vs)[i]	356.4, 68.9[c]	4

[a] Data from ref 3d. [b] Recorded in toluene. [c] Recorded in C_6D_6. [d] Recorded in toluene-d_8. [e] Recorded in CH_2Cl_2. [f] Recorded in CD_2Cl_2. [g] $J_{P^{119}Sn}$ = 399, 108, $J_{P^{117}Sn}$ = 382, 103. [h] $J_{P^{119}Sn}$ = 531, 455, $J_{P^{117}Sn}$ = 498, 437. [i] Recorded in petroleum ether.

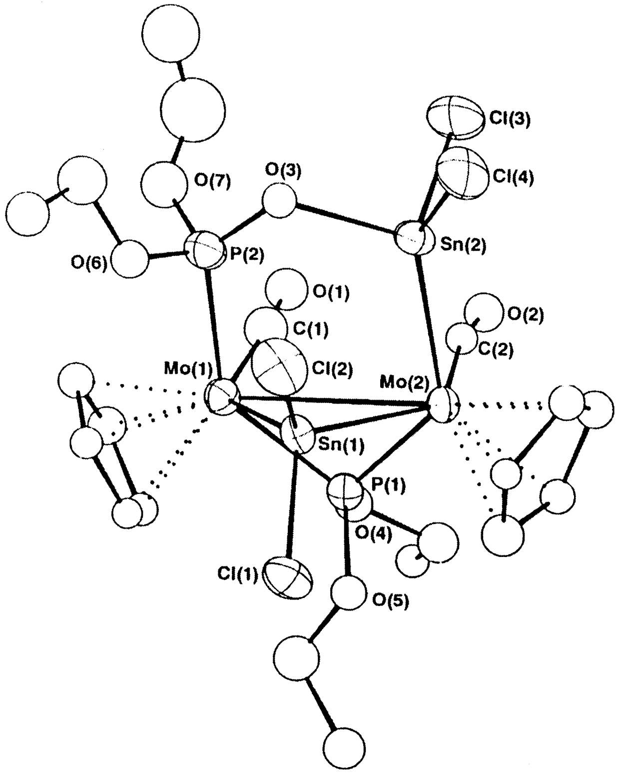

Figure 1. CAMERON diagram of the molecular structure of compound **3**. Ellipsoids represent 30% probability.

Table 2. Selected Bond Distances and Angles for 3

	d (Å)		θ (deg)
Mo(1)–Mo(2)	3.412(6)	Sn(1)–Mo(1)–P(1)	75.9(3)
Mo(1)–P(1)	2.41(1)	Sn(1)–Mo(1)–P(2)	82.7(4)
Mo(1)–Sn(1)	2.683(5)	Sn(1)–Mo(1)–C(1)	130.0(18)
Mo(1)–P(2)	2.47(2)	Sn(1)–Mo(2)–Sn(2)	82.2(2)
Mo(2)–Sn(1)	2.731(5)	Sn(1)–Mo(2)–P(1)	75.1(3)
Mo(2)–P(1)	2.40(1)	Sn(1)–Mo(2)–C(2)	133.7(14)
Mo(2)–Sn(2)	2.680(5)	Sn(1)–Mo(2)–P(1)	75.1(3)
Sn(2)–O(3)	2.11(3)	P(1)–Mo(1)–P(2)	135.8(5)
Mo(1)–C(1)	1.92(7)	Mo(1)–Sn(1)–Mo(2)	78.1(2)
Mo(2)–C(2)	1.91(5)	P(1)–Mo(2)–Sn(2)	126.1(4)
P(1)–O(4)	1.61(3)	Mo(1)–Mo(2)–Sn(2)	83.3(1)
P(1)–O(5)	1.62(3)	Mo(2)–Sn(2)–O(3)	115.1(9)
P(2)–O(3)	1.52(3)	Sn(2)–O(3)–P(2)	123.1(19)
P(2)–O(6)	1.59(4)	Mo(1)–P(2)–O(3)	123.9(15)
Sn(1)–Cl(1)	2.38(1)	Cl(1)–Sn(1)–Cl(2)	92.9(5)
Sn(1)–Cl(2)	2.37(1)	Cl(3)–Sn(2)–Cl(4)	95.6(6)
Sn(2)–Cl(3)	2.35(2)		
Sn(2)–Cl(4)	2.36(1)		

