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Chemistry of Unsaturated Group 6 Metal Complexes with Bridging Hydroxy and Methoxycarbyne Ligands. 5. Heterometallic Clusters Derived from the Neutral Complex [$Mo_2(\eta^5$-$C_5H_5)_2(\mu$-COMe)-(μ-$PCy_2)(\mu$-CO)]

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The unsaturated complex [$Mo_2Cp_2(\mu$-COMe)(μ-PCy_2)(μ-CO)] (**1**) reacts with the solvate manganese complexes [MnL$(CO)_2$(THF)] (L = Cp, η^5-C_5H_4Me) rapidly at room temperature in toluene solution to give the corresponding electron-precise clusters [$MnMo_2Cp_2L(\mu_3$-COMe)(μ-PCy_2)$(CO)_4$] (Mo−Mo = 2.986(1) Å when L = Cp), which follow from the addition of the manganese fragment to compound **1** and further spontaneous carbonylation. In contrast, the incorporation of the group 8 metal fragments $M(CO)_4$ occurs selectively either at room temperature (reaction with [$Fe_2(CO)_9$]) or under photochemical activation (reaction with [$Ru_3(CO)_{12}$]) to give the 46-electron derivatives [$Mo_2MCp_2(\mu_3$-COMe)(μ-PCy_2)$(CO)_5$] (M = Fe, Ru), which follow from the addition of the $M(CO)_4$ fragment to compound **1** and carbonyl migration from M to molybdenum. Simple addition of a metal fragment to the triple intermetallic bond of **1** is observed in its reaction with CuCl, which gives the unsaturated derivative [$CuMo_2ClCp_2(\mu_3$-COMe)(μ-PCy_2)(μ-CO)]. Compound **1** can also yield tetranuclear derivatives. Thus, it reacts with [$Co_2(CO)_8$] at room temperature to give a mixture of the clusters [$Co_2Mo_2Cp_2(\mu_3$-COMe)(μ-PCy_2)(μ-CO)$_2(CO)_4$] and [$Co_2Mo_2Cp_2(\mu_3$-COMe)(μ-PCy_2)-(μ-CO)$(CO)_6$]. The heptacarbonyl compound has the expected composition, i.e., the one resulting from the addition of a $Co_2(CO)_6$ fragment to compound **1**, but not the expected structure, since the PCy_2 ligand is found as bridging one Mo−Co edge of the tetrahedral metal core, according to an X-ray diffraction study. In contrast, the hexacarbonyl cluster roughly has the expected structure, but has one carbonyl below the number that might have been anticipated, with the resulting unsaturation being mainly located at the Mo−Mo bond (2.686(1) Å) of this tetrahedral cluster.

Introduction

Transition-metal carbyne complexes constitute a large and extensively studied family of compounds within organometallic chemistry. The carbyne ligand in these complexes is a quite reactive site in either the terminal or the edge-bridging coordination modes, as a result of the multiple nature of the corresponding metal−carbon bonds,[1] and this can be further increased in the latter case by the presence of multiple metal−metal bonds (Chart 1). Further interest in the chemistry of carbyne complexes stems from their involvement in several industrial processes such as CO hydrogenation[2] and alkyne metathesis.[3] Compared to this state of knowledge, the chemistry of alkoxycarbyne compounds is considerably less developed. Most of the complexes described so far contain the COR ligand acting as a μ_2- or μ_3-bridging group on electron-precise di- or trinuclear complexes,[4] and therefore the behavior of the alkoxycarbyne ligand in the presence

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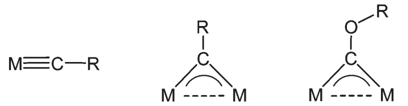
Chart 1



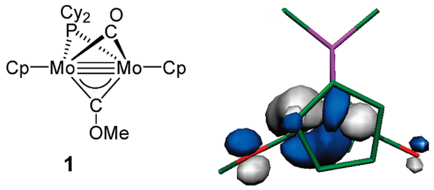


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Figure 1. Structure of compound **1** and a drawing of the HOMO−2 orbital (DFT) of this complex,[8] viewed along the metal−metal axis, with H atoms and cyclohexyl rings (except the C^1 atoms) omitted for clarity.

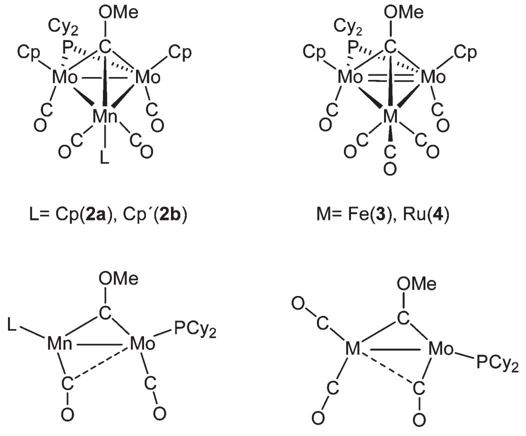

Figure 2. Structures of compounds **2**, **3**, and **4** and schematic drawings of the same structures (below) as viewed along the corresponding Mo−Mo axis so as to emphasize the distinct conformation of the carbonyl ligands, with Cp(Mo) ligands omitted for clarity.

of multiple metal−metal bonds remains almost unknown. We thus initiated a systematic study of the reactivity of unsaturated COR-bridged species, focused first on cationic binuclear complexes with 32- and 30-electron counts, which, due to their positive charge, display a dominant electrophilic behavior.[5−7] In contrast to these cations, the neutral 30-electron complex [$Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\mu\text{-CO})$] (**1**) (Cp = η^5-C_5H_5, Figure 1) is a more electron-rich species and should display a substantial nucleophilic behavior. Indeed, we have shown previously that compound **1** can be easily protonated or alkylated at the oxygen atom of its bridging carbonyl ligand to give the corresponding cations having new hydroxy- or alkoxycarbyne groups, respectively.[8] This is in agreement with a DFT calculation on compound **1**, indicating that the largest negative charge in this molecule is placed at that particular site. However, the same calculation revealed that the frontier orbitals of **1** do not involve that oxygen atom but rather the metal atoms and the bridgehead carbon atoms of the carbyne and carbonyl ligands.[8] Interestingly the HOMO−2 orbital, having δ (metal−metal) and π (metal−carbyne) bonding character, seems well-suited for enabling the complex to act as a base under conditions of orbital control, that is, when faced to soft acids, since it concentrates a large electron density on the relatively accessible region between the carbonyl and methoxycarbyne bridges (Figure 1). Thus we concluded that compound **1** might be a useful building block for the rational synthesis of heterometallic clusters if it is basic enough to add different coordinatively unsaturated metal fragments. This has been an efficient synthetic strategy extensively developed by Stone and co-workers mainly using mononuclear carbyne complexes as starting subtrates[1a,1b,1e] and is based on the isolobal analogies existing between different metal-based and carbon-based fragments, these allowing to compare, for instance, the reactivity of the C≡C, M≡C, and M≡M triple bonds with each other. In this paper we report our results on the reactions of compound **1** toward different transition-metal carbonyl complexes and related species to give heterometallic clusters having trinuclear and tetranuclear metal cores. One of these reactions was previously reported in a short communication.[9]

Results and Discussion

Incorporation of 16-Electron Metal Fragments. Compound **1** reacts readily with several carbonyl complexes of Mn, Fe, and Ru, which are able to generate 16-electron fragments of the type $M(CO)_n$ or $MCp(CO)_n$ to give trinuclear clusters containing a μ_3-bridging methoxycarbyne ligand, but the electron count of the product is strongly dependent on the metal being added. Thus, the reaction of **1** with the solvate manganese complexes [$MnL(CO)_2(THF)$] (L = η^5-C_5H_5, η^5-C_5H_4Me) takes place rapidly at room temperature in toluene solution to give the corresponding electron-precise (48-electron) clusters [$MnMo_2Cp_2L(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_4$] [L = η^5-C_5H_5 (**2a**), η^5-C_5H_4Me (**2b**)] (Figure 2). The formation of these molecules can be understood as following from the addition of the corresponding 16-electron fragment $MnL(CO)_2$ to the unsaturated Mo_2C center of **1** (interaction with the HOMO−2 orbital, see Figure 1) and further spontaneous carbonylation of the electron-deficient cluster (46-electron) thus generated, which could not be detected. This is possible due to the availability of CO in solution derived from the thermal decomposition of the excess [$MnL(CO)_2(THF)$] used in these reactions.

