Reactivity of the Unsaturated Hydride $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ toward 17- and 16-Electron Metal Carbonyl Fragments: Rational Synthesis of Electron-Deficient Heterometallic Clusters

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Reactions of the 30-electron hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$) with the 17-electron-fragment precursors $[M_2Cp_2(CO)_n]$ (M = Mo, W, $n = 6$; M = Ru, $n = 4$) or $[Mn_2(CO)_{10}]$ lead to the 46-electron clusters $[Mo_2MCp_3(\mu\text{-}PCy_2)(\mu_3\text{-}CO)(CO)_4]$ (M = Mo, W), $[Mo_2RuCp_3(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_3]$, and $[MnMo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_5]$. The structure of the trimolybdenum cluster was confirmed by an X-ray diffraction study and displays two long (ca. 3.1 Å) and one short Mo−Mo distance (2.743(1) Å). The title unsaturated hydride also proved to be highly reactive toward the appropriate precursors of 16-electron fragments such as $M(CO)_5$ (M = Cr, Mo, W) and $MnCp'(CO)_2$ ($Cp' = \eta^5\text{-}C_5H_4CH_3$), then leading to the 46-electron hydride clusters $[MMo_2Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7]$ (M = Cr, Mo, W) and $[MnMo_2Cp_2Cp'(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$. The structures of the compounds having Mo_2W and Mo_2Mn skeletons were also determined by X-ray diffraction methods, both of them displaying Mo−Mo distances (ca. 2.6 Å) somewhat shorter than expected for double Mo═Mo bonds and Mo−M distances longer than the corresponding single-bond lengths. A similar reaction takes place with the 12-electron compound CuCl, to give the hydride $[CuMo_2ClCp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$. In contrast, the reaction of the title hydride with $[Fe_2(CO)_9]$, a precursor of the 16-electron fragment $Fe(CO)_4$, gives the heterodinuclear complex $[FeMo(\mu\text{-}PCy_2)(CO)_6]$ (Fe−Mo = 2.931(1) Å).

Introduction

In our preliminary exploration of the reactivity of the triply bonded hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**) we noticed the ability of this unsaturated species to incorporate the 16-electron fragment $MnCp'(CO)_2$, as well as the 17-electron fragment $MoCp(CO)_3$, this suggesting the opportunity to develop rational synthetic methods to prepare electron-deficient heterometallic clusters that might be difficult or impossible to prepare through more conventional preparative procedures.[1] Several rational methods for the synthesis of heterometallic clusters have been developed during the last three decades, some of them inspired by the isolobal relationships existing between metal fragments and organic molecules.[2] However, the high reactivity of unsaturated hydride-bridged compounds has not been fully exploited for this purpose. Among these substrates, only a few complexes having doubly bonded $M_2(\mu\text{-}H)_2$ cores (M = Mn, Re, Os) have been studied in detail. For example, we have analyzed the reactions of the 32-electron dimanganese hydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = (EtO)_2POP(OEt)_2$, $Ph_2PCH_2PPh_2$) toward the appropriate precursors of 16-electron fragments such as $Fe(CO)_4$ and $M(CO)_5$ (M = Cr, Mo, W) (isolobal to either CH_2 or CH_3^+)[2] to obtain trinuclear clusters.[3] These hydrides are also reactive toward $[Au(PPh_3)]^+$ [4] (a fragment isolobal to H^+)[5] and other group 11 and 12 compounds, such as CuX (X = halogen),[6] Zn(Hg),[6] or [M(C≡CPh)] (M = Au, Cu, Ag),[7] thus allowing the synthesis of different trinuclear (M = Au, Ag, Zn), pentanuclear (M = Au), or hexanuclear (M = Cu, Ag) Mn_2M_x clusters. Extensive studies have also been carried out with the isoelectronic dirhenium complex $[Re_2(\mu\text{-}H)_2(CO)_8]$, which reacts easily with different transition-metal complexes such as the metal carbonyl anions $[M(CO)_x]^-$ (M = Mn, Re, Ir; x = 4, 5)[8] and $[Re_2H(CO)_9]^-$ [8a,9] or the neutral late transition-metal compounds $[Pt(PPh_3)_2(C_2H_4)]$,[10] $[Pt(COD)_2]$,[11]

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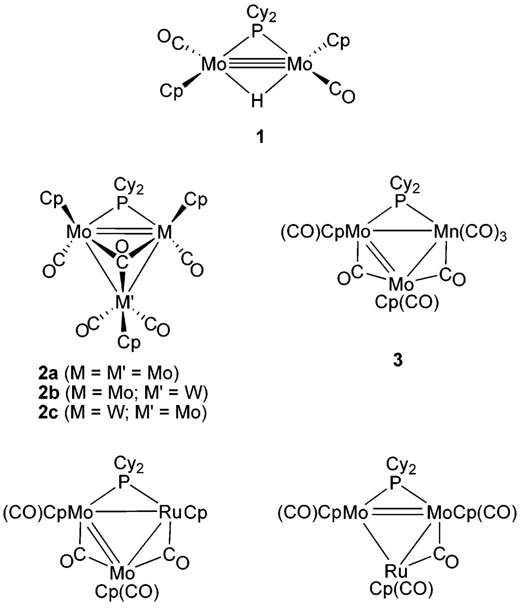
or [Ir(CO)(η^5-C_9H_7)(η^2-C_8H_{14})],[12] to give new tri- or tetranuclear clusters. Finally, the reactivity of the triosmium dihydride [Os_3(μ-H)$_2$(CO)$_{10}$] toward organometallic fragments has been also widely studied, allowing the synthesis of heterometallic clusters with higher nuclearity and incorporating transition-metal atoms from groups 6,[13,14] 8,[15−17] 9,[18−20] 10,[19a,21] 11,[19a,22] and 12.[23]

During the last decades, organometallic clusters have had an important role in chemistry, not only because of their singular bonding and structures but also because of their potential application in homogeneous catalysis (as catalysts or precursors) and heterogeneous catalysis (anchored to solid supports) or in the synthesis of homo- and heterometallic nanoparticles.[24] Yet, the synthesis of these species is not a matter completely solved, and the implementation of new rational synthetic procedures remains a valuable target. In this sense, the high reactivity of the 30-electron hydride **1** provided us with an excellent opportunity to explore synthetic routes for new heterometallic clusters having molybdenum and other transition or post-transition metals. In this paper we report our full results on the use of **1** as a precursor of such species. Two main synthetic routes have been developed. In one of them, the hydride ligand in **1** is replaced by a 17-electron metal fragment, which is generated in situ through the homolytic cleavage of a metal−metal bond. In the second one, a 16-electron metal fragment just adds to the multiple bond present in **1** (a similar result is obtained using 12-electron fragments such as CuCl or [Au(PPh_3)]$^+$). In all cases, electron-deficient trinuclear clusters are formed.

Results and Discussion

Incorporation of 17-Electron Metal Fragments. Several precursors of 17-electron metal fragments were reacted with the unsaturated hydride **1**, such as the cyclopentadienyl dimers [$M_2Cp_2(CO)_n$] (M = Mo, W, n = 6; M = Fe, Ru, n = 4) or the carbonyl dimers [$M_2(CO)_n$] (M = Mn, Re, n = 10; M = Co, n = 8). Except for the cobalt complex, no reaction occurred in the absence of light, even in refluxing toluene (ca. 383 K). However, rapid reactions took place under visible or UV irradiation. It is well known that the dimers [$M_2Cp_2(CO)_6$] (M = Mo, W) undergo homolytic cleavage of the metal−metal bond under photochemical conditions. This process competes with decarbonylation and is favored, in relative terms, when irradiating with visible rather than UV light.[25a,b] A similar effect is observed for the binary carbonyls [$M_2(CO)_n$].[25a,c] Therefore, it seems that the homolytic cleavage of the metal−metal bond in these substrates is the critical step for the reaction to proceed, a matter that will be discussed later on.