the most relevant bond distances and angles. The coordination geometry around each metal center can be considered of the "four-legged piano stool" type, if we exclude the metal–metal bond, where the μ-$SnCl_2$ ligand has a *trans* disposition with respect to the CO ligands, whereas the μ-$P(OEt)_2$ ligand exhibits a *trans* disposition with respect to the μ-$(EtO)_2POSnCl_2$ ligand. We note that the CO ligands in compound **3** adopt a *cis* relative geometry, while they are mutually *trans* in the starting compound, so an isomerization must occur at some step of the reaction between **3** and $SnCl_2$. This *cis* arrangement of CO ligands has been observed before for the isoelectronic compounds [$W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)$]($PF_6$) (X = F, Cl),[10] and it is considered to be the result of an important thermodynamic preference for this geometry. The Mo–Mo distance in **3** [3.412(6) Å] is consistent with the presence of a formally single Mo–Mo bond, it being somewhat longer than those found at the related neutral compounds [$Mo_2Cp_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)$] [3.327(1) Å][11] and [$W_2Cp_2(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}$] [3.2731(6) Å].[3d] The alkoxyphosphido ligand exhibits a symmetric coordination with respect to the molybdenum atoms [d(Mo–P) 2.40(1) and 2.41(1) Å]. However, the μ-$SnCl_2$ group displays an asymmetric coordination [d(Mo–Sn) 2.683(5) and 2.731(5) Å], surely due to the intrinsic asymmetry of the phosphonate-stannyl bridging ligand $(EtO)_2POSnCl_2$. A similar effect has been previously observed at the Mn_2Zn cluster [$Mn_2(CO)_6\{\mu\text{-}Zn(bipy)\}\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6$],[12] which contains three closely related bridging ligands. Although a few complexes displaying SnX_2 groups bonded to two metal fragments have been structurally characterized, such as the neutral [$\{MoCp(CO)_3\}_2(\mu\text{-}SnX_2)$][13a,b] or the anions [$\{Mo(CO)_5\}_2(\mu\text{-}SnX_2)$]$^{2-}$ (X = Cl, Br, I),[13c] they all show open-chain trimetal cores. Thus, compound **3** seems to be the first one having a $SnCl_2$ group incorporated as part of a metal triangle. The resulting interaction seems to be particularly strong, as deduced from the values of the Mo–Sn distances in **3** (ca. 2.70 Å on average), which are considerably shorter than those found in open Mo_2-Sn chains (i.e., 2.9831(10) and 3.0186(11) Å for [$\{MoCp(CO)_3\}_2(\mu\text{-}SnI_2)$]).[13a] Other internuclear distances in compound **3** have normal values.

Spectroscopic data in solution for **3** are consistent with the structure found in the crystal. In the first place, the relative intensities of the CO stretching bands (strong and weak, in order of decreasing frequency) are indicative of their mutual, almost parallel, *cis* arrangement.[14] Second, the relative arrangement of the three bridging

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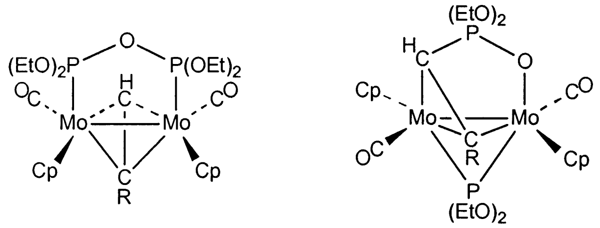
Chart 2



4 **5**

ligands seems to be retained in solution, as deduced from the P−Sn couplings. Thus, the phosphido group displays quite different couplings to each of the tin atoms (ca. 400 and 100 Hz), in agreement with their quite different bond angles [P(1)−Mo(2)−Sn(1) = 75.1(3)° and P(1)−Mo(2)−Sn(2) = 126.1(4)°, or *cis* and *trans*, respectively]. Analysis of P−Sn couplings in the phosphonate-stannyl resonance cannot be done easily, as they involve both P−Mo−Sn and P−O−Sn bond pathways, even if ignoring three-bond pathway contributions.

Reaction of Compound 1 with HCC(*p*-C_6H_4Me-4). We have also used the isolobal[5] relationship between multiple M−M and C−C bonds in order to examine the potential of compound **1** to form new Mo−C bonds. First, the reaction with CH_2N_2 was examined, but that was found to lead to complex mixtures of compounds that could not be characterized. We then examined the reactions with some simple olefins and alkynes, the 2+2 organic addition being its model. Although no reaction was observed at room temperature between olefins or internal alkynes and **1**, reaction of the latter with a terminal alkyne such as HCC(*p*-tol) [*p*-tol = C_6H_4Me-4] proceeds smoothly at room temperature to give a mixture of isomers [$Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-HCC}(p\text{-tol})\}\{\mu\text{-(EtO)}_2\text{POP(OEt)}_2\}(CO)_2$] (**4**) and [$Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa^1{:}\eta^2\text{-OP(OEt)}_2\text{CH=C}(p\text{-tol})\}\{\mu\text{-P(OEt)}_2\}(CO)_2$] (**5**) (Chart 2), in a 1:4 ratio. Surprisingly, this ratio was rather insensitive to experimental conditions such as temperature or excess of alkyne used. Reactions with other terminal alkynes HCCR having nonaromatic R groups were tried, but no reaction was observed at room temperature in these cases.