In contrast, the incorporation of the group 8 metal fragments $M(CO)_4$ leads selectively to 46-electron derivatives as expected. Indeed either the room-temperature reaction of **1** with [$Fe_2(CO)_9$] in tetrahydrofuran solution or the photochemical reaction of **1** with [$Ru_3(CO)_{12}$] yielded the pentacarbonyl derivatives [$Mo_2MCp_2(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_5$] [M = Fe (**3**), Ru (**4**)] in good yields (Figure 2). However, the structures of these clusters are not exactly the ones anticipated on the basis of the initial interaction between the reacting fragments, as will be discussed below.

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Surprisingly, no reaction was observed between **1** and the photochemically generated group 6 metal complexes $[M(CO)_5(THF)]$ (M = Mo, W) under various conditions. This can be hardly due to any intrinsic lack of stability in the expected derivatives $[Mo_2MCp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(CO)_6]$, since we have recently reported the preparation of the strongly related methylidyne-bridged trimolybdenum cluster $[Mo_3Cp_2(\mu\text{-}CH)(\mu\text{-}PCy_2)(CO)_7]$, this even having one more CO ligand.[10] We trust that our failure to prepare Mo_3 or Mo_2W clusters derived from **1** does not have an electronic origin but possibly arises from unfavorable kinetic barriers to the approach of the sterically more demanding $M(CO)_5$ fragments (when compared to the $M(CO)_4$ ones). The electronic effects obviously must be relevant in other cases. For instance, compound **1** failed to react with the solvate adduct $[ReCp(CO)_2(THF)]$ under conditions similar to those used to prepare the manganese clusters **2**, an observation that could hardly be ascribed to any steric effect.

Solid-State and Solution Structure of Compounds 2. The structure of **2a** in the crystal was reported in a previous communication.[9] It displays a Mo_2Mn triangle bridged by the COMe ligand in an essentially symmetrical way, if we allow for the ca. 0.1 Å difference in the covalent radii of Mo and Mn, and the molecule is completed with one cyclopentadienyl ligand on each metal atom (defining a cisoid conformation) and with one (Mo) or two (Mn) terminal CO ligands (Figure 3).[9] Within the methoxycarbyne group, the O−C (carbyne) length of 1.383(3) Å is substantially elongated with respect to the corresponding length in the binuclear complex $[Mo_2Cp_2(\mu\text{-}COEt)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (1.332(5) Å),[11] thus implying that upon going from the μ_2 to the μ_3 coordination modes, the π-bonding contribution to the O−C(carbyne) bond is fully suppressed, thus leaving a single C−O bond. In fact, the $C(sp^2)$−O single bonds in organic molecules are ca. 1.35 Å long,[12] and the C−OMe lengths in the dimethoxyacetylene complexes of the type $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}\eta^2{:}\eta^2\text{-}MeOCCOMe)(L_2)]^+$ are ca. 1.37 Å,[7a,7b] so we might consider the O−C(carbyne) distance in **2a** even a bit longer than expected for a single C−O bond. The Mn-bound CO ligands are involved in bent-semibridging interactions with the Mo atoms [Mo(2)−C(5) = 2.391(3) Å, Mo(1)−C(6) = 2.472(3) Å], thus balancing the electron densities at the Mo and Mn atoms, since the local electron counts would be 17.5 and 19 electrons, respectively, for a structure with only terminal CO ligands. The Mo−Mo length of 2.986(1) Å in **2a** is comparable to that measured in the electron-precise (48-electron) trimolybdenum cluster ($[Mo_3Cp_2(\mu\text{-}CH)(\mu\text{-}PCy_2)(CO)_7]$ mentioned above (2.9283(3) Å), and it is substantially longer than the corresponding lengths in the 46-electron clusters $[MnMo_2Cp_2Cp'(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ ($Cp' = \eta^5\text{-}C_5H_4Me$, Mo−Mo = 2.6448(8) Å)[13] and $[Mo_3Cp_3(\mu_3\text{-}CO)(\mu\text{-}PCy_2)(CO)_4]$ (Mo−Mo = 2.743(1) Å),[14] as expected. Incidentally, we note that the latter trimolybdenum species displays a structure very similar to that in **2a**, if we only replace the bridging carbonyl ligand by a methoxycarbyne group and one of the molybdenum atoms by manganese. Besides this, we should also remark that the Mn−Mo lengths of ca. 2.83 Å in **2a** are significantly shorter than some reference single-bond values, such as those measured in the binuclear complexes $[MnMoCp(CO)_8]$ (3.083(5) Å),[15a] $[MnMoCp(CO)_7\{P(OMe)_3\}]$ (3.112(1) Å),[15b] and $[MnMoCp(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ (3.088(1) Å),[15c] and even shorter than those measured in the tetranuclear complex $[Mo_2Mn_2Cp(CO)_7(\mu_3\text{-}Se)_4]$, a compound displaying a Mo_2Mn triangle triply bridged by two selenide ligands with Mo−Mn lengths of ca. 2.97 Å.[16] We attribute the shortness of the Mn−Mo bonds in **2a** to the presence of small-sized C-donor bridging ligands, notably the triply bridging methoxycarbyne ligand, but also to the carbonyl ligands acting as semibridging groups over each of the Mn−Mo edges. We finally note that, apart from the mentioned compounds, no other complexes having a triangular Mo_2Mn skeleton appear to have been reported previously.

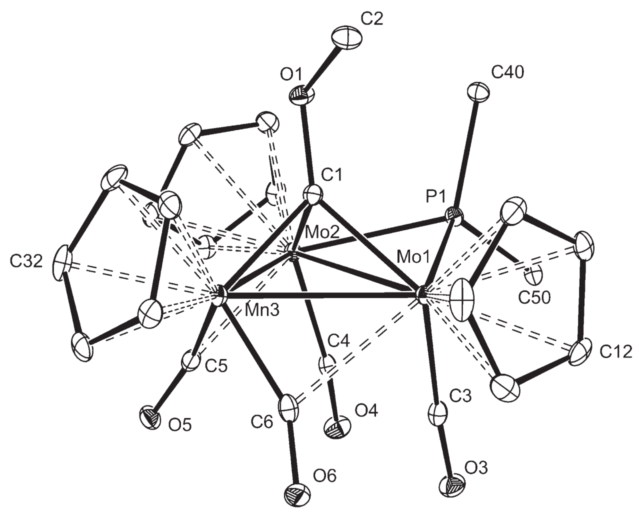

Figure 3. ORTEP diagram of compound **2a**, with H atoms and cyclohexyl rings (except the C^1 atoms) omitted for clarity (reproduced from ref 9). Selected bond lengths (Å): Mo(1)−Mo(2) = 2.986(1), Mo(1)−Mn(3) = 2.824(1), Mo(2)−Mn(3) = 2.830(1), Mo(1)−C(1) = 2.085(3), Mo(2)−C(1) = 2.136(2), Mn(3)−C(1) = 1.989(3), Mo(1)−P(1) = 2.438(1), Mo(2)−P(1) = 2.453(1), Mo(1)−C(3) = 1.968(3), Mo(2)−C(4) = 1.959(3), Mn(3)−C(5) = 1.819(3), Mo(2)−C(5) = 2.391(3), Mn(3)−C(6) = 1.811(3), Mo(1)−C(6) = 2.472(3), C(1)−O(1) = 1.383(3), O(1)−C(2) = 1.429(3). Selected bond angles (deg): Mn(3)−C(5)−O(5) = 150.6(2), Mn(3)−C(6)−O(6) = 154.0(2), C(1)−O(1)−C(2) = 119.2(2).