Chart 1



2a (M = M' = Mo)
2b (M = Mo; M' = W)
2c (M = W; M' = Mo)

4a

4b

Compound **1** reacts slowly at 288 K with [$Mo_2Cp_2(CO)_6$] upon exposure to visible light to give the trimolybdenum cluster [Mo_3Cp_3(μ-PCy_2)(μ_3-CO)(CO)$_4$] (**2a**) in good yield after 5 h. Compound **1** reacts similarly with [$W_2Cp_2(CO)_6$] to give a mixture of the heterometallic clusters of formula [Mo_2WCp_3(μ-PCy_2)(μ_3-CO)(CO)$_4$] (**2b**, **2c**) (Chart 1 and Scheme 1). Isomers **2b** and **2c** differ in the position of the dicyclohexylphosphide bridge on the Mo_2W metal skeleton and are obtained in a equilibrium ratio showing only a modest dependence on the solvent (see Experimental Section).

Compound **1** is also reactive toward metal−metal bonded binary carbonyls, but most of the products obtained were rather unstable and could not be properly purified and characterized. The reaction with [$Co_2(CO)_8$] proceeds at room temperature in the absence of light, but no heterometallic cluster could be identified in the complex mixture of unstable products formed. The reaction of **1** with [$Re_2(CO)_{10}$] required visible−UV irradiation to proceed, but it was more selective. Unfortunately, it led to a mixture of several Mo_2Re clusters that could not be properly characterized due to decomposition during attempts of purification (chromatography, crystallization). In contrast, the

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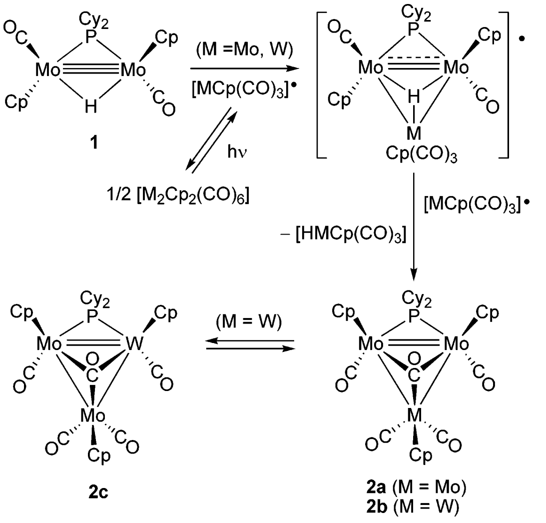
Scheme 1. Reaction Pathway Proposed for the Formation of Compounds 2



reaction with [$Mn_2(CO)_{10}$] under the same conditions gave almost quantitatively the manganese−molybdenum cluster [$MnMo_2Cp_2(\mu$-$PCy_2)(\mu$-$CO)_2(CO)_5$] (**3**) after 10 min. This allowed the spectroscopic characterization of the product even when it could not be isolated in a completely pure form nor characterized through X-ray diffraction methods, due to its progressive decomposition upon manipulation.

Iron and ruthenium cyclopentadienyl dimers [$M_2Cp_2(CO)_4$] also react with hydride **1** under photochemical conditions, but with very different results. The reaction with the iron dimer gave no detectable heterometallic cluster, but led instead to the tetracarbonyl complex [$Mo_2Cp_2(\mu$-$H)(\mu$-$PCy_2)(CO)_4$][26] as the only carbonyl-containing species. The latter compound is obviously formed by reaction of the photogenerated CO with **1** (in fact, this electron-precise hydride is always obtained in variable amounts as a side product in all photochemical reactions here reported). In contrast, visible−UV irradiation of a toluene solution of **1** and [$Ru_2Cp_2(CO)_4$] for 10 min gives a mixture of the heterometallic clusters of formula [$Mo_2RuCp_3(\mu$-$PCy_2)(\mu$-$CO)(CO)_3$] (**4a**, **4b**). As it was the case of the Mo_2W clusters, isomers **4a** and **4b** differ in the position of the dicyclohexylphosphide bridge on the Mo_2Ru metal skeleton (Chart 1). Even though in this case two different brown fractions could be separated upon chromatography in alumina (activity IV) at 253 K, the IR and NMR spectra of the resulting solutions at room temperature (see below) proved them to have the same composition, suggesting that fast isomerization occurs on the laboratory time scale to reach an equilibrium ratio between isomers, which is ca. 1:1 for these ruthenium clusters, with no significant dependence on the solvent, as deduced from the integration of the ^1H NMR spectra recorded in $CDCl_3$, C_6D_6, and $(CD_3)_2CO$ solutions.

Solid State and Solution Structure of Compounds 2. The structure of compound [$Mo_3Cp_3(\mu$-$PCy_2)(\mu_3$-$CO)(CO)_4$] (**2a**) was confirmed through a single-crystal X-ray diffraction study and previously reported (Figure 1).[1] The molecule displays two MoCp(CO) groups and one $MoCp(CO)_2$ moiety, all bound together to form a Mo_3 triangle, which is asymmetrically capped by a carbonyl ligand. The MoCp(CO) fragments are bridged by a dicyclohexylphosphide ligand and all three Cp ligands, and the bridging carbonyls are placed on the same side of the Mo_3 plane, which implies a trans to cis rearrangement in the hydride **1** upon reaction. The Mo(1)−Mo(3) and Mo(2)−Mo(3) distances, 3.085(1) and 3.094(1) Å, respectively, are in good agreement with the presence of single Mo−Mo bonds, whereas the Mo(1)−Mo(2) distance (2.743(1) Å) is significantly shorter and close to the values found for double Mo−Mo bonds in related systems (for example, 2.713(1) Å for the bis(diphenylphosphide) complex [$Mo_2Cp_2(\mu$-$PPh_2)_2(CO)_2$]).[27] So it seems that the electronic unsaturation of the cluster is rather localized on just a pair of metal atoms. Interestingly, a similar localization effect occurs in the isolectronic cluster [$Mo_3Cp^*_3(\mu_2$-$H)(\mu_3$-$O)(CO)_4$],[28] which appears to be the only other 46-electron Mo_3 cluster structurally characterized so far, since it displays Mo−Mo distances of 2.916(1), 2.917(1), and 2.660(1) Å. In the case of **2a**, the asymmetrically triply bridging carbonyl plays an active role in defining the intermetallic separations. The corresponding Mo−C distances are 2.275(6) [Mo(1)−C(3)], 2.197(6) [Mo(2)−C(3)], and 2.042(6) Å [Mo(3)−C(3)], so this carbonyl can be viewed as involved in a normal (for a bridging group) bond to the Mo(3) atom [the Mo(3)−C(3)−O(3) angle is 139.9(5)°] and in weaker interactions (of semibridging type) with the other two metal atoms. This implies an additional electron transfer from the original $MoCp(CO)_3$ moiety to the unsaturated $Mo_2Cp_2(\mu$-$PCy_2)$ fragment, in agreement with the intermetallic separations. In the absence of such a bridging carbonyl, the $MoCp(CO)_3$ fragment would behave much as the hydride ligand in **1** does, and then shorter Mo(1)−Mo(2) and longer Mo−Mo(3) lengths would have been expected.

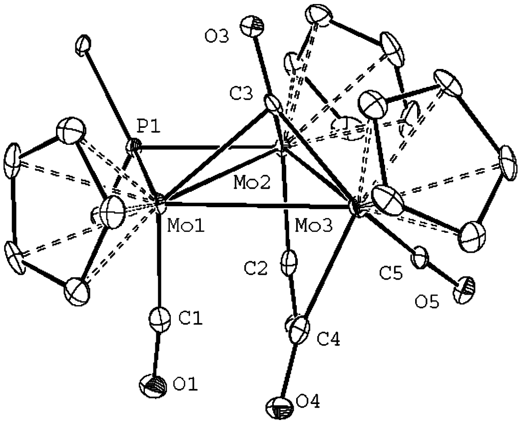


Figure 1. ORTEP diagram (30% probability) of compound **2a**,[1] with H atoms and Cy rings omitted for clarity, except the C^1 atoms. Selected bond lenghts (Å): Mo(1)−Mo(2) 2.743(1); Mo(1)−Mo(3) 3.085(1); Mo(2)−Mo(3) 3.094(1); Mo(1)−P(1) 2.399(2); Mo(2)−P(1) 2.398(2); Mo(1)−C(3) 2.275(6); Mo(2)−C(3) 2.197(6); Mo(3)−C(3) 2.042(6).