Compound **4** is the result of a P−O bond reductive elimination between phosphido and phosphonate ligands at the starting substrate and coordination of the incoming alkyne as a 4 e^- ligand to the resulting tetraethylpyrophosphite-bridged fragment. The presence of two carbonyl ligands in the molecule is denoted by the presence of two absorptions in the CO stretching region of the IR spectrum (1929 and 1857 cm^{-1}, Table 1). These bands present almost the same intensity, this being indicative of CO ligands arranged at approximately 90° angles.[14] The $^{31}P\{^1H\}$ NMR of **4** exhibits a single resonance at 175.7 ppm (Table 1), with a chemical shift compatible with the presence of a tetraethylpyrophosphite group bridging a dimolybdenum cyclopentadienyl center.[3d,15] The presence of the new ligand allows the metal centers to be symmetry-related, which implies the chemical equivalence of both Cp or carbonyl ligands. This is clearly apparent in the ^1H or $^{13}C\{^1H\}$ NMR spectra, which exhibit single resonances for these ligands (an AXX′ multiplet is observed for the carbonyl groups). As for the alkyne ligand, it gives rise to a triplet resonance in the ^1H NMR spectrum ($\delta = 5.32$ ppm, $J = 5$ Hz), while the metal-bonded carbon atoms give resonances at 90.8 (singlet, internal acetylenic carbon) and 86.7 ppm (triplet, $J_{PC} = 16$ Hz, terminal acetylenic carbon), in the region observed for similar compounds of the type [$Mo_2Cp_2(\mu\text{-}\eta^2{:}\eta^2\text{-RCCR}')(CO)_4$].[2b] Both the observed PH and PC couplings are structurally informative. In the first place, because these couplings are equal to both phosphorus atoms, a coordination mode of the alkyne ligand perpendicular to the intermetallic bond must be proposed for **4**. Second, it is known that PC couplings in cyclopentadienyl complexes of the type [$MCpX(CO)_2(PR_3)$] (M = Mo, W; X = halogen, alkyl, hydride, etc.) follow the order $|^2J_{cis}| > |^2J_{trans}|$,[16] where *cis* and *trans* refer to angles between ligands around 80° and 120°, respectively. On the basis of this information, we then propose that the internal acetylenic carbon is coordinated *trans* with respect the phosphorus atoms, which leaves the terminal acetylenic carbon *cis* to them, thus explaining its higher PC coupling. This conformation would be also expected on the basis of steric considerations, if the repulsive interaction between the alkyne and bridging diphosphite is to be minimized.

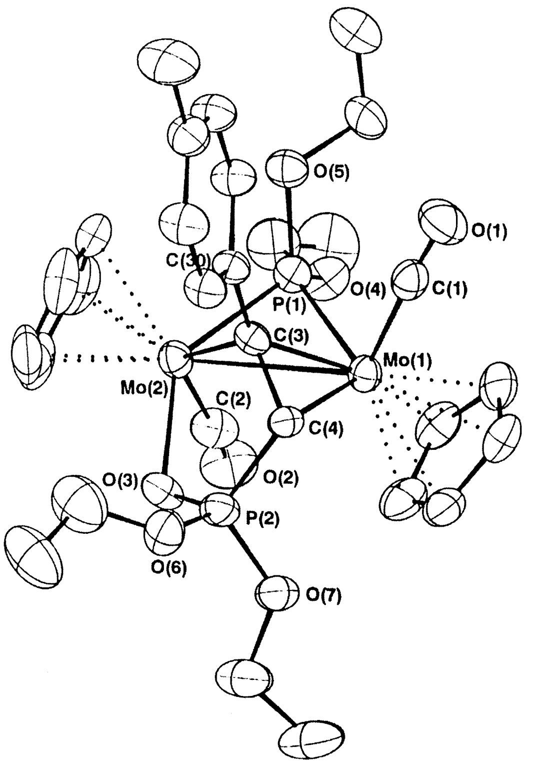


Figure 2. CAMERON diagram of the molecular structure of compound **5**. Ellipsoids represent 30% probability.

The structure of **5** has been solved through an X-ray study, and it is depicted in Figure 2, while Table 3 lists the most relevant bond distances and angles. The molecule displays two cyclopentadienyl carbonyl molybdenum moieties arranged so that the carbonyl ligands

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Table 3. Selected Bond Distances and Angles for 5

	d (Å)		θ (deg)
Mo(1)−Mo(2)	2.991(1)	Mo(2)−C(3)−Mo(1)	85.6(3)
Mo(1)−P(1)	2.366(3)	C(3)−Mo(1)−P(1)	78.8(2)
Mo(1)−C(3)	2.154(9)	C(3)−Mo(2)−P(1)	77.4(2)
Mo(1)−C(4)	2.214(9)	C(3)−Mo(1)−C(1)	78.8(4)
Mo(2)−C(3)	2.245(9)	C(3)−Mo(2)−C(2)	125.5(4)
Mo(2)−P(1)	2.350(3)	C(4)−Mo(1)−P(1)	115.3(2)
P(2)−C(4)	1.702(9)	O(3)−Mo(2)−P(1)	134.9(2)
C(3)−C(4)	1.46(1)	O(3)−Mo(2)−C(3)	79.0(3)
Mo(1)−C(1)	1.90(1)	C(1)−Mo(1)−Mo(2)	115.3(3)
Mo(2)−C(2)	1.95(1)	C(2)−Mo(2)−Mo(1)	84.3(4)
Mo(2)−O(3)	2.230(6)	Mo(1)−P(1)−Mo(2)	78.72(8)
C(3)−C(30)	1.48(1)	Mo(2)−O(3)−P(2)	117.6(3)
P(2)−O(3)	1.491(7)	O(3)−P(2)−C(4)	108.4(4)
P(2)−O(6)	1.570(7)	C(30)−C(3)−C(4)	118.7(8)
P(2)−O(7)	1.566(7)	C(3)−C(4)−P(2)	115.1(6)
P(1)−O(4)	1.628(6)	C(3)−C(4)−Mo(1)	68.3(5)
P(1)−O(5)	1.617(7)	P(2)−C(4)−Mo(1)	117.9(5)