Spectroscopic data in solution for compounds **2a** and **2b** are very similar to each other (Table 1 and Experimental Section), and they are also consistent with the structure of **2a** in the crystal. The IR spectra of these compounds display four C−O stretching bands, with that at higher frequency (the symmetric stretch) being by far the most intense one, in agreement with the cisoid arrangement of all carbonyl ligands in the cluster.[17] Moreover, the low frequency of the fourth band (ca. 1760 cm^{-1}) is fully consistent with the retention of semibridging carbonyls in solution. This is

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Table 1. Selected IR[a] and NMR[b] Data for New Complexes

	ν(CO)	δ(P)	δ(μ-COMe) [J_{CP}]
[$Mo_2Cp_2(\mu$-COMe)(μ-$PCy_2)(\mu$-CO)] (**1**)[c]	1674 (s)	228.5	352.0 [15]
[$MnMo_2Cp_3(\mu_3$-COMe)(μ-$PCy_2)(CO)_4$] (**2a**)	1928 (vs), 1862 (w), 1800 (w), 1749 (w)	143.7	
[$MnMo_2Cp_2Cp'(\mu_3$-COMe)(μ-$PCy_2)(CO)_4$] (**2b**)	1936 (vs), 1875 (w), 1815 (w), 1771 (w)[d]	141.5[e]	314.5 [28][e]
[$FeMo_2Cp_2(\mu_3$-COMe)(μ-$PCy_2)(CO)_5$] (**3**)	2009 (vs), 1945 (s), 1913 (m)[d]	183.0	357.0 [3]
[$Mo_2RuCp_2(\mu_3$-COMe)(μ-$PCy_2)(CO)_5$] (**4**)	2036 (vs), 1970 (s), 1936 (m), 1918 (w)[f]	181.6	339.3
[$CuMo_2ClCp_2(\mu_3$-COMe)(μ-$PCy_2)(\mu$-CO)] (**5**)	1676 (s)	207.0[g]	330.5 [16][g]
[$Co_2Mo_2Cp_2(\mu_3$-COMe)(μ-$PCy_2)(\mu$-CO$)_2(CO)_4$] (**6**)	2013 (vs), 1983 (vs), 1959 (m), 1855 (w), 1809 (w), 1765 (w)	184.7	
[$Co_2Mo_2Cp_2(\mu_3$-COMe)(μ-$PCy_2)(\mu$-CO)$(CO)_6$] (**7**)	1993 (vs), 1966 (m), 1893 (w), 1823 (w), 1785 (m)[f]	340.5[g]	347.4[g]

[a] Recorded in dichloromethane solution, ν(CO) in cm^{-1} for carbonyl ligands. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 (^{31}P) or 75.48 (^{13}C) MHz, unless otherwise stated; δ in ppm relative to internal TMS (^{13}C) or external 85% aqueous H_3PO_4 (^{31}P), J in Hz. [c] Data taken from ref 11. [d] In toluene solution. [e] In C_6D_6 solution. [f] In petroleum ether solution. [g] Recorded at 233 K.

further confirmed by the $^{13}C\{^1H\}$ NMR spectrum of **2b**, which displays a single and quite deshielded resonance (for Mn-bound carbonyls) at 253.8 ppm for the two equivalent Mn-CO ligands, while the also equivalent Mo-bound ligands give rise to a doublet resonance at 238.9 ppm ($J_{PC} = 10$) in the usual region of terminal carbonyls bound to molybdenum. The existence of an effective symmetry plane relating both Mo fragments is further revealed in this spectrum by the appearance of single resonances for the Cp ligands and for each pair of diastereotopic C atoms of the C_5H_4 and cyclohexyl groups. All this is possible only if there is fast rotation of the OMe group around the O−C(carbyne) bond on the NMR time scale, a movement now facilitated by the absence of any π-bonding component in that bond, as indicated by the X-ray data discussed above. In contrast, the presence of some multiplicity in the O−C bonds of the edge-bridging alkoxycarbyne ligands has been shown previously to restrict at some extent the rotation of the alkoxy group around this bond (see ref 5b and previous work cited therein). Finally we note that the chemical shift of the carbyne ligand in **2b** (314.5 ppm) is substantially lower than that in the precursor **1** (352.0 ppm).[11] This shielding effect is a general trend found for carbyne ligands when comparing μ_2- and μ_3-bridging ligands, and the magnitude of the effect for **2b** (ca. 40 ppm) is comparable to that found for the pair [$Fe_2(\mu$-COEt)-{μ-CPhCHPh}$(CO)_6$]/[$Fe_3(\mu_3$-COMe)$(CO)_9$] (383.8 ppm/345.9 ppm).[18]

Solid-State and Solution Structure of Compounds 3 and 4. A single-crystal X-ray study of the Mo_2Fe cluster **3** was carried out. However, due to poor crystal quality and twinning, a satisfactory refinement of the structure could not be achieved (the lowest R_1 being ca. 0.18, see Experimental Section). Even so, the available data give full support to the structure proposed on the basis of the spectroscopic data (Figure 2), with a metal triangle defined by two MoCp(CO) fragments (in a cisoid conformation) and one pyramidal $Fe(CO)_3$ fragment, the triangle being bridged by a methoxycarbyne bridge (Mo−C ca. 2.10 Å, Fe−C ca. 1.82 Å). The molecule thus can be viewed as resulting from the addition of a methylene-like $Fe(CO)_4$ fragment to the unsaturated Mo_2C center of **1** (interaction with the HOMO−2 orbital, see Figure 1), this being followed by a carbonyl transfer from Fe to Mo. The resulting cluster is unsaturated (46-electron), and our crystallographic data suggest that this unsaturation is mainly located on the Mo−Mo bond, since the Mo−Fe lengths (ca. 2.79 Å) are only moderately shorter than those measured in related electron-precise $FeMo_2$ clusters such as [$FeMo_2L_2(\mu_3$-S)$(CO)_7$] (L = η^5-C_5H_4Me; Mo−Fe ca. 2.82 Å)[19a] and [$FeMo_2Cp_2(\mu_3$-PPh)$(CO)_7$] (ca. 2.92 Å),[19b] whereas the Mo−Mo length in **3** (2.69 Å) is ca. 0.3 Å shorter than the corresponding distance in the electron-precise complex **2a** and even shorter than the corresponding distance in the 46-electron cluster [$Mo_3Cp_3(\mu_3$-CO)(μ-$PCy_2)(CO)_4$] (2.743(1) Å).[14] Yet, the iron center remains somewhat unsaturated (a formal count of 17 electrons in a structure with only terminal carbonyls), this explaining the distinct conformation of the Mo-CO ligands in **3** (when compared to those in **2a**), since now these are directed toward the iron atom in an incipient semibridging interaction so as to partially relieve the unsaturation at the iron center (Figure 2).