Spectroscopic data in solution for compounds **2a**−**c** (Table 1 and Experimental Section) are essentially consistent with the solid structure of **2a**, but reveal the presence of dynamic processes in solution. The IR spectra for **2a** and that for the mixture of **2b** and **2c** are similar and display five CO stretching bands in CH_2Cl_2 in each case, as expected. The ^{31}P spectra for these clusters exhibit in each case singlet resonances with chemical shifts of 178.3 (**2a**), 170.9 (**2b**), and 143.5 (J_{PW} = 319 Hz) (**2c**). The relative shielding and the appearance of a large ^{31}P−^{183}W coupling in the latter resonance is a clear indication that the phosphide bridge in **2c** is placed over the

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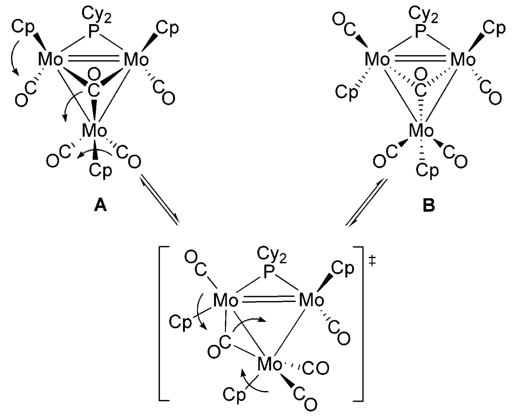
Table 1. Selected IR[a] and $^{31}P\{^{1}H\}$ NMR[b] Data for New Compounds

compound	ν(CO)	δ_P
$[Mo_3Cp_3(\mu\text{-}PCy_2)(\mu_3\text{-}CO)(CO)_4]$ (**2a**)	1954 (vs), 1915 (m), 1890 (m), 1866 (m), 1814 (w)	178.3[c] (185.4, 150.2)[d]
$[Mo_2WCp_3(\mu\text{-}PCy_2)(\mu_3\text{-}CO)(CO)_4]$ (**2b**,**c**)	1952 (vs), 1916 (m), 1885 (m), 1864 (m), 1808 (w)	170.9[e] (**2b**) 143.5[e] [319],[f] (**2c**)
$[MnMo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_5]$ (**3**)	2015 (m), 1946 (m, sh), 1926 (vs), 1842 (w), 1797 (w)	207.0[c]
$[Mo_2RuCp_3(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_3]$ (**4a**,**b**)	1956 (s), 1935 (s, sh), 1921 (s), 1891 (vs), 1812 (s), 1769 (vs)	224.1[e] (**4a**) 169.1[e] (**4b**)
$[CrMo_2Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7]$ (**5a**)	2050 (m), 1931 (vs)[g]	207.4[e]
$[Mo_3Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7]$ (**5b**)	2062 (m), 1941 (vs), 1908 (m, sh)[g]	208.4[e]
$[Mo_2WCp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7]$ (**5c**)	2058 (s), 1969 (w, sh), 1934 (vs), 1908 (m, sh), 1848 (w), 1832 (w, sh)	205.0
$[MnMo_2Cp_2Cp'(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**6**)	1915 (vs), 1875 (m, sh), 1851 (s), 1833 (m, sh)	167.5[h]
$[FeMoCp(\mu\text{-}PCy_2)(CO)_6]$ (**7**)	2065 (s), 2009 (m), 1989 (vs), 1981 (s), 1934 (s), 1867 (s)[i]	199.1
$[CuMo_2ClCp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**8**)	1905 (m), 1850 (vs)	230.8[e]

[a] Recorded in dichloromethane solution, unless otherwise stated, ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz, unless otherwise stated, δ in ppm relative to external 85% aqueous H_3PO_4. [c] In $CDCl_3$ at 81.04 MHz. [d] Isomer mixture at 193 K and 162.01 MHz (see text). [e] In $CDCl_3$. [f] J_{PW} in Hz. [g] The rest of the C−O stretching bands could not be assigned unambiguously. [h] In C_6D_6. [i] In petroleum ether.

Scheme 2. Isomerization Equilibrium Proposed for Compound 2a in Solution



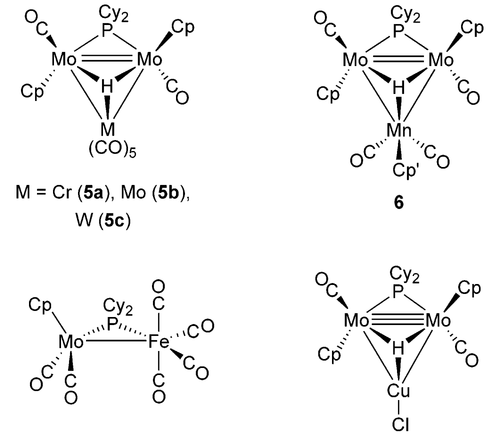
Mo and W atoms. We note that the P−W coupling constant is close to those found for the unsaturated compounds $[W_2Cp_2(\mu\text{-}PR_2)_2(CO)_2]$,[26] which exhibit similar coordination environments around the W and P atoms. The ^{1}H NMR spectra for **2a** and **2b** are in good agreement with the solid structure found for **2a**, both exhibiting two signals in a 2:1 ratio for the three Cp ligands, consistent with the presence of a symmetry plane making both MoCp(CO) fragments equivalent. In contrast, **2c** exhibits three different cyclopentadienyl resonances, since all three metal fragments are now inequivalent. All the above data are themselves consistent with the rigid structures based on the crystal structure of **2a**. However, the $^{13}C\{^{1}H\}$ NMR spectrum of **2a** recorded at room temperature is not consistent with that structure, since it displays just one broad carbonyl resonance at 256.3 ppm and four signals for the cyclohexyl carbon atoms, while, according to the solid structure, there should be three carbonyl and up to eight distinct cyclohexyl resonances present. All this suggests the operation of dynamic processes in these solutions, which proved to be due to the presence of two interconverting isomers. Thus, on cooling a solution of **2a**, its $^{31}P\{^{1}H\}$ NMR resonance at ca. 178 ppm first broadens and then eventually splits into two different signals (185.4 ppm for isomer **A** and 150.2 ppm for isomer **B** at 193 K, ratio **A**/**B** = 1.7). From the ill-defined coalescence point (T_c ca. 218 K) we can estimate an average activation barrier of 36 ± 1 kJ mol^{-1}, which is a fairly low figure. Unfortunately, the ^{1}H NMR spectra do not exhibit informative changes over that temperature range, apart from a general broadening of all resonances. In order to explain the above spectroscopic observations, we propose the operation in these solutions of a fast isomerization equilibrium between two of the possible conformers for **2a**. By considering the large ^{31}P chemical shift difference between these isomers (ca. 35 ppm), we propose that only a cis/trans rearrangement at the $Mo_2(\mu\text{-}PCy_2)$ center can account for such a large shift difference (Scheme 2). Indeed, we have shown previously that the unsaturated complex *cis*-$[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBu_2)(CO)_2]$[26] displays a ^{31}P shift some 40−50 ppm above that of its trans isomer, thus allowing us to identify the major and more deshielded isomer **A** as that one exhibiting a cis arrangement around the $Mo_2(\mu\text{-}PCy_2)$ center, as found in the crystal. The exchange between isomers **A** and **B** would possibly imply a transition state whereby the μ_3-CO ligand becomes edge-bridging, then allowing the $MoCp(CO)_x$ fragments to rotate. In this way, not only are the isomers **A** and **B** interconverted, but also a generalized carbonyl scrambling results (not shown in the scheme). Of course, in the absence of further data, we cannot exclude other possibilities at present.

Reaction Pathways in the Formation of Compounds 2. As stated above, no reaction between **1** and the cyclopentadienyl dimers $[M_2Cp_2(CO)_6]$ occurs in the absence of light, even in refluxing toluene. On the other hand, a separate experiment proved that compound **1** does not experience any significant change when irradiated with visible light. Thus, in light of the known photochemistry of these dimers,[25a,b] it is reasonable to propose that these reactions are initiated by the homolytic cleavage of their single metal−metal bonds to yield the corresponding 17-electron radicals $[MCp(CO)_3]^{\bullet}$, which then would rapidly add to the hydride **1** to yield a transient paramagnetic cluster, which spontaneously would lose a hydrogen atom to afford the diamagnetic clusters **2a**,**b** (Scheme 1). An NMR monitoring experiment carried out using C_6D_6 as solvent revealed the essentially quantitative formation of $[WHCp(CO)_3]$, identified by its characteristic proton resonances [δ_H = −7.2 ppm, J_{HW} = 37 Hz; δ_{Cp} = 4.9 ppm]. This proves that these reactions imply eventually the complete H atom transfer from **1** to the photogenerated $[MCp(CO)_3]^{\bullet}$ radicals. The radical attack on **1** would be facilitated by the presence of multiple metal−metal bonding in this substrate, which provides it with empty, low-lying antibonding orbitals not present in related electron-precise complexes. Finally, in order to explain the formation of **2c**, we propose that, once formed, the dimolybdenum−tungsten cluster **2b** rearranges by exchanging CO and PCy_2 ligands between molybdenum and tungsten atoms to reach a thermodynamic equilibrium between isomers **2b** and **2c**. Given the almost identical atom sizes and covalent radii of the Mo and W atoms, the relative amounts of these isomers are likely to be governed by the relative strengths of the corresponding M−C and W−P bonds.