are in a transoid disposition. Both metal atoms are bridged by two ligands. The first one is the diethoxyphosphido group already present in the starting compound. The other one is a phosphonoalkenyl ligand formed by insertion of the terminal acetylenic carbon into the P−Mo bond of the former phosphonate ligand, which retains its coordination through the oxygen atom, thus formally providing a total of 5 e^- to the dimetal center. The alkenyl end of the ligand is σ bonded to the molybdenum atom O-bonded [Mo(2)], and it displays π coordination to the other metal atom [Mo(1)]. In a formal sense, compound **5** is a 34 e^- complex, so that a single Mo−Mo bond must be formulated for this molecule. This is in agreement with the intermetallic separation, which displays a quite short value, 2.991(1) Å, comparable to those in related singly bonded binuclear cations of the group 6 metals, such as the halide complexes $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$ (X = F, Cl) [2.945(1) and 3.040(3) Å][10] or the alkenyl $[W_2Cp_2\{\mu\text{-}C(OMe){=}CH_2\}(\mu\text{-}CH_2)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$ [2.965(1) Å].[17] The interatomic distances involving the alkenyl moiety in **5** [relatively short Mo−C lengths, around 2.20 Å, and a relatively large C−C length, 1.46(1) Å] are indicative of strongly σ and π binding of the ligand to the molybdenum atoms.[17] Although there are only a few structural studies on complexes bearing related zwitterionic PX_3-substituted alkenyl bridges (X = R or OR)[18] to be compared with, and none of them involve Mo or W complexes, this seems to be a general feature for this type of alkenyl ligand. In the case of compound **5**, the considerable strength of the π interaction is deduced from the low value of the Mo(1)−C(4) separation, 2.214(9) Å, in the lower part of the range (2.20−2.30 Å) found for $\mu\text{-}\eta^1{:}\eta^2$-alkenyl dimolybdenum complexes.[17] This can be understood by considering the increased electronic charge in the carbon atoms, resulting from the donor−acceptor interaction between the P and C atoms of the former phosphonate and alkyne groups. This is also consistent with the short P(2)−C(4) length in **5** [1.702(9) Å], considerably shorter than those found for normal $C{-}P(O)(OR)_2$ bonds, such as 1.785(3) Å for $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}C(Me){=}C(H)P(O)(OMe)_2\}]$.[19]

Spectroscopic data for **5** indicate that this compound retains in solution its solid state structure. The IR spectrum of **5** has two absorptions in the carbonyl region [1899 (w), 1886 (vs) cm^{-1}, Table 1] with relative intensities characteristic of $M_2(CO)_2$ oscillators with a transoid geometry.[14] The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits two resonances at 356.4 and 68.9 ppm (Table 1). The first one, due to the diethoxyphosphido bridge, appears at a chemical shift almost identical to that of compound **1** (356.0 ppm).[3d] On the other hand, the signal at 68.9 ppm is out of the range found for our previous dimolybdenum phosphonate compounds (125−200 ppm), in agreement with its coordination to the C atom of the alkyne. Indeed, the chemical shift of this resonance is close to the values for the phosphonium salts of phosphites $[RP(OR)_3]^+$ (ca. 50 ppm).[20] The ^1H NMR spectrum of **5** shows a doublet at 2.00 ppm [$J_{HP} = 31$ Hz] due to the terminal acetylenic proton, which was not detected by the X-ray study. The high PH coupling for this H atom at **5** (31 Hz) is considerably higher than that observed at **4** (5 Hz), in agreement with the smaller number of bonds between the proton and the phosphorus atom. The assignment of that high coupling to the P (phosphonate) nucleus was confirmed through a selectively decoupled $^1H\{^{31}P\}$ NMR experiment.