The spectroscopic data in solution for compounds **3** and **4** are very similar to each other (Table 1 and Experimental Section). The IR spectrum exhibits in each case three strong C−O stretching bands, as expected from the presence of a pyramidal $M(CO)_3$ oscillator under local C_s symmetry,[17] while the Mo-bound carbonyls seem to give rise to very weak absorptions barely hinted at in the baseline of the spectra. This is not unusual in this type of heterometallic clusters; actually, the related (even if electron-precise) cluster [$FeMo_2Cp_2(\mu$-$PPh_2)(\mu_3$-CCPh)$(CO)_5$] also displays just three similar C−O stretching bands at 2028 (vs), 1989 (s), and 1961 (m) cm^{-1}.[20] The NMR data for compounds **3** and **4** reveal the presence of an effective symmetry plane relating both Mo fragments, as found for compounds **2**. The equivalent molybdenum-bound carbonyl ligands, however, give rise now to a relatively deshielded ^{13}C resonance (ca. 250 ppm), which is suggestive of an incipient semibridging character, in full agreement with our crystallographic analysis of **3**. In contrast, the iron- and ruthenium-bound carbonyls give rise in each case to a single resonance (δ 218.3 and 202.8 ppm, respectively) in the corresponding terminal regions. This of course requires the existence of a dynamic process, fast on the NMR time scale, effectively exchanging the chemical environments of the three carbonyl ligands bound to the group 8 metal atom in each case. This is a very common phenomenon for di- and polynuclear carbonyl complexes having pyramidal $M(CO)_3$ units and was not further investigated. As for the carbyne resonance, this was found much more deshielded than that in the electron-precise **2b**, actually slightly below (339.3 ppm for **4**) or even above (357.0 ppm for **3**) the corresponding resonance in the parent compound **1**. It would be tempting to conclude that the multiple intermetallic bonding in these trinuclear compounds might be having a deshielding effect on the carbyne resonance, thus

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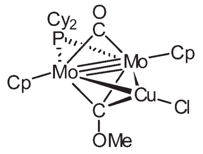
counterbalancing the shielding effect derived from the change (from μ_2 to μ_3) in the coordination mode occurring upon cluster formation. However, similar deshielded resonances are also observed for an electron-precise Mo_2Co_2 cluster to be discussed later, this being an indication that the carbyne shielding in these clusters cannot be interpreted in such simple terms. Fortunately, the ^{31}P resonances of the dicyclohexylphosphide ligands seem to better correlate with the electron count of the molecule. As it can be deduced from the data in Table 1, all of the electron-deficient clusters described in this work give rise to relatively deshielded $Mo_2(\mu\text{-}PCy_2)$ resonances in the range 180−210 ppm, while the electron-precise clusters **2a**,**b** give rise to much more shielded resonances (ca. 140 ppm). This is in agreement with the ^{13}P NMR data obtained recently by us on different 46-electron trinuclear derivatives of the hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$, all of them exhibiting $Mo_2(\mu\text{-}PCy_2)$ resonances in the range 170−210 ppm.[13]

Incorporation of Group 11 Metal Fragments. Heterometallic compounds containing bonds between transition metals and group 11 elements can often be formed by the reaction of basic transition-metal complexes (either neutral or anionic) with the pertinent metal(I) halides MX or related derivatives such as the neutral complexes $[MXL_n]$ or the cations $[ML_m]^+$ (L = two-electron donor ligand).[21] Since compound **1** is basic enough to react with protons or 16-electron metal fragments, it was worth examining its ability to form new bonds with the group 11 elements. Indeed, compound **1** reacts rapidly with the gold(I) cations $[Au(PR_3)]^+$ (R = Ph, Me; prepared in situ from $[AuCl(PR_3)]$ and $TlPF_6$), but a complex mixture of compounds was formed. A similar result was obtained when using the neutral complex [AuCl(THT)] (THT = tetrahydrothiophen). In contrast, compound **1** reacted cleanly with solid CuCl in dichloromethane solution to give the corresponding 1:1 adduct $[CuMo_2ClCp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**5**). Although the formation of compound **5** is selective, this cluster is rather unstable in solution, and it slowly decomposes at room temperature to give the chloro complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PCy_2)(CO)_2]$,[11] along with other uncharacterized species. Thus, no crystalline sample suitable for an X-ray analysis could be obtained for this compound.

The spectroscopic data in solution for **5** indicate that little rearrangement in the structure of the parent compound **1** has occurred upon addition of the CuCl fragment. Thus, the carbonyl ligand in **5** gives rise to a C−O stretching band only marginally more energetic than that of **1**, thus indicating the retention of its bridging character (Table 1). This is further confirmed by the appearance of a quite deshielded ^{13}C resonance for this ligand (287.6 ppm, to be compared to 305.0 ppm for **1**). Besides this, the carbyne resonance appears at 330.5 ppm, only some 20 ppm more shielded than the corresponding resonance in the parent compound **1**. All of this is consistent with a binding (possibly not a very strong one) of the acidic CuCl fragment to the unsaturated Mo_2C center of **1** (interaction with the HOMO−2 orbital, see Figure 1) without any further substantial rearrangement. This of course implies the retention of a symmetry plane relating both Mo fragments, as it can be deduced from the chemical equivalences apparent from the number of ^1H and ^{13}C NMR resonances (see Experimental Section). Under this interpretation, the acidic CuCl fragment would be acting essentially as an acceptor group, and therefore the intermetallic bond order would only be marginally reduced with respect to that in the parent compound, as a result of the dominant Cu−HOMO−2 orbital interaction. This is consistent with the fact that the chemical shift of the P nucleus in **5** is still quite high (207.0 ppm) and comparable to those found for the unsaturated hydride clusters $[MMo_2Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7]$ (M = Cr, Mo, W).[13] Interestingly, the structure of the latter clusters could also be described as the result of a simple donor−acceptor interaction between a triply bonded complex (the donor, the hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$) and a coordinatively unsaturated mononuclear metal fragment (the acceptor, the pentacarbonyls $[M(CO)_5]$). We note that an isolable adduct could also be obtained between $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ and CuCl, apparently also with little rearrangement of the dimolybdenum center in that case.[13]

Chart 2



5

Tetranuclear Derivatives. Compounds having triple bonds between metal atoms and carbon, as is the case of mononuclear carbyne complexes, have been shown to react with dimetal carbonyl complexes having triple metal−metal bonds or synthetic equivalents of them (for example, $[Co_2(CO)_8]$) to give the corresponding heterometallic derivatives having trimetallatetrahedrane central cores as a result of the corresponding eight-electron interactions.[22] More recently this strategy has also been applied to substrates having metal−phosphorus triple bonds, to give heterometallic derivatives having phosphatrimetallatetraedrane cores.[23] Thus it was conceivable that the triply bonded complex **1** might experience similar reactions to give tetranuclear derivatives exhibiting tetrahedral metal cores. Unfortunately, no reaction was observed between compound **1** and the triply bonded tetracarbonyl $[Mo_2Cp_2(CO)_4]$ even in refluxing toluene solutions or under visible−UV light irradiation. In contrast, a rapid reaction takes place between **1** and $[Co_2(CO)_8]$ at room temperature to give a mixture of two tetranuclear clusters in similar amounts, these being the hexacarbonyl $[Co_2Mo_2Cp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_4]$ (**6**) and the heptacarbonyl $[Co_2Mo_2Cp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_6]$ (**7**) (Chart 2). The latter compound has the expected composition, i.e., the one resulting from the addition of a $Co_2(CO)_6$ fragment to compound **1**, but not the expected structure, as will be discussed below. In contrast, the hexacarbonyl cluster **6** roughly has the expected structure, but one carbonyl below the number that might have been anticipated. Although we have not studied in detail the carbonylation/decarbonylation processes that