Solution Structure of Compounds 3 and 4. Unfortunately, no suitable crystals for X-ray diffraction could be grown for either of these rather unstable compounds, so our structural proposal for these species must be based on limited spectroscopic data recorded in solution. The IR spectrum of the $MnMo_2$ cluster **3** displays five CO stretching bands, with the position and high intensity of the band at highest frequency (2015 cm^{-1}) being indicative of the presence of a facial $Mn(CO)_3$ oscillator,[29] then discarding the presence of a *cis*-$Mn(CO)_4$ group, for which the highest-frequency band appears typically in the range 2060−2090 cm^{-1}.[29,30] On the other hand, the presence of low-frequency bands (<1800 cm^{-1}) suggests that there is at least one bridging carbonyl in the molecule. In fact, we propose for **3** a structure with two bridging (or semibridging) CO ligands, in order to fulfill the EAN formalism in an equilibrated way (Chart 1). The proposal of the PCy_2 ligand in **3** as bridging Mo and Mn atoms is based on the fact that its ^{31}P NMR resonance appears at a relatively high chemical shift (207.0 ppm in C_6D_6) and it is abnormally broad at room temperature. The latter is a well-known effect caused by the quadrupolar ^{55}Mn nucleus on ^{31}P nuclei bonded to it, while there is also a general trend for phosphide ligands to exhibit more deshielded ^{31}P resonances when bridging over lighter transition-metal atoms.[31]

The mixture of isomers **4a** and **4b** exhibits six stretching CO bands ranging from 1769 to 1956 cm^{-1}, this alone suggesting that there is more than one compound in solution, since the expected product would have only four CO ligands and therefore no more than four stretching bands. Moreover, the positions of the lowest bands in frequency (1812 and 1769 cm^{-1}) suggest the presence of bridging or semibridging CO ligands in both isomers. These isomers are characterized by quite separated ^{31}P NMR resonances, which appear at 224.1 (**4a**) and 169.1 (**4b**) ppm, while the proton NMR spectrum reveals the lack of any element of symmetry in both cases, since three distinct Cp resonances are observed in each case, therefore excluding any symmetrical structure similar to that found for **2b**. Thus, the large difference in the ^{31}P chemical shifts of isomers **4a** and **4b** is taken as an indication that the PCy_2 ligand might be bridging a Mo_2 vector in one isomer (**4b**, by comparison with the shifts for **2b**) and a MoRu one in the other isomer (**4a**, this structure being comparable to that of **3**, after replacing the $Mn(CO)_3$ fragment in the latter by the isoelectronic RuCp one). We can compare the shift in **4a** with those of the Mo_2Ru clusters [$Mo_2RuCp_2(\mu_3\text{-}C{=}CRH)(\mu\text{-}PPh_2)_2(CO)_4$] and [$Mo_2RuCp_2(\mu_3\text{-}CCH_2R)(\mu\text{-}PPh_2)(CO)_5$] (R = H, Me), ranging from 188 to 202 ppm.[32] Taking into account that PCy_2 shifts tend to be higher than those of PPh_2, the value of 224.1 ppm seems to be a reasonable figure for compound **4a**. Finally, we should note that while a number of trinuclear clusters having Mo_2Ru cores have been reported previously, most of them are electron-precise species (48 electrons). In fact, we are only aware of another family of 46-electron Mo_2Ru species, these being the above-mentioned [$Mo_2RuCp_2(\mu_3\text{-}CCH_2R)(\mu\text{-}PPh_2)(CO)_5$] clusters (R = H, Me).[32]

Chart 2



M = Cr (**5a**), Mo (**5b**), W (**5c**)

6

7

8

Incorporation of 16-Electron Metal Fragments. These metal fragments can be generated in a number of ways, for example, through either thermal or photochemical decarbonylation of suitable carbonyl complexes, by displacement of labile ligands, etc. These well-established strategies have been used to test the ability of the unsaturated hydride **1** to generate new heterometallic clusters by addition of 16-electron fragments of the groups 6, 7, and 8 metals to its multiple metal−metal bond, in a process similar to the organic cyclopropanation reaction.[2b]

Compound **1** reacts rapidly with the group 6 hexacarbonyls [$M(CO)_6$] (M = Cr, Mo, W) in toluene solution under visible−UV irradiation to give the corresponding 46-electron clusters [$MMo_2Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7$] [M = Cr (**5a**), Mo (**5b**), W (**5c**)] (Chart 2), along with significant amounts of the tetracarbonyl complex [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$][26] as a side product. Attempts to prepare these clusters by the thermal reaction of **1** and the solvates [$M(CO)_5(THF)$] gave no detectable amounts of the trinuclear clusters, which suggests that the hydride **1** has only a moderate electron-donor ability. Compounds **5a** and **5b** were very unstable and decomposed progressively upon manipulation to give mixtures of compound **1** and its tetracarbonyl derivative. Fortunately, the Mo_2W tungsten cluster was more stable and could be completely characterized both in solution and in the solid state (see below).

Group 7 metal cyclopentadienyl fragments could be introduced using tetrahydrofuran adducts. Thus, a THF solution of the adduct [$MnCp'(CO)_2(THF)$] (Cp′ = $\eta^5\text{-}C_5H_4CH_3$) reacts with compound **1** at room temperature to give the trinuclear cluster [$MnMo_2Cp_2Cp'(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] (**6**) with good yield, along with variable amounts of the tetracarbonyl [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] as a side product. Compound **6**, which could be characterized through an X-ray diffraction study (see below), is a rare example of a Mo_2Mn cluster. In fact there appears to be just another cluster (apart from **3**) having a triangular Mo_2Mn core, this being the electron-precise cluster [$Mo_2Mn_2Cp_2(\mu_3\text{-}Se)_4(CO)_7$].[33] For this reason, we examined also the reaction of **1** with the rhenium adduct [$ReCp(CO)_2(THF)$], but this turned out to give a mixture of unstable compounds, which could be neither isolated nor characterized properly.

Compound **1** is also very reactive toward [$Fe_2(CO)_9$], which is a classical precursor of the $Fe(CO)_4$ fragment. However, this

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(29) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, UK, 1975.

(30) See for example: (a) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1983**, 205. (b) Horton, A. D.; Kemball, A. C.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2953.

(31) Carty, A. J.; McLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 16.

(32) Adams, H.; Bailey, N. A.; Gill, L. J.; Morris, M. J.; Sadler, N. D. *J. Chem. Soc., Dalton Trans.* **1997**, 3041.

(33) Adams, R. D.; Kwon, O.-S. *Inorg. Chem.* **2003**, *42*, 6175.