Reaction Pathways Prevalent for Compound 1. Compound **1** has a coordinative and electronic unsaturation and expectedly behaves as a good ligand acceptor, as confirmed through the experiments discussed above. All reagents examined in this work are themselves (or act as source of) at least 2 e^- donors that might first coordinate to the double metal−metal bond to reduce those coordinative and electronic unsaturations (intermediates **A** and **A′**, Schemes 2 and 3). Then, these intermediates would evolve differently in each case. The synthesis of **2** just requires ejection of a CO molecule after the addition of the $Fe(CO)_4$ fragment, thus giving a 46 e^- cluster. As stated before, this thermodynamic preference for an unsaturated rather than saturated 48 e^- trimetal cluster has been observed previously. The formation of compound **3** can be understood by starting at the same intermediate **A**, followed by reductive elimination of a Sn−O bond to give a second intermediate **B**. This is not an expected isomerization, because it forms an unsaturated intermediate, but there is some precedent for such a process. In fact, we have found previously that the anion $[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6]^{2-}$ reacts with Cl_2SnPh_2 to give first the expected derivative having a $\mu\text{-}SnPh_2$ bridge, which then evolves spontaneously to the complex $[Mn_2\{\mu\text{-}(EtO)_2POSnPh_2\}\{\mu\text{-}P(OEt)_2\}(CO)_7]$, characterized through an X-ray study.[21] In both cases it is reasonable to assume that the driving force for these Sn−O reductive eliminations would be the fact that a strong Sn−O bond is formed. The formation of compound **3** is then completed by addition of a second molecule of $SnCl_2$ to the double Mo═Mo bond in intermediate **B**. As stated

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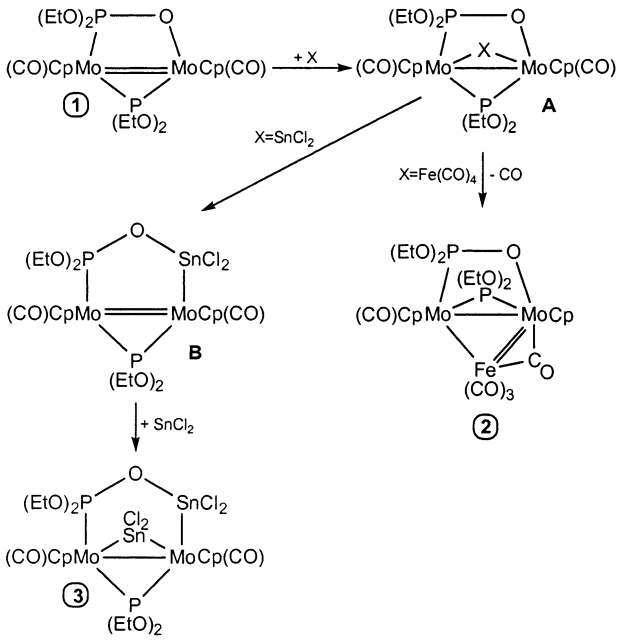
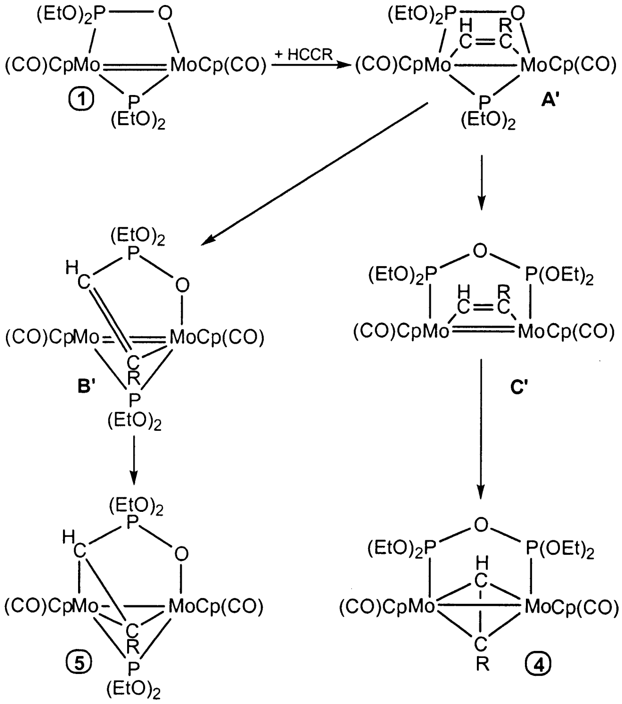
Scheme 2. Proposed Reaction Pathways in the Formation of Compounds 2 and 3



Scheme 3. Proposed Reaction Pathways in the Formation of Compounds 4 and 5



before, this double addition of $SnCl_2$ on compound **1** is strongly favored, irrespective of the available amount of $SnCl_2$ in the reaction mixture.