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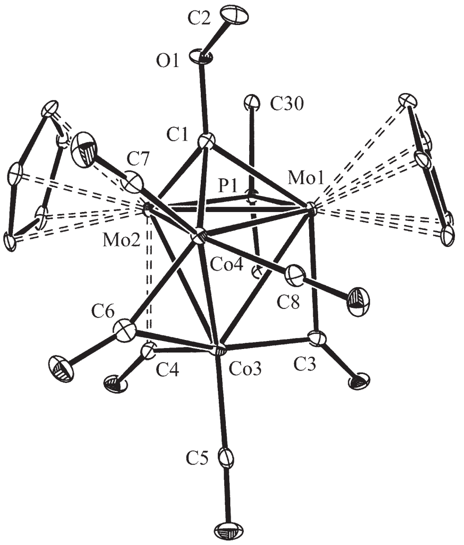


Figure 4. ORTEP diagram (30% probability) of compound **6**, with H atoms and Cy rings (except the C^1 atoms) omitted for clarity.

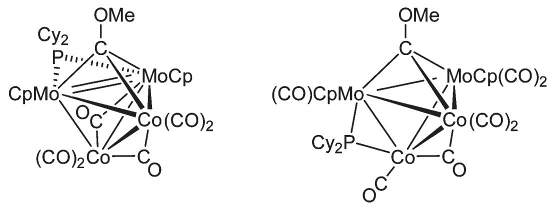
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Mo(1)−Mo(2)	2.6857(6)	C(1)−O(1)−C(2)	118.9(4)
Mo(1)−Co(3)	2.7422(8)	Mo(1)−C(3)−O(3)	138.4(4)
Mo(1)−Co(4)	2.7679(8)	Co(3)−C(3)−O(3)	137.0(4)
Mo(2)−Co(3)	2.7013(8)	Co(3)−C(4)−O(4)	151.7(4)
Mo(2)−Co(4)	2.7710(8)	Co(3)−C(5)−O(5)	176.2(5)
Co(3)−Co(4)	2.4147(9)	Co(3)−C(6)−O(6)	133.3(4)
Mo(1)−P(1)	2.4007(11)	Co(4)−C(6)−O(6)	151.1(4)
Mo(2)−P(1)	2.3997(11)	Co(4)−C(7)−O(7)	176.5(4)
Mo(1)−C(1)	2.189(4)	Co(4)−C(8)−O(8)	176.6(4)
Mo(2)−C(1)	2.030(4)	Mo(1)−P(1)−Mo(2)	68.04(3)
Co(4)−C(1)	1.883(5)	Co(3)−C(6)−Co(4)	75.5(2)
Co(3)−C(3)	1.896(4)	Mo(1)−C(1)−Mo(2)	79.0(2)
Mo(1)−C(3)	2.168(5)	Mo(2)−C(1)−Co(4)	90.1(2)
Co(3)−C(4)	1.777(5)	Co(4)−C(1)−Mo(1)	85.3(2)
Mo(2)−C(4)	2.364(4)	P(1)−Mo(2)−C(1)	96.2(1)
Co(3)−C(5)	1.749(5)	C(1)−Co(4)−C(7)	96.6(2)
Co(3)−C(6)	2.084(5)	C(1)−Co(4)−C(6)	128.7(2)
Co(4)−C(6)	1.847(5)	C(6)−Co(3)−C(3)	159.1(2)
Co(4)−C(7)	1.778(5)	C(6)−Co(3)−C(4)	97.4(2)
Co(4)−C(8)	1.773(5)	C(6)−Co(3)−C(5)	94.4(2)
C(1)−O(1)	1.345(5)	C(6)−Co(4)−C(7)	92.5(2)
O(1)−C(2)	1.436(6)		

might convert one compound into the other under forcing conditions, we note that none of these compounds transforms spontaneously into the other one in solution at room temperature. Thus, we conclude that there are two independent pathways in the room-temperature reaction of compound **1** with $[Co_2(CO)_8]$.

Solid-State and Solution Structure of Compound 6. The structure of this cluster in the crystal is shown in Figure 4, while the most relevant bond distances and angles are collected in Table 2. The molecule exhibits a quite regular Mo_2Co_2 tetrahedral metal core, with the methoxycarbyne ligand bridging one of the Mo_2Co faces and the dicyclohexylphosphide ligand bridging the Mo−Mo edge, as expected. Each of the molybdenum atoms bears a cyclopentadienyl ligand, and there are two rather asymmetric bridging carbonyl ligands, one over the Co−Co edge and another one over the Co(3)−Mo(1) edge. The Co(3) atom also bears a terminal carbonyl and another carbonyl involved in a weak semibridging interaction with the Mo(2) atom (C(4)···Mo(2) = 2.364(5) Å). The different strength of the interaction of the Mo atoms with the bridging and semibridging carbonyls is compensated by the carbyne ligand, which binds the Mo(2) atom more strongly (Mo(2)−C(1) = 2.031(5) Å, Mo(1)−C(1) = 2.188(5) Å). Finally, the Co(4) atom bears two terminal carbonyl ligands. Overall, compound **1** is a 58-electron cluster, two below the 60 electrons needed for an electron-precise tetrahedral cluster such as the dodecacarbonyls $[M_4(CO)_{12}]$ (M = Co, Rh, Ir), and therefore is unsaturated. A systematic search in the Cambridge Structural Database[24] revealed that the intermetallic distances in electron-precise clusters with Co_2Mo_2 cores usually display Mo−Co lengths in the range 2.64−2.79 Å and Co−Co lengths in the range 2.45−2.75 Å, with the shorter bonds usually being those bridged by carbonyl ligands. In compound **1** the Mo−Co lengths fall in the range 2.70−2.77 Å and must be therefore considered as normal, single-bond lengths. This also applies to the Co−Co length of 2.415(1) Å, after taking into account the presence of a bridging ligand over that bond. However, the Mo−Mo length in **6** (2.686(1) Å) is almost identical to that measured in the unsaturated (46-electron) Mo_2Fe cluster **3** and 0.30 Å shorter than the corresponding distance in the electron-precise (48-electron) Mo_2Mn cluster **2a**. Thus we conclude once more that the unsaturation in **6** is mainly concentrated on the Mo−Mo bond, which can be formally identified as a double bond (Chart 3).

Chart 3



6 **7**

The spectroscopic data in solution for compound **6** are essentially consistent with its solid-state structure, except for some fine details. Thus, its IR spectrum in the C−O stretching region is very similar to that recorded for the solid in a Nujol mull (see Experimental Section), thus indicating that the carbonyl arrangement found in the solid is essentially retained in solution. However, the ^1H NMR spectrum of **6** suggests that the actual symmetry in solution must be somewhat higher than that in the solid, since the Cp ligands give rise to a single resonance. This can be easily accomplished with a minimum distortion of the solid-state structure, so as to yield two equivalent Co(3)−CO···Mo semibridging interactions that would be compensated by a symmetrical share of the carbyne ligand between molybdenum atoms. We note finally that the ^{31}P spectrum of **6** is also consistent with its solid-state structure since it exhibits a quite deshielded resonance (184.7 ppm), with a chemical shift comparable to those of the clusters **3** and **4**, which also display dicyclohexylphosphide ligands bridging Mo−Mo double bonds.