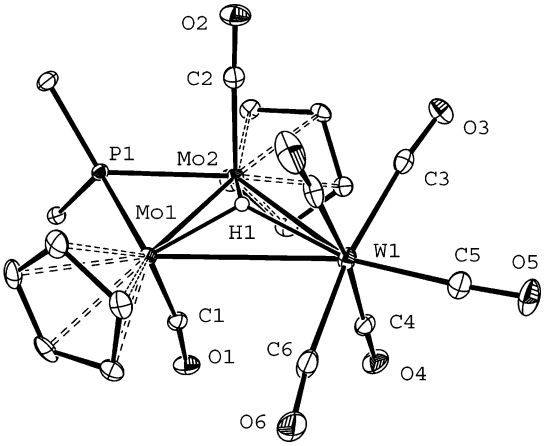

Figure 2. ORTEP diagram (30% probability) of compound **5c**, with H atoms and Cy rings omitted for clarity, except the C^1 atoms and the hydride ligand.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 5c

Mo(1)−Mo(2)	2.6351(5)	Mo(1)−Mo(2)−W(1)	68.00(2)
Mo(1)−W(1)	3.3714(5)	Mo(2)−W(1)−Mo(2)	46.44(2)
Mo(2)−W(1)	3.3103(6)	W(1)−Mo(1)−Mo(2)	65.56(3)
Mo(1)−P(1)	2.380(1)	C(1)−Mo(1)−Mo(2)	72.5(1)
Mo(2)−P(1)	2.386(1)	C(2)−Mo(2)−Mo(1)	95.6(1)
Mo(1)−C(1)	1.924(4)	Mo(1)−P(1)−Mo(2)	67.14(3)
Mo(2)−C(2)	1.965(4)	O(1)−C(1)−Mo(1)	170.7(3)
Mo(2)−C(1)	2.755(4)	O(2)−C(2)−Mo(2)	176.7(3)
Mo(1)−H(1)	1.80(5)	P(1)−Mo(1)−H(1)	96(2)
Mo(2)−H(1)	1.92(5)	P(1)−Mo(2)−H(1)	92(1)
W(1)−H(1)	2.02(5)		

reaction proceeds readily with **1** in toluene at room temperature to give with good yield the heterodinuclear compound [FeMoCp(μ-PCy$_2$)(CO)$_6$] (**7**) along with the dimer [Mo$_2$Cp$_2$(CO)$_6$], rather than the expected trinuclear cluster. No intermediate species could be reproducibly detected by IR or ^{31}P NMR monitoring of the corresponding reaction mixtures. In contrast, the reaction of **1** with Ru$_3$(CO)$_{12}$ under visible−UV irradiation (this acting as a precursor of the Ru(CO)$_4$ fragment) led to complex mixtures of products that could not be isolated.

Solid State and Solution Structure of Compounds 5. The crystal structure of [Mo$_2$WCp$_2$(μ_3-H)(μ-PCy$_2$)(CO)$_7$] (**5c**) was determined through a single-crystal X-ray diffraction study (Figure 2 and Table 2). The molecule can indeed be viewed as resulting from the addition of a W(CO)$_5$ moiety to the dimetal center in the hydride **1** with little distortion of the dimolybdenum substrate. Thus, the Cp groups remain placed on opposite sides of the Mo$_2$P plane, as do the carbonyl ligands. However, the hydride ligand is significantly perturbed upon binding of the tungsten fragment, since it is now located as triply bridging the metal triangle in an asymmetrical way (closer to the molybdenum atoms). The intermetallic Mo−Mo distance, 2.6351(5) Å, is slightly shorter (ca. 0.03 Å) than that measured for the 46-electron cluster [Mo$_3$Cp*$_3$(μ_2-H)(μ_3-O)(CO)$_4$][28] and much shorter (ca. 0.11 Å) than the formally double Mo−Mo length measured for **2a**. On the other side, this distance is 0.06 to 0.1 Å longer than those measured in the 30-electron compounds [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-SnPh$_3$)(CO)$_2$] and **1**, respectively, for which triple Mo−Mo bonds can be proposed under the EAN formalism.[1] In summary, the Mo−Mo interaction for compound **5c** might be viewed both as a short double bond and as a long triple bond. This suggests that the W(CO)$_5$ fragment might be acting essentially as an acceptor group (isolobal to CH$_3^+$ rather than to CH$_2$).[2] In this case, a 3c-2e interaction (rather than 3c-4e) would be a better description for the binding in the Mo$_2$W core, whereby the electron donor (the multiple Mo−Mo bond) just shares a bonding electron pair with the acceptor (the tungsten atom). This description is consistent not only with the Mo−Mo separation found in **5c** but also with the rather long Mo−W distances, 3.3714(5) and 3.3103(6) Å, significantly much longer than the single-bond Mo−Mo distances in related compounds (e.g., ca. 3.10 Å for **2a**).

Scheme 3. Fluxional Process Proposed for Compounds 5, 6, and 8 in Solution

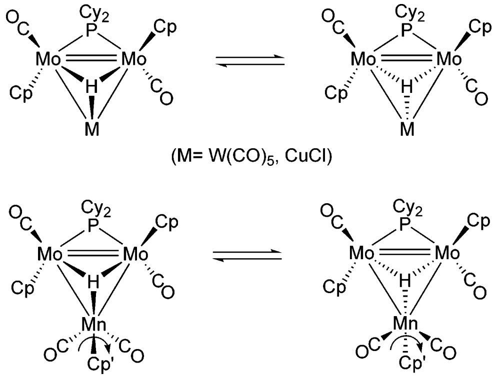

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Mo(1)−Mo(2)	2.6448(8)	Mo(1)−Mo(2)−Mn(1)	65.25(2)
Mo(1)−Mn(1)	3.135(1)	Mo(2)−Mn(1)−Mo(1)	50.01(2)
Mo(2)−Mn(1)	3.122(1)	Mn(1)−Mo(1)−Mo(2)	64.74(3)
Mo(1)−P(1)	2.386(2)	C(1)−Mo(1)−Mo(2)	88.8(2)
Mo(2)−P(1)	2.368(2)	C(2)−Mo(2)−Mo(1)	74.8(2)
Mo(1)−H(1)	1.86(6)	Mo(1)−P(1)−Mo(2)	67.62(5)
Mo(2)−H(1)	1.85(6)	O(1)−C(1)−Mo(1)	176.5(6)
Mn(1)−H(1)	1.64(7)	O(2)−C(2)−Mo(2)	172.3(6)
C(2)−Mo(2)	1.929(8)	P(1)−Mo(1)−H(1)	97(2)
C(2)−Mo(1)	2.835(7)	P(1)−Mo(2)−H(1)	98(2)
C(1)−Mo(1)	1.952(7)	C(3)−Mn(1)−C(4)	86.4(6)

Spectroscopic data in solution for compounds **5a**−**c** are essentially consistent with the structure found in the solid state for **5c**, although dynamic processes are present once more, and only limited data are available for compounds **5a**,**b** due to their low stability. In fact, only for compound **5c** could the C−O stretching bands in the IR spectra be unambiguously assigned, since for the other complexes some of these bands are overlapping with those of compound **1** and its tetracarbonyl derivative, these being formed upon manipulation of the new clusters. Nevertheless, the IR spectra clearly display in all cases a strong band in the range 2050−2060 cm^{-1}, characteristic of the presence of M(CO)$_5$ fragments (M = Cr, Mo, W).[29] As for the ^{31}P NMR spectra, compounds **5a**−**c** exhibit single resonances ranging from 205 to 208 ppm. These chemical shifts are significantly higher than those for other clusters having the PCy$_2$ ligand over formally double Mo=Mo bonds discussed in this paper (Table 1), but are lower than the chemical shift in the triply bonded **1** (232.3 ppm).[34] This is consistent with a retention in solution of the same 3c-2e interaction at the Mo$_2$W metal skeleton that is found in the crystal. The ^{1}H NMR spectrum reflects the significant modification operating in the hydride environment upon coordination (from the μ_2- to the μ_3-mode), since the unusually deshielded resonance in **1** (−6.94 ppm) moves into a more shielded region upon coordination of the new metal atom [δ_H = −16.88 (**5a**), −13.34 (**5b**), −12.46

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[34] García, M. E.; Melón, S.; Ramos. A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983.

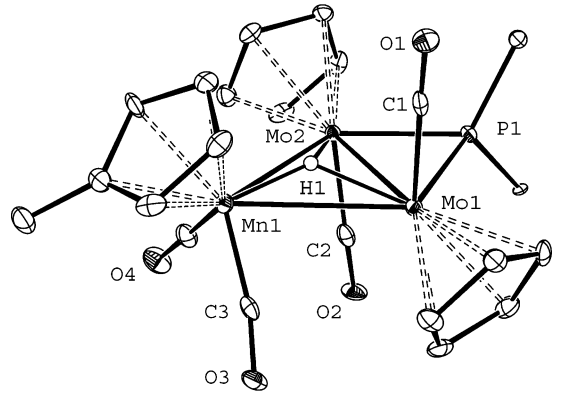

Figure 3. ORTEP diagram (30% probability) of one of the two independent molecules in the unit cell of compound **6**, with H atoms and Cy rings omitted for clarity, except the C^1 atoms and the hydride ligand.

ppm (**5c**)], as expected. However, these spectra exhibit in each case a single resonance for both cyclopentadienyl groups, itself inconsistent with the solid state structure of **5c**. The same is concluded from the ^{13}C NMR spectrum of **5c**, which displays a single resonance for each of the inequivalent pairs of MoCO and cyclopentadienyl groups (but not for the diastereotopic C^2 and C^3 cyclohexyl carbon atoms). Therefore, a dynamic process creating a false C_2 symmetry axis bisecting the Mo_2W triangle must be operative in solution for these compounds, which we propose to involve just a shift of the hydride ligand from one side to the other of the metal triangle (Scheme 3). Although we have not studied this process in detail, we note that it should be of an intramolecular nature, since H−P and H−W couplings are retained under fast exchange conditions. Besides we also note the appearance of just one resonance at 197.6 ppm for the five carbonyls attached to the tungsten atom, which suggests the occurrence of a further exchange process inside the pentacarbonyl fragment, which is also fast on the NMR time scale at room temperature.