The formation of compounds **4** and **5** is also likely to be initiated by addition of 1 equiv of HCC(*p*-tol) to the double Mo=Mo bond in **1** to obtain the intermediate **A′**, proposed to have an alkyne molecule coordinated in the μ-η^1:η^1-fashion (Scheme 3). This coordination mode has been frequently found upon insertion of alkynes into metal–metal bound A-frame dimers and related species.[22] Intermediate **A′** could display two different structures (isomers) depending on the position of the organic residue, but only that with the CH group close to the phosphonate P atom can lead to the formation of **5** by reductive elimination of a P–C bond, by first giving a new intermediate **B′**. There are some precedents for the insertion of alkynes into M–P bonds of phosphine complexes. This is the case of the reactions leading to the alkenyl-bridged cation $[Pt_2Pd(\mu\text{-dpmp})\{\mu\text{-dpmp-CH}{=}C(CO_2Et)\}(XylNC)_2]^{2+}$ (dpmp = $Ph_2PCH_2P(Ph)CH_2PPh_2$)[18c] or the mononuclear complexes $[PdCl_2(\mu\text{-}Ph_2PCH_2P(Ph)_2CH{=}C(Ph)]$[23] and $[Mo(\eta^3\text{-CHCHPPh}_2CH_2CH_2PPh_2\text{-}C,C',P)(NCMe)_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$.[24] To our knowledge, the formation of **5** is the first example of akyne insertion into a metal–P (phosphonate) bond. The η^1-vinyl intermediate **B′** thus formed would finally give the electron-precise **5** after coordination of its C=C bond, a rearrangement expected to be facile.

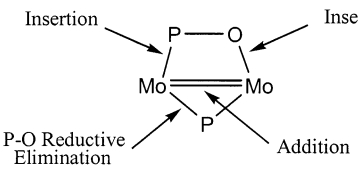


Figure 3. Reactivity patterns exhibited by compound **1**.

The formation of compound **4** can also be understood starting from **A′** (whichever of the possible isomers) after reductive elimination of a P–O bond to generate an unsaturated diphosphite-bridged intermediate **C′**, which then would experience alkyne rearrangement from the μ-η^1:η^1 to the μ-η^2:η^2 mode so as to achieve a saturated structure. The above P–O bond reductive elimination has been observed previously in one instance, this requiring some thermal activation (ca. 90–100°). The novel feature of the P–O bond formation here disclosed is that it occurs readily at room temperature.

From the above considerations it can be concluded that the key step in the reactions of **1** is the evolution of the 34 e^- intermediates (**A** and **A′**) formed after the initial addition process. Starting at this point, either P–C, O–Sn, or P–O reductive eliminations induce the formation of a wide range of compounds. We notice that the only precedent for a related P–O bond reductive elimination was postulated to occur at a 34 e^- intermediate, the tricarbonyl $[Mo_2Cp_2\{\mu\text{-OP(OEt)}_2\}\{\mu\text{-P(OEt)}_2\}(\mu\text{-CO})(CO)_2]$. Why is it that these saturated intermediates experience rather unexpected reductive elimination processes to give unsaturated compounds is not clear at present, but further studies will hopefully bring new data so as to understand this unusual behavior.

Conclusion

Compound **1** experiences under mild conditions a wide variety of processes (Figure 3). As expected for a substrate having a double metal–metal bond, addition of donors to the dimetal center occurs readily, thus reducing the metal–metal bond order to one ($Fe(CO)_4$) or even to zero (CO), but this is generally followed by other reactions. Further processes include the insertion of the incoming molecule into the Mo–O bond ($SnCl_2$) or Mo–P [HCC(*p*-tol)] bond of the phosphonate ligand, giving unusual bridging groups. A final process involves

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the diethoxyphosphido/phosphonate P−O reductive elimination [observed in the reaction with HCC(*p*-tol)] to give a diphosphite-bridged derivative at room temperature. In summary, the chemical behavior of compound **1** is quite different from that of the isoelectronic $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$, a complex unreactive toward 16 e^- metal fragments, alkynes, or CO.[3b,4] This difference can be attributed to the smaller size and higher electron-withdrawing power of the phosphonate and alkoxyphosphido ligands in **1**, when compared to the related phosphinomethyl and diphenylphosphido bridges, respectively.

Experimental Section

General Comments. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were purified according to standard literature procedures[25] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65−70 °C. Compound **1** was prepared by literature methods.[3d] Other reagents were obtained from the usual commercial suppliers and used without further purification. Filtrations were carried out using diatomaceous earth, and alumina for column chromatography was deactivated by appropriate addition of water to the commercial material (Aldrich, neutral, activity I). NMR spectra were recorded at 400.13 (^1H), 81.03 ($^{31}P\{^1H\}$), or 100.62 MHz ($^{13}C\{^1H\}$), at room temperature unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. $^{13}C\{^1H\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonate)chromium(III) as a relaxation reagent.