Solid-State and Solution Structure of Compound 7. The structure of this cluster in the crystal is shown in the Figure 5, while the most relevant bond distances and angles are collected in Table 3. The molecule displays a somewhat distorted tetrahedral Mo_2Co_2 core, with the methoxycarbyne ligand symmetrically bridging one of the Mo_2Co faces as expected, but with the dicyclohexylphosphide ligand now bridging a Mo(1)−Co edge rather than the molybdenum atoms.

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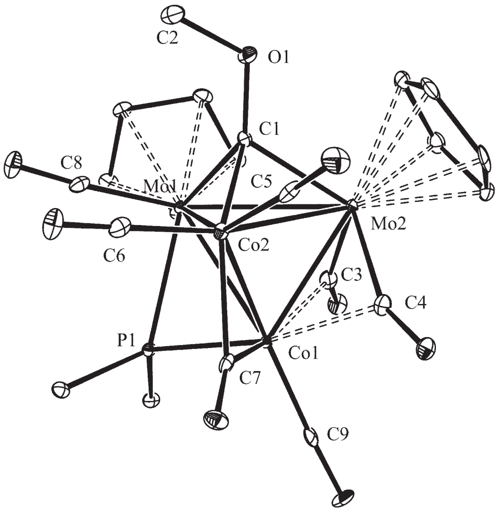

Figure 5. ORTEP diagram (30% probability) of compound **7** (only one of the two independent molecules shown), with H atoms and Cy rings (except the C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 7

Mo(1)−Mo(2)	2.9667(9)	C(1)−O(1)−C(2)	117.3(4)
Mo(1)−Co(1)	2.8174(8)	Mo(1)−C(8)−O(8)	171.6(4)
Mo(2)−Co(1)	2.5816(9)	Mo(2)−C(3)−O(3)	155.6(4)
Mo(1)−Co(2)	2.7825(9)	Mo(2)−C(4)−O(4)	157.3(4)
Mo(2)−Co(2)	2.7276(9)	Co(1)−C(9)−O(9)	175.8(5)
Co(1)−Co(2)	2.4927(10)	Co(1)−C(7)−O(7)	143.3(4)
Mo(1)−P(1)	2.4355(13)	Co(2)−C(7)−O(7)	137.9(4)
Co(1)−P(1)	2.1849(15)	Co(2)−C(6)−O(6)	175.5(4)
Mo(1)−C(1)	2.119(5)	Co(2)−C(5)−O(5)	176.5(4)
Mo(2)−C(1)	2.109(5)	Mo(1)−P(1)−Co(1)	74.92(4)
Co(2)−C(1)	1.921(5)	Co(1)−C(7)−Co(2)	78.5(2)
Mo(1)−C(8)	1.952(5)	Mo(1)−C(1)−Mo(2)	89.1(2)
Mo(2)−C(3)	2.001(5)	Mo(1)−C(1)−Co(2)	86.9(2)
Co(1)−C(3)	2.181(5)	Mo(2)−C(1)−Co(2)	85.1(2)
Mo(2)−C(4)	2.004(5)	C(1)−Mo(1)−C(8)	86.9(2)
Co(1)−C(4)	2.195(5)	C(1)−Mo(1)−P(1)	124.8(1)
Co(1)−C(9)	1.746(5)	C(1)−Mo(2)−C(3)	111.6(2)
Co(1)−C(7)	1.902(5)	C(1)−Mo(2)−C(4)	114.9(2)
Co(2)−C(7)	2.036(5)	C(3)−Mo(2)−C(4)	91.2(2)
Co(2)−C(6)	1.764(5)	C(7)−Co(2)−C(6)	91.4(2)
Co(2)−C(5)	1.784(5)	C(7)−Co(2)−C(5)	103.5(2)
C(1)−O(1)	1.349(5)	C(7)−Co(1)−P(1)	95.9(2)
O(1)−C(2)	1.434(6)	C(7)−Co(1)−C(9)	99.2(2)

Table 4. Crystal Data for Compounds 6 and 7

	6	7
mol formula	$C_{30}H_{35}Co_2Mo_2O_7P$	$C_{31}H_{35}Co_2Mo_2O_8P$
mol wt	848.29	876.3
cryst syst	monoclinic	monoclinic
space group	$P2_1$	Pc
radiation (λ, Å)	0.71073	0.71073
a, Å	9.887(2)	9.790(2)
b, Å	16.178(3)	17.122(4)
c, Å	10.307(2)	19.337(5)
α, deg	90	90
β, deg	114.510(3)	104.332(4)
γ, deg	90	90
V, Å^3	1500.1(5)	3140.5(13)
Z	2	4
calcd density, g cm^{-3}	1.878	1.853
absorpt coeff, mm^{-1}	2.003	1.919
temperature, K	100	100
θ range, deg	2.17−27.87	2.15−27.88
index ranges (h, k, l)	−13, 11; −21, 21; 0, 13	−12, 12; 0, 22; −25, 25
no. of reflns collected	27832	57021
no. of indep reflns	7002 [R_{int} = 0.050]	15098 [R_{int} = 0.053]
reflns with $I > 2\sigma(I)$	6287	12498
R indexes	R_1 = 0.0338	R_1 = 0.0369
[data with $I > 2\sigma(I)$]	wR_2 = 0.0708^{a,b}	wR_2 = 0.0842^{a,c}
GOF	1.089	1.069
Flack param	−0.011(16)	−0.001(11)
no. of restraints/params	1/379	2/795
$\Delta\rho$ (max,min), e Å^{-3}	0.566, − 0.986	1.577, −1.11

[a] $wR=1/[\sum w(|F_o|^2-|F_c|^2)/\sum w|F_o|^2]^{1/2}$, with $w=1/[\sigma^2(F_o)^2+(aP)^2+bP]$, where $P=(F_o^2+2F_c^2)/3$. [b] $a=0.0299$, $b=1.4940$. [c] $a=0.0479$, $b=0.0000$.

This is compensated by the different number of carbonyls bound to these metal atoms, one terminal (on Mo(1)) and two semibridging ones (on Mo(2)), respectively. As found for **6**, the cobalt atoms in **7** are bridged by a carbonyl ligand, and there are also three terminal carbonyls, one on Co(1) and two on the Co(2) atom. Overall, the molecule is an electron-precise (60-electron) tetrahedral cluster, and all the metal−metal interactions should be described as single bonds, in agreement with the measured intermetallic lengths of 2.58−2.82 Å (Mo−Co bonds), 2.493(1) Å (Co−Co), and 2.967(1) Å (Mo−Mo). Note that the latter figure is very close to the corresponding value measured in the electron-precise Mo_2Mn cluster **2a** (2.986(1) Å), as expected.

The spectroscopic data in solution for compound **7** are in full agreement with the asymmetric structure found in the solid state. Thus the ^1H and $^{13}C\{^1H\}$ NMR spectra reveal the retention of inequivalent Cp ligands in solution. The methoxycarbyne ligand gives rise to a quite deshielded (for an electron-precise molecule) resonance at 347.4 ppm, and seven different resonances are observed in the carbonyl region, with chemical shifts that allow their identification with the different coordination sites found in the crystal. The most deshielded resonance is unambiguously assigned to the carbonyl ligand bridging the Co atoms (271.2 ppm), this being followed by the resonances of the molybdenum-bound carbonyls, two semibridging ones (resonances at 255.1 and 242.6 ppm) and one terminal (231.5 ppm), and finally by the resonances of the three cobalt-bound terminal carbonyls (211.5, 207.2, and 202.3 ppm). In agreement with this, the IR spectra of **7** both in solution and in the solid state exhibit a high number of C−O stretching bands (see Table 1 and Experimental Section), including several ones at low frequencies, as expected for a low-symmetry molecule having three bridging or semibridging carbonyls.