Solid State and Solution Structure of Compound 6. The crystal structure of **6** was also confirmed through a single-crystal X-ray diffraction study (Table 3 and Figure 3). The structure is very similar to that found for **5c**, if the $W(CO)_5$ fragment is replaced by the isoelectronic $MnCp'(CO)_2$ group, with the methylcyclopentadienyl ligand and the triply bridging hydride on the same side of the Mo_2Mn plane. The intermetallic separations are also comparable to those of the Mo_2W tungsten cluster, suggesting that the binding within the metal triangle might also be described in terms of a 3c-2e interaction (H^+-like behavior of the $MnCp'(CO)_2$ fragment). However, the Mo−Mo distance (2.6448(8) Å) is a bit longer than that in **5c**, whereas the Mo−Mn distances (3.135(1) and 3.122(1) Å) are now closer to the reference single-bond lengths (cf. 3.11 Å in [$MnMoCp(CO)_7\{P(OMe)_3\}$][35] or 3.09 Å in [$MnMoCp(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6$]).[36] This suggests that, compared to the $W(CO)_5$ fragment, the $MnCp'(CO)_2$ fragment binds more tightly to the hydride **1**, surely due to its higher electron density at the metal center, derived from the presence of the methylcyclopentadienyl ligand. This could make a Mn-based electron pair become more available for cluster binding (CH_2-like behavior of the metal fragment).

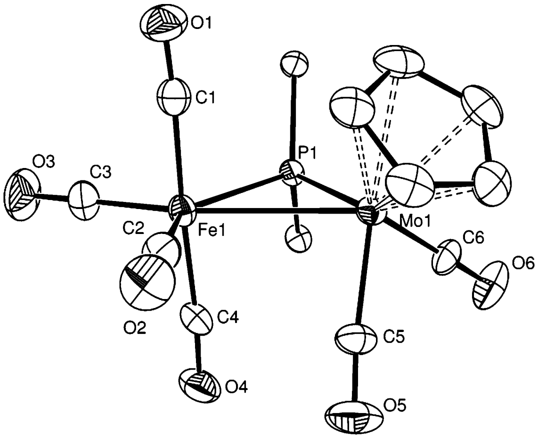

Figure 4. ORTEP diagram (30% probability) of one (B) of the two independent molecules in the unit cell of compound **7**, with H atoms and Cy rings omitted for clarity, except the C^1 atoms.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 7 [molecule B]

Mo(1)−Fe(1)	2.929(1)	Mo(1)−P(1)−Fe(1)	77.16(3)
Mo(1)−P(1)	2.412(1)	C(1)−Fe(1)−C(3)	90.5(1)
Fe(1)−P(1)	2.283(1)	C(1)−Fe(1)−C(4)	176.9(1)
Fe(1)−C(1)	1.803(3)	C(1)−Fe(1)−C(2)	90.8(1)
Fe(1)−C(2)	1.806(3)	C(3)−Fe(1)−C(4)	91.7(1)
Fe(1)−C(3)	1.786(3)	C(3)−Fe(1)−C(2)	109.8(1)
Fe(1)−C(4)	1.810(3)	C(4)−Fe(1)−C(2)	90.5(1)
Mo(1)−C(5)	1.946(3)	C(5)−Mo(1)−C(6)	78.7(1)
Mo(1)−C(6)	1.938(3)	C(5)−Mo(1)−Fe(1)	84.7(1)
		C(6)−Mo(1)−Fe(1)	119.5(1)

Spectroscopic data in solution for compound **6** are in quite good agreement with the solid structure but again reveal the presence of dynamic effects. The IR spectrum displays four CO stretching bands, itself in accordance with the low symmetry of this tetracarbonylic cluster, the ^{31}P NMR spectrum exhibits a resonance at 167.5 ppm, a shift similar to those found for other $Mo_2(\mu\text{-}PCy_2)$ moieties discussed in this work (Table 1), and the hydride resonance appears at −15.82 ppm, therefore consistent with a triply bridging position. However, the Cp ligands exhibit just one ^1H or ^{13}C NMR resonance at room temperature, while the Mo-bound carbonyls (but not the Mn-bound ones) and both cyclohexyl groups appear as equivalent groups too (but not the diastereotopic pairs of C^2 and C^3 atoms in each ring). Therefore, the dynamic process is generating a false C_2 axis, as found for compounds **5**. Indeed, at 233 K that process is slowed enough so as to yield separate ^{13}C resonances for the Cp ligands. In order to explain all these spectroscopic features, we must assume for **6** the operation of a dynamic process similar to that proposed for the heptacarbonyl clusters **5**, that is, a shift of the hydride ligand between both sides of the metal triangle. However, in the case of **6** this needs to be accompanied by a simultaneous rotation of the manganese fragment (Scheme 3), since otherwise the process would be an isomerization (not observed).

Structure of Compound 7. In the crystals of **7** two crystallographically independent molecules (A and B), even if very similar, are present. The structure of one of them (molecule B) is shown in Figure 4, while Table 4 collects some relevant structural parameters of both molecules. The molecule displays $MoCp(CO)_2$ and $Fe(CO)_4$ moieties bound through a dicyclohexylphosphide bridge, and a metal−metal bond, strictly comparable to those found in the diphenylphosphide-bridged

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[35] Ingham, W. L.; Billing, D. G.; Levendis, D. C.; Coville, N. J. *Inorg. Chim. Acta* **1991**, *187*, 17.

[36] Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 247.

compounds [$FeMoCp(\mu\text{-}PPh_2)(CO)_5L$] (L = CO,[37] $P(OMe)_3$).[38] The iron fragment displays a pseudo-octahedral geometry, if the Mo atom is considered as a coordination position. Under the analogous assumption, the molybdenum atom displays then the classical piano stool geometry. The Mo−Fe distance (2.934(1) and 2.929(1) Å for molecules A and B, respectively) is consistent with the single Mo−Fe bond formulated for this molecule under the EAN formalism and is similar to the bond lengths measured in the mentioned MoFe complexes. Other bond lengths and angles are also similar to those found in the above diphenylphosphide compounds and thus deserve no further comments.

Spectroscopic data in solution for **7** are fully consistent with its solid structure. The IR spectrum in petroleum ether, for instance, shows six CO stretching bands, with a pattern similar to that measured in the solid state for [$FeMoCp(\mu\text{-}PPh_2)(CO)_6$].[37] The ^{31}P NMR spectrum for **7** exhibits a singlet at 199.1 ppm, a chemical shift ca. 40 ppm higher than that measured for the above diphenylphosphide complex, as expected for PCy_2 and PPh_2 chemical shifts in comparable structures.

Reaction with CuCl. Since the interaction of hydride **1** with 16-electron transition-metal fragments of the type $M(CO)_5$ and $MCp(CO)_2$ seems to point to an essentially acceptor role of the heterometal fragment and a donor role of the unsaturated dimolybdenum center, we examined the possibility of synthesizing Mo_2−group 11 clusters by reacting the hydride **1** with neat electron acceptors such as the gold cations [$Au(PR_3)$]$^+$ or the neutral copper(I) halides. Indeed, both reactions take place readily at room temperature, but only that with CuCl gave a reasonably stable and pure product, identified as the trinuclear cluster [$CuMo_2ClCp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (**8**).