Preparation of $[FeMo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(\mu\text{-}CO)(CO)_4]$ (2). A toluene solution (10 mL) of compound **1** (0.046 g, 0.07 mmol) was treated with $[Fe_2(CO)_9]$ (0.030 g, 0.08 mmol) and the mixture stirred at room temperature for 20 h. Solvent was then removed under vacuum and the residue dissolved in a minimum of toluene and chromatographed on a tap-water refrigerated alumina column (activity II, 15 × 2.5 cm) prepared in petroleum ether. Elution with toluene gave two green fractions. The first fraction contained $[Fe_3(CO)_{12}]$ and was discarded. The second fraction gave, after removal of solvent under vacuum, compound **2** as a green powder (0.040 g, 74%). Anal. Calcd for $C_{23}H_{30}O_{10}P_2FeMo_2$: C, 35.59; H, 3.90. Found: C, 35.46; H, 3.79. ^1H NMR (300.13 MHz, toluene-d_8): δ 5.12 (d, $J_{HP} = 1$, 5H, Cp), 4.99 (s, 5H, Cp), 4.24 (m, 1H, CH_2), 4.07−3.87 (m, 2H, CH_2), 3.87−3.50 (m, 4H, CH_2), 3.42 (m, 1H, CH_2), 1.32, 1.20, 1.19, 1.09 (4 × t, $J_{HH} = 7$, 4 × 3H, Me). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8): δ 356.0 (d, $J_{PP} = 3$, μ-P), 129.0 (d, $J_{PP} = 3$, μ-OP). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 243.8 (d, $J_{CP} = 12$, μ-CO), 238.1 (dd, $J_{CP} = 24, 17$, MoCO), 214.9 (dd, $J_{CP} = 10, 6$, FeCO), 213.2 (d, $J_{CP} = 8$, FeCO), 202.7 (t, $J_{CP} = 4$, FeCO), 93.9, 87.0 (2 × s, Cp), 65.7 (d, $J_{CP} = 11$, CH_2), 64.2 (d, $J_{CP} = 9$, CH_2), 58.8 (d, $J_{CP} = 10$, CH_2), 58.6 (s, CH_2), 16.6 (d, $J_{CP} = 7$, Me), 16.3 (d, $J_{CP} = 4$, Me), 16.2 (d, $J_{CP} = 7$, Me), 15.7 (d, $J_{CP} = 9$, Me).

Preparation of $[Mo_2Cp_2\{\mu\text{-}(EtO)_2POSnCl_2)\}\{\mu\text{-}P(OEt)_2\}(CO)_2(\mu\text{-}SnCl_2)]$ (3). A toluene solution (8 mL) of compound **1** (0.046 g, 0.07 mmol) was treated with $SnCl_2$ (0.040 g, 0.21 mmol), and the mixture was stirred at room temperature for 1 h and then filtered through diatomaceous earth. Removal of solvent under vacuum from the filtrate gave compound **3** as an orange powder (0.044 g, 75%). The crystals used in the X-ray diffraction study were grown by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **3** at room temperature. Anal. Calcd for $C_{20}H_{30}O_7P_2Cl_4Mo_2Sn_2$: C, 23.66; H, 2.98. Found: C, 23.59; H, 2.95. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 5.22 (s, 5H, Cp), 5.18 (d, $J_{HP} = 1$, 5H, Cp), 4.20−3.55 (m, 8H, CH_2), 1.37, 1.26, 1.24, 1.15 (4 × t, $J_{HH} = 7$, 4 × 3H, Me). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): δ 357.5 (d, $J_{PP} = 22$, $J_{P^{119}Sn} = 399, 108$, $J_{P^{117}Sn} = 382, 103$, μ-P), 138.9 (d, $J_{PP} = 22$, $J_{P^{119}Sn} = 521, 455$, $J_{P^{117}Sn} = 498, 437$, μ-OPSn).

Table 4. Crystal Data for Compounds 3 and 5

	3	**5**
mol formula	$C_{20}H_{30}Cl_4Mo_2O_7P_2Sn_2$	$C_{29}H_{38}Mo_2O_7P_2$
mol wt	1015.47	752.44
cryst syst	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
cryst color	orange	orange
cryst shape	parallelepiped	parallelepiped
radiation (λ, Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
a, Å	20.608(8)	10.706(2)
b, Å	18.696(9)	10.886(2)
c, Å	17.154(5)	15.432(4)
α, deg		70.57(2)
β, deg		79.17(2)
γ, deg		69.55(1)
V, Å^3	6609(8)	1584(11)
Z	4	2
calcd density, g cm^{-3}	2.04	1.58
μ(Mo Kα), cm^{-1}	26.82	9.1
diffractometer	Philips-PW 1100	Nonius CAD4
temperature, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
θ limits, deg	1−25	1−25
scan width	$0.8 + 0.345 \tan \theta$	$0.8 + 0.345 \tan \theta$
total no. of data collected	6429	5791
no. of unique total data	5830	5561
no. of unique data used	1038 $[(F_o)^2 > 2.5\sigma(F_o)^2]$	2721 $[(F_o)^2 > 3\sigma(F_o)^2]$
R^a	0.057	0.041
$R_w{}^b$	0.065	0.045
abs coeff corr (min., max.)	0.94, 1.14	0.76, 1.21
no. of variables	199	362
$\Delta\rho_{min}$ (e/Å^3)	−0.76	−0.39
$\Delta\rho_{max}$ (e/Å^3)	0.75	0.63