The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **7** displays an unusually deshielded and broad resonance at 333.7 ppm that becomes a sharp singlet at about the same shift (340.5 ppm) when recorded at 223 K. The broadening effect of this resonance and its temperature dependence are characteristic of nuclei bound (and scalar coupled) to quadrupolar nuclei,[25] as is the case of the ^{59}Co nucleus ($I = 7/2$, natural abundance 100%). The very strong deshielding of this resonance, however, cannot be just attributed to the coordination position of the phosphorus-donor ligand between Mo and the light Co atom. Indeed, related complexes having PR_2 ligands bridging Mo−Co bonds exhibit only moderately deshielded resonances, as is the case of the cluster $[Co_2MoCp\{\mu_3\text{-}C(C_6H_4Me)\}(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ ($\delta_P = 196.4$ ppm),[26a] or several binuclear complexes of the type $[CoMoCp(\mu\text{-}PPh_2CR{=}CCO_2Me)(\mu\text{-}PPh_2)(CO)_3]$

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(R = H, CO_2Me; δ_P = 160−205 ppm).[26b] Since the geometrical parameters around the PCy_2 ligand in the crystals of **7** are unremarkable, we trust that the unusual deshielding of the P nucleus might be due to a particularly strong cluster effect in this molecule. Indeed it has been shown in several instances that upon increasing the nuclearity of some PR_2-bridged clusters there is a general increase in the ^{31}P chemical shifts, an effect that can be attributed to the progressive decrease of the HOMO−LUMO gap of the corresponding clusters.[27] The reason that this effect should be much stronger in the heptacarbonyl **7** than in the hexacarbonyl **6** remains, however, unclear to us at the moment.

Concluding Remarks

The unsaturated methoxycarbyne complex **1** is a useful building block for the rational synthesis of heterometallic clusters having triangular or tetrahedral metal cores, since it is basic enough to add different coordinatively unsaturated metal fragments. The structure of the resulting clusters can be interpreted in all cases as derived from an initial interaction of the HOMO−2 orbital of the dimolybdenum substrate with the relevant acceptor orbital of the metal fragment being added, but further rearrangements (carbonyl or dicyclohexylphosphide migrations) or reactions (carbonylation and decarbonylation processes) usually follow, depending on the metal being added. In all cases, the methoxycarbyne ligand ends up as a triply bridging group on an heterometallic Mo_2M triangle, as expected from the Mo−C π-bonding character of the mentioned frontier orbital of complex **1**.

Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to their use.[28] Petroleum ether refers to that fraction distilling in the range 338−343 K. Compound $[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\mu\text{-CO})]$ (**1**)[11] and tetrahydrofuran (THF) solutions of the manganese solvate complexes $[MnL(CO)_2(THF)]$ (L = η^5-C_5H_5, η^5-C_5H_4Me)[29] were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, and kept at the desired temperature with a cryostat. A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all the experiments. Chromatographic separations were carried out using jacketed columns. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were carried out using diatomaceous earth. IR stretching frequencies were measured in solution or Nujol mulls, are referred to as ν (solvent) or ν (Nujol), respectively, and are given in wavenumber units (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), or 75.47 ($^{13}C\{^1H\}$) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (*J*) are given in Hz.

Preparation of $[MnMo_2Cp_3(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_4]$ (2a). Compound **1** (0.040 g, 0.068 mmol) was added to a freshly prepared THF solution (10 mL) of $[MnCp(CO)_2(THF)]$ (ca. 0.2 mmol). The solvent was then removed under vacuum, the residue dissolved in toluene (10 mL), and the resulting solution then stirred for 15 min. The solvent was removed under vacuum again, the brown residue was then extracted with dichloromethane−petroleum ether (1:7), and the extracts were chromatographed on alumina (activity IV) at 253 K. Elution with the same solvent mixture gave a yellow fraction containing $[MnCp(CO)_3]$. Elution with dichloromethane−petroleum ether (1:1) gave a brown fraction, which yielded, after removal of solvents under vacuum, compound **2a** as an orange solid (0.035 g, 65%). The crystals used in the X-ray study of this compound were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at room temperature, and the corresponding crystallographic data can be found in ref 9. Anal. Calcd for $C_{34.5}H_{43}Cl_3MnMo_2O_5P$ (**2a**$\cdot 1.5CH_2Cl_2$): C, 44.94; H, 4.67. Found: C, 45.11; H, 4.81. ^1H NMR: δ 5.15 (s, MoCp, 10H), 4.61 (s, MnCp, 5H), 3.85 (s, OMe, 3H), 2.20−1.10 (m, Cy, 22H).

Preparation of $[MnMo_2Cp_2Cp'(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_4]$ (2b). The procedure is completely analogous to that described above for **2a**, but using a freshly prepared THF solution (10 mL) of $[MnCp'(CO)_2(THF)]$ (ca. 0.2 mmol; Cp′ = η^5-C_5H_4Me). After similar workup, compound **2b** was obtained as an orange solid (0.032 g, 58%). Anal. Calcd for $C_{34}H_{42}MnMo_2O_5P$: C, 50.51; H, 5.24. Found: C, 50.57; H, 5.30. ^1H NMR (C_6D_6): δ 4.95 (s, MoCp, 10H), 4.24 (s, C_5H_4, 2H), 3.71 (s, br, C_5H_4, 2H), 3.37 (s, OMe, 3H), 2.22 (s, Me, 3H), 2.20−1.10 (m, Cy, 22H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 314.5 (d, J_{CP} = 28, μ-*C*OMe), 253.8 (s, 2× MnCO), 238.9 (d, J_{CP} =10, 2×MoCO), 102.2 [s, $C^1(C_5H_4)$], 90.5 (s, Cp), 90.0, 89.6 [2*s*, $C^2(C_5H_4)$ and $C^3(C_5H_4)$], 65.9 (s, OMe), 50.4 [d, J_{CP} = 10, C^1(Cy)], 49.0 [d, J_{CP} = 5, C^1(Cy)], 34.9 [s, 2× C^2(Cy)], 28.9 [d, J_{CP} = 9, C^3(Cy)], 28.5 [d, J_{CP} = 10, C^3(Cy)], 26.6 [s, 2× C^4(Cy)], 12.2 (s, Me).

Preparation of $[FeMo_2Cp_2(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_5]$ (3). Solid $[Fe_2(CO)_9]$ (0.025 g, 0.096 mmol) was added to a toluene solution (10 mL) of compound **1** (0.040 g, 0.068 mmol), and the mixture was stirred at room temperature for 1 h to give a green solution, which was filtered. The solvent was then removed under vacuum from the filtrate, and the residue was recrystallized from dichloromethane and petroleum ether to give compound **3** as a green powder (0.048 g, 93%). The crystals used in the X-ray study of this compound were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K and were of poor quality. Selected crystal data: green crystals, triclinic ($P\bar{1}$), *a* = 10.407(3) Å, *b* = 10.975(4) Å, *c* = 12.614(4) Å, α = 90.472(7)°, β = 94.85(3)°, γ = 90.20(4)°, *V* = 1435.5(8) Å^3, *T* = 120 K, *Z* = 2, *R* = 0.1771 (observed data with $I > 2\sigma(I)$), GOF = 1.12. Anal. Calcd for $C_{29}H_{35}FeMo_2O_6P$: C, 45.93; H, 4.65. Found: C, 46.12; H, 4.86. ^1H NMR: δ 5.12 (s, Cp, 10H), 4.10 (s, OMe, 3H), 2.60−0.80 (m, Cy, 22H). $^{13}C\{^1H\}$ NMR: δ 357.0 (d, J_{CP} = 3, μ-*C*OMe), 254.4 (d, J_{CP} = 6, 2 × MoCO), 218.3 (s, 3 × FeCO), 89.5 (s, Cp), 67.8 (s, OMe), 47.9 [d, J_{CP} = 22, C^1(Cy)], 43.7 [d, J_{CP} = 16, C^1(Cy)], 33.8, 33.1 [2s, 2 × C^2(Cy)], 28.2 [d, J_{CP} = 10, C^3(Cy)], 28.15 [d, J_{CP} = 12, C^3(Cy)], 26.8, 26.6 [2s, 2 × C^4(Cy)].