Although no suitable crystals for a diffractometric study could be grown for **8**, the spectroscopic data suggest a structure related to those of the hydride clusters **5** and **6** just discussed, perhaps with a more pronounced donor−acceptor interaction to sustain the heterometallic Mo_2Cu framework (Chart 2). In the first place, the IR spectrum for **8** shows two CO stretching bands with a pattern (well-separated medium and strong bands, in order of decreasing frequency) different from that in **1** and very similar to that found for the molybdenum−tin derivative [$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnPh_3)(CO)_2$].[1] This indicates that the carbonyl ligands are still in a transoid arrangement, but a distorted one in order to better accommodate the bridging group. Interestingly, the average C−O stretching frequencies for **1** and **8** in tetrahydrofuran solution are 1854 and 1878 cm^{-1}, respectively, which gives support to our idea that these hydride-bridged heterometallic clusters derived from **1** are essentially supported by a donor−acceptor interaction from the hydride substrate to the heterometal fragment. This interaction is possibly the strongest in the case of the Mo_2Cu cluster **8**. In fact, the chemical shift of the phosphorus nucleus in **8** (230.8 ppm) is much higher than those for clusters **5** or **6** (Table 1) and similar to the chemical shifts found for PCy_2 ligands bridging triple Mo−Mo bonds.[1,26,34] All this is consistent with a negligible electron contribution of the CuCl group to the bonding in the cluster.

As observed for the hydride clusters **5** and **6**, the ^1H spectrum of **8** at room temperature displays just one cyclopentadienyl resonance, which is not consistent with the transoid arrangement of the MoCp(CO) fragments clearly deduced from its IR spectrum. Presumably, a fluxional process similar to those already discussed is also operative for this compound (Scheme 3). We note finally that compound **8** exhibits a relatively little shielded resonance (δ −6.71 ppm, J_{PH} = 4 Hz), not very different from that for the starting hydride **1** (δ −6.94 ppm, J_{PH} = 11 Hz). It is tempting to conclude from this that the hydride ligand in **8** might be edge-bridging the molybdenum atoms, rather than triply bridging the Mo_2Cu face. However, we must consider that hydride ligands are themselves relatively deshielded when bridging to copper atoms. For example, in the cluster [$CuMn_2(\mu\text{-}H)_3(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}(PPh_3)$] the chemical shifts for the hydride ligands are −26.2 (Mn−Mn) and −9.0 ppm (Mn−Cu).[6] Therefore, in the absence of further structural data, we must assume that the hydride ligand in **8** is likely to be placed bridging (even if asymmetrically) the trimetal skeleton of the cluster.

Concluding Remarks

The 30-electron dinuclear hydride **1** readily reacts with 17-electron metal fragments of type $MCp(CO)_3$ or $M(CO)_x$ to give 46-electron trinuclear clusters after formal replacement of the hydride ligand by the isolobal metal fragment. On the other hand, compound **1** adds easily to 16-electron metal fragments of the type $M(CO)_x$ or $MCp(CO)_2$ to give the corresponding unsaturated trinuclear clusters in which the hydride ligand bridges the three metal atoms. The structure and bonding interaction in the hydride-bridged clusters can be essentially described in terms of a 3c-2e donor−acceptor interaction between the multiply metal−metal bonded hydride (donor) and the heterometal fragment (acceptor). In any case, all the above reactions proved to be efficient and rational synthetic routes for electron-deficient trinuclear clusters, although some of them were found to be quite unstable species.

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 use.[39] Compounds [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$][34] (**1**) and [$Ru_2Cp_2(CO)_4$][40] were prepared according to literature procedures, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338−343 K. Photochemical experiments were performed using jacketed Pyrex Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp (as source of visible−UV light) or conventional 200 W lamp (as source of visible light) both placed ca. 1 cm away from the Schlenk tube were used for these experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water. Commercial aluminum oxide (Aldrich, 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. IR stretching frequencies of CO ligands were measured in solution and are referred to as ν(CO) (solvent). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), or 75.47 MHz ($^{13}C\{^1H\}$) 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 solutions (^{31}P). Coupling constants (J) are given in hertz.

Preparation of [$Mo_3Cp_3(\mu\text{-}PCy_2)(\mu_3\text{-}CO)(CO)_4$] (2a). A toluene solution (10 mL) of compound **1** (0.030 g, 0.05 mmol) and [Mo$_2$-

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$Cp_2(CO)_6$] (0.050 g, 0.1 mmol) was irradiated with visible light for 5 h at 288 K. Solvent was then removed from the solution under vacuum, the residue was extracted with dichloromethane−petroleum ether (1:4), and the extracts were chromatographed on an alumina column (activity IV) at 253 K. Elution with dichloromethane−petroleum ether (1:1) gave a brown fraction. Removal of solvents from the latter under vacuum gave compound **2a** (0.025 g, 61%) as a dark brown solid. The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether and diethyl ether into a toluene solution of the complex at 253 K. Anal. Calcd for $C_{32}H_{37}Mo_3O_5P$: C, 46.85; H, 4.55. Found: C, 47.13, H, 4.82. $^{31}P\{^1H\}$ NMR (81.04 MHz, $CDCl_3$): δ 178.3 (s, μ-P). $^{31}P\{^1H\}$ NMR (162.01 MHz, CD_2Cl_2, 193 K): δ 185.4 (s, br, μ-P, isomer **A**), 150.2 (s, br, μ-P, isomer **B**), ratio **A**/**B** = 1.7. ^1H NMR (200.13 MHz, $CDCl_3$): δ 5.31 (s, 5H, Cp), 5.07 (s, 10H, Cp), 2.50−1.00 (m, 22H, Cy) ppm. ^1H NMR (400.13 MHz, 193 K): δ 5.36 (s, 5H, Cp), 5.11 (s, 10H, Cp), 2.40−1.00 (m, 22H, Cy) ppm. $^{13}C\{^1H\}$ NMR: δ 256.3 (s, br, CO), 93.0 (s, Cp), 90.0 (s, 2 × Cp), 47.3 (d, J_{CP} = 18, C^1-Cy), 32.7 (s, C^2-Cy), 28.0 (d, J_{CP} = 12, C^3-Cy), 26.6 (C^4-Cy) ppm.

Reaction of 1 with [$W_2Cp_2(CO)_6$]. The procedure is identical to that above-described for **2a**, but using [$W_2Cp_2(CO)_6$] (0.055 g, 0.08 mmol) instead. Irradiation of the mixture for 2 h gave 0.025 g (59%) of the isomers [$Mo_2WCp_3(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_4$] (**2b**,**c**). The equilibrium ratio, measured by ^1H NMR, was somewhat dependent on the solvent, being **2b**/**2c** = 2.0 ($CDCl_3$), 1.7 (C_6D_6), or 1.3 [$(CD_3)_2CO$]. $^{31}P\{^1H\}$ NMR (81.04 MHz, $CDCl_3$): δ 170.9 (s, μ-P, **2b**), 143.5 (s, J_{PW} = 319, μ-P, **2c**) ppm. ^1H NMR (200.13 MHz, $CDCl_3$, **2b**): δ 5.38 (s, 5H, Cp), 5.05 (d, J_{PH} = 0.7, 10H, Cp) ppm. Signals due to the cyclohexyl groups are mixed with those of the other isomer, in the range 2.50−1.00 ppm. ^1H NMR (200.13 MHz, $CDCl_3$, **2c**): δ 5.32 (s, 5H, Cp), 5.19 (d, J_{PH} = 1, 5H, Cp), 5.10 (d, J_{PH} = 1, 5H, Cp) ppm. Signals due to the cyclohexyl groups are mixed with those of the other isomer, in the range 2.50−1.00 ppm.

Preparation of [$MnMo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_5$] (3). A toluene solution (10 mL) of compound **1** (0.040 g, 0.070 mmol) and [$Mn_2(CO)_{10}$] (0.022 mg, 0.056 mmol) was irradiated at 288 K with visible−UV light for 10 min to yield a brown-orange solution containing similar amounts of **3** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$].[26] Solvents were then removed under vacuum, and the residue was extracted with CH_2Cl_2−petroleum ether (1:1 mixture) and chromatographed on alumina (activity IV) at 253 K. Elution with the latter mixture gave a brown fraction, which yielded, after removal of solvents, compound **3** as a brown, highly air-sensitive solid decomposing progressively upon manipulation. $^{31}P\{^1H\}$ NMR (81.03 MHz, C_6D_6): δ 207.0 (s, μ-P) ppm. ^1H NMR (200.13 MHz, C_6D_6): δ 4.85, 4.80 (2 × s, 2 × 5H, Cp) ppm. Signals due to cyclohexyl groups could not be assigned unambiguously because of the presence of cyclohexyl-containing impurities in the NMR sample.