[a] $R = \sum|F_o - |F_c||/\sum F_o$. [b] $R_w = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Reaction of Compound 1 with HCC(*p*-tol). A toluene solution (12 mL) of compound **1** (0.090 g, 0.14 mmol) was treated with HCC(*p*-tol) (40 μL, 0.14 mmol), and the mixture was stirred at room temperature for 24 h. Solvent was then removed under vacuum, and the residue was dissolved in a minimum of petroleum ether and chromatographed on a tap-water refrigerated alumina column (activity II, 15 × 2.5 cm) prepared in petroleum ether. Elution with CH_2Cl_2/petroleum ether (1:4) gave two red fractions. Removal of the solvent under vacuum from the first fraction gave 0.016 g (15%) of $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HCC(p\text{-tol})\}\{\mu\text{-}(EtO)_2POP(OEt)_2\}(CO)_2]$ (**4**) as an orange solid. Anal. Calcd for $C_{29}H_{38}O_7P_2Mo_2$: C, 46.29; H, 5.09. Found: C, 46.12; H, 4.97. ^1H NMR (CD_2Cl_2): δ 7.25, 7.04 (2 × d, $J_{HH} = 8$, 2 × 2H, $C_6\mathit{H}_4Me$), 5.32 (t, $J_{HP} = 5$, 1H, CH), 4.85 (s, 10H, Cp), 4.15−3.85 (m, 4H, CH_2), 3.75−3.65 (m, 4H, CH_2), 2.22 (s, 3H, $C_6H_4\mathit{Me}$), 1.16, 0.96 (2 × t, $J_{HH} = 7$, 2 × 6H, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 175.7 (s, μ-POP). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 234.6 (false t, (AXX′), $J_{AX} + J_{AX'} = 19$, CO), 149.9, 132.9, 130.4, 128.5 (4 × s, C_6H_4Me), 90.8 (s, $HC\mathit{C}R$), 88.2 (s, Cp), 86.7 (t, $J_{CP} = 16$, $H\mathit{C}CR$), 61.6 (s, CH_2), 59.8 (s, CH_2), 21.0 (s, $C_6H_4\mathit{Me}$), 16.5, 16.4 (s, $OCH_2\mathit{Me}$). Removal of the solvent under vacuum from the second fraction gave compound $[Mo_2Cp_2\{\mu\text{-}\eta^1,\kappa^1{:}\eta^2\text{-}OP(OEt)_2CH{=}C(p\text{-tol})\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (**5**) (0.072 g, 68%) as an orange solid. The crystals used in the X-ray diffraction study were grown by slow

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diffusion of petroleum ether into a solution of **5** in CH_2Cl_2 at -20 °C. Anal. Calcd for $C_{29}H_{38}O_7P_2Mo_2$: C, 46.29; H, 5.09. Found: C, 46.17; H, 4.93. ^1H NMR (CD_2Cl_2): δ 7.40 (br, 2H, C_6H_4Me), 7.00 (d, $J_{HH} = 8$, 2H, C_6H_4Me), 5.20 (s, 5H, Cp), 4.77 (d, $J_{HP} = 1$, 5H, Cp), 4.10−3.99 (m, 1H, CH_2), 3.98−3.75 (m, 5H, CH_2), 3.71−3.64 (m, 2H, CH_2), 2.30 (s, 3H, C_6H_4Me), 2.00 (d, $J_{HP} = 31$, 1H, CH), 1.33, 1.31 (2 × t, $J_{HH} = 7$, 2 × 3H, OCH_2Me), 1.29 (t, $J_{HH} = 7$, 6H, OCH_2Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 356.4 (d, $J_{PP} = 4$, μ-P), 68.9 (d, $J_{PP} = 4$, μ-OP).

X-ray Structure Determination for Compounds 3 and 5. A selected crystal was set up on an automatic diffractometer in each case. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other information are summarized in Table 4. Corrections were made for Lorentz and polarization effects. Empirical absorption correction (Difabs)[26] were applied. A secondary extinction correction was unnecessary.

Computations were performed by using the PC version of CRYSTALS.[27] Atomic form factors for neutral Sn, Mo, P, Cl, O, C, and H were taken from ref 28. Real and imaginary parts of anomalous dispersion were taken into account. The structures were solved by direct methods (SHELXS 86)[29] and successive Fourier maps. Because of the few number of reflections, in the case of **3**, hydrogen atoms were not found on difference maps nor introduced in calculations, and only Sn, Mo, Cl, and P atoms were anisotropically refined. For compound **5**, almost all hydrogen atoms could be found on difference maps, others were geometrically located, and all of them were given an overall isotropic thermal parameter, while non-hydrogen atoms were anisotropically refined.

Refinements were carried out in three blocks by minimizing the function $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. Models reached convergence with R and R_w having values defined and listed in Table 4. The weighting scheme was unity. Figures 2 and 3 represent CAMERON[30] views of compounds **3** and **5** respectively.

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología of Spain for financial support (Projects BQU2000-0220 and BQU2000-0944) and the Universidad de Oviedo for a grant to C.M.A.

Supporting Information Available: Tables of atomic coordinates for non-hydrogen atoms, for hydrogen atoms, anisotropic thermal parameters and bond lengths and angles for compounds **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0301886

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