Preparation of $[Mo_2RuCp_2(\mu_3\text{-COMe})(\mu\text{-PCy}_2)(CO)_5]$ (4). A toluene solution (10 mL) of compound **1** (0.040 g, 0.068 mmol) and $[Ru_3(CO)_{12}]$ (0.045 g, 0.07 mmol) was irradiated with UV−visible light in a Pyrex Schlenk tube at 288 K for 20 min to give a green solution. The solvent was then removed under vacuum, the residue was extracted with petroleum ether, and the extracts were chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane−petroleum ether (1:8) gave a green fraction, which yielded, after removal of solvents under vacuum, compound **4** as a green solid (0.045 g, 82%). Anal. Calcd for $C_{29}H_{35}Mo_2O_6PRu$: C, 43.35; H, 4.39. Found: C, 43.51; H, 4.67. ^1H NMR: δ 5.13 (s, Cp, 10H), 3.87 (s, OMe, 3H), 2.70−0.80 (m, Cy, 22H). $^{13}C\{^1H\}$ NMR: δ 339.3 (s, μ-*C*OMe), 247.5 (d, J_{CP} = 6,

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2 × MoCO), 202.8 (s, 3×RuCO), 89.1 (s, Cp), 68.1 (s, OMe), 47.3 [d, J_{CP} = 23, C^1(Cy)], 43.5 [d, J_{CP} = 15, C^1(Cy)], 33.9, 33.0 [2*s*, 2× C^2(Cy)], 28.3 [d, J_{CP} = 10, C^3(Cy)], 28.2 [d, J_{CP} = 12, C^3(Cy)], 26.9, 26.6 [2*s*, 2×C^4(Cy)].

Preparation of $[CuMo_2ClCp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (5). Solid CuCl (0.007 g, 0.071 mmol) was added to a dichloromethane (5 mL) or CD_2Cl_2 (1 mL) solution of compound **1** (0.030 g, 0.051 mmol), and the mixture was stirred at room temperature for 1 min to give a blue-black solution, which was filtered. The solvent was then removed under vacuum from the filtrate to give compound **5** as a black, air-sensitive solid. All attempts to further purify this crude product resulted in its progressive decomposition to give the chloro complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}PCy_2)(CO)_2]$[11] and other uncharacterized species. The cleanest NMR spectra of **5** were obtained when preparing the complex in the deuterated solvent and keeping the solution at low temperature. ^{1}H NMR (243 K): δ 5.87 (s, Cp, 10H), 3.75 (s, OMe, 3H), 2.10−0.40 (m, Cy, 22H). ^{13}C{^{1}H} NMR (100.63 MHz, 233 K): δ 330.5 (d, J_{CP} = 16, μ-*C*OMe), 287.6 (d, J_{CP} = 9, μ-CO), 94.0 (s, Cp), 66.2 (s, OMe), 40.2 [d, J_{CP} = 19, C^1(Cy)], 39.2 [d, J_{CP} = 20, C^1(Cy)], 32.8, 32.2 [2s, 2× C^2(Cy)], 26.9 [d, J_{CP} = 10, 2×C^3(Cy)], 25.8, 25.6 [2s, 2×^{4}(Cy)].

Reaction of Compound 1 with $[Co_2(CO)_8]$. Solid $[Co_2(CO)_8]$ (0.035 g, 0.103 mmol) was added to a toluene solution (10 mL) of compound **1** (0.050 g, 0.085 mmol), and the mixture was stirred at room temperature for 15 min to give a black solution shown (by NMR) to be a mixture of the compounds $[Co_2Mo_2Cp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_4]$ (**6**) and $[Co_2Mo_2Cp_2(\mu_3\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_6]$ (**7**) in similar amounts. The solvent was then removed under vacuum, the residue was extracted with dichloromethane−petroleum ether (1:5), and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a green-brown fraction, which yielded, after removal of solvents under vacuum, compound **6** as a brown solid (0.030 g, 42%). Elution with dichloromethane−petroleum ether (1:1) gave a brown fraction, which yielded analogously compound **7** as a dark brown solid (0.033 g, 44%). The crystals used in the X-ray study of these two compounds were grown in each case by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the corresponding complex at 253 K. *Data for compound* **6**: Anal. Calcd for $C_{30}H_{35}Co_2Mo_2O_7P$: C, 42.47; H, 4.16. Found: C, 42.21; H, 3.98. ν_{CO} (Nujol): 2004 (s), 1864 (s), 1943 (s), 1829 (w), 1759 (m). ^{1}H NMR: δ 5.13 (s, Cp, 10H), 4.01 (s, OMe, 3H), 2.50−0.80 (m, Cy, 22H). *Data for compound* **7**: Anal. Calcd for $C_{31}H_{35}Co_2Mo_2O_8P$: C, 42.49; H, 4.02. Found: C, 42.28; H, 3.87. ν_{CO} (Nujol): 2006 (m), 1964 (vs), 1892 (m), 1844 (m), 1809 (m), 1740 (m). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 5.42, 4.99 (2s, Cp, 2×5H), 4.05 (s, OMe, 3H), 2.50−1.25 (m, Cy, 22H). ^{1}H NMR (400.13 MHz, 223 K): δ 5.46, 4.99 (2s, Cp, 2×5H), 3.93 (s, OMe, 3H), 2.50−1.20 (m, Cy, 22H). ^{13}C{^{1}H} NMR (100.63 MHz, 223 K): δ 347.4 (s, br, μ-*C*OMe), 271.2 (s, br, μ-CO), 255.1, 242.6, 231.5 (3s, 3×MoCO), 211.5, 207.2, 202.3 (3s, 3 × CoCO), 97.5, 90.9 (2s, Cp), 68.7 (s, OMe), 58.2 [s, br, C^1(Cy)], 53.0 [s, br, C^1(Cy)], 34.9 [s, br, C^2(Cy)], 34.7 [s, br, 2×C^2(Cy)], 31.9 [s, br, C^2(Cy)], 28.5 [s, br, 2 × C^3(Cy)], 28.3 [s, br, 2 × C^3(Cy)], 26.5 [s, 2×C^4(Cy)].

X-ray Structure Determination for Compounds 6 and 7. The X-ray intensity data for compounds **6** and **7** were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 100 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART[30] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[30] and a multiscan absorption correction was applied with SADABS.[31] Using the program suite WinGX,[32] the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least-squares on F^2 with SHELXL97.[33] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically located, and they were given an overall isotropic thermal parameter. The final refinement on F^2 proceeded by full-matrix least-squares calculations. In the case of compound **6** the methyl group was modeled as disordered over two positions. For compound **7** two independent molecules are present in the unit cell, these having very similar geometrical parameters.

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Supporting Information Available: CIF file giving the crystallographic data for the structural analysis of compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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