Reaction of 1 with [$Ru_2Cp_2(CO)_4$]. A toluene solution (10 mL) of compound **1** (0.060 g, 0.104 mmol) and [$Ru_2Cp_2(CO)_4$] (0.049 mg, 0.110 mmol) was irradiated with visible−UV light for 5 min at 288 K to obtain a brown solution containing the isomers [$Mo_2RuCp_3(\mu\text{-}PCy_2)(\mu\text{-}CO)(CO)_3$] (**4a**,**b**) (1:1 ratio). Solvents were then removed under vacuum, the residue was extracted with CH_2Cl_2−petroleum ether (1:4 mixture), and the extracts were chromatographed on alumina (activity IV) at 253 K. Elution with CH_2Cl_2−petroleum ether (1:1 mixture) gave two separated brown fractions both containing, after removal of solvents, a 1:1 mixture of compounds **4a** and **4b**, as a brown, highly air-sensitive solid (overall yield 0.057 g, 69%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 224.1 (s, μ-P, **4a**), 169.1 (s, μ-P, **4b**) ppm. ^1H NMR ($CDCl_3$, **4a**): δ 5.31, 5.01, 4.99 (3 × s, 3 × 5H, Cp) ppm. Signals due to the cyclohexyl groups are mixed with those of the other isomer, in the range 2.60−1.10 ppm. ^1H NMR ($CDCl_3$, **4b**): δ 5.22, 5.08 (2 × s, 2 × 5H, Cp), 4.96 (d, J_{PH} = 1, 5H, Cp) ppm. Signals due to the cyclohexyl groups are mixed with those of the other isomer, in the range 2.60−1.10 ppm.

Preparation of [$CrMo_2Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7$] (5a). A toluene solution (10 mL) of compound **1** (0.030 g, 0.052 mmol) and [$Cr(CO)_6$] (0.016 g, 0.073 mmol) was irradiated with visible−UV light for 10 min at 288 K to yield an orange solution containing similar amounts of **5a** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$].[26] Solvents were then removed under vacuum, the residue was extracted with CH_2Cl_2−petroleum ether (1:9 mixture), and the extracts were chromatographed on alumina (activity IV) at 253 K. Elution with the latter mixture gave an orange fraction, which yielded, after removal of solvents, compound **5a** contaminated with small amounts of **1** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$]. Compound **5a** is an unstable, air-sensitive compound, and further attempts to purify or isolate it led to its progressive decomposition (to yield the above-mentioned compounds). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 207.4 (s, μ-P) ppm. ^1H NMR ($CDCl_3$): δ 5.25 (s, 10H, Cp), −16.88 (d, J_{PH} = 5, 1H, μ-H) ppm. Signals due to the cyclohexyl groups were mixed with those of **1** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$].

Preparation of [$Mo_3Cp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7$] (5b). A toluene solution (10 mL) of compound **1** (0.030 g, 0.052 mmol) and [$Mo(CO)_6$] (0.015 g, 0.057 mmol) was irradiated with visible−UV light for 10 min at 288 K to yield an orange solution containing similar amounts of **5b** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$].[26] Workup as described above for **5a** yielded **5b** as an unstable, air-sensitive, orange solid contaminated with small amounts of **1** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 208.4 (s, μ-P) ppm. ^1H NMR ($CDCl_3$): δ 5.24 (s, 10H, Cp), −13.34 (d, J_{PH} = 4, 1H, μ-H) ppm. Signals due to the cyclohexyl groups were mixed with those of **1** and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$].

Preparation of [$Mo_2WCp_2(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_7$] (5c). A toluene solution (10 mL) of compound **1** (0.040 g, 0.070 mmol) and [$W(CO)_6$] (0.030 mg, 0.085 mmol) was irradiated with visible−UV light for 8 min at 288 K to yield an orange solution containing compound **5c** as the major product. After removal of solvents under vacuum, the orange residue was extracted with CH_2Cl_2−petroleum ether (1:10 mixture) and the extracts were chromatographed on alumina (activity IV) at 243 K. Elution with the same solvent mixture gives an orange fraction, yielding, after removal of solvents, compound **5c** as an orange, microcrystalline solid (0.040 g, 63%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a toluene solution of the complex at 253 K. Anal. Calcd for $C_{29}H_{33}Mo_2O_7PW$: C, 38.69; H, 3.69. Found: C, 38.43, H, 3.77. $^{31}P\{^1H\}$ NMR: δ 205.0 (s, μ-P) ppm. ^1H NMR: δ 5.27 (s, Cp, 10H), 2.50−1.20 (m, Cy, 22H), −12.46 (d, J_{PH} = 3, J_{WH} = 36, μ-H, 1H) ppm. $^{13}C\{^1H\}$ NMR: δ 245.2 (d, J_{CP} = 13, MoCO), 197.6 (s, J_{CW} = 125, WCO), 90.7 (s, Cp), 51.9 (d, J_{CP} = 17, C^1-Cy), 33.6 (d, J_{CP} = 5, $C^{2,6}$-Cy), 32.5 (d, J_{CP} = 3, $C^{6,2}$-Cy), 28.3 (d, J_{CP} = 12, $C^{3,5}$-Cy), 28.1 (d, J_{CP} = 10, $C^{5,3}$-Cy), 26.5 (s, C^4-Cy) ppm.

Preparation of [$MnMo_2Cp_2Cp'(\mu_3\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] (6). A THF solution of [$MnCp'(CO)_2(THF)$] (Cp′ = $C_5H_4CH_3$) was prepared from [$MnCp'(CO)_3$] (50 μL, 0.3 mmol) according to literature procedures.[41] Compound **1** (0.030 g, 0.05 mmol) was then added to this solution, and the mixture was stirred for 30 min at room temperature. Solvent was then removed from the solution under vacuum to yield a brown residue, which was extracted with CH_2Cl_2−petroleum ether (1:4). The extracts were then chromatographed on an alumina column (activity IV) at 253 K. Elution with the same solvent mixture gave a green fraction, which yielded, after removal of solvents under vacuum, compound **6** (0.023 g, 60%) as a green solid. The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a toluene solution of the complex at 253 K. Anal. Calcd for $C_{32}H_{40}MnMo_2O_4P$: C, 50.15; H, 5.26. Found: C, 50.38; H, 5.40. $^{31}P\{^1H\}$ NMR (C_6D_6):

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(41) Herrmann, W. A. *Angew. Chem.* **1974**, *86*, 345.

Table 5. Crystal Data for Compounds 5c, 6, and 7

	5c	**6**	**7**
mol formula	$C_{29}H_{33}Mo_2O_7PW$	$C_{32}H_{40}MnMo_2O_4P$	$C_{23}H_{27}FeMoO_6P$
mol wt	900.25	766.43	582.21
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1/c$
radiation (λ, Å)	0.71073	0.71073	0.71073
a, Å	12.047(2)	9.9059(18)	18.725(5)
b, Å	15.280(3)	22.193(4)	16.262(5)
c, Å	16.888(3)	13.832(2)	17.103(5)
α, deg	90	90	90
β, deg	101.172(3)	100.521(3)	107.51(5)
γ, deg	90	90	90
V, Å^3	3049.8(10)	2989.7(9)	4967(2)
Z	4	4	8
calcd density, g cm^{-1}	1.961	1.703	1.557
absorp coeff, mm^{-1}	4.668	1.332	1.188
temperature, K	120(2)	120(2)	293(2)
θ range, deg	1.81 to 28.28	1.50 to 28.33	3.04 to 30.00
index ranges (h, k, l)	−16, 15; 0, 20;0, 22	−13, 12; −29, 28; 0, 18	0, 26; 0, 22; −24, 22
no. of reflns collected	74 749	37 847	14 865
no. of indep reflns (R_{int})	7797 (0.0492)	14 379 (0.0658)	14 468
no. of reflns with $I > 2\sigma(I)$	6083	10 652	8385
R indexes (data with $I > 2\sigma(I)$)[a]	$R_1 = 0.0235$	$R_1 = 0.0444$	$R_1 = 0.0356$
	$wR_2 = 0.0433^b$	$wR_2 = 0.0644^c$	$wR_2 = 0.0780^d$
R indexes (all data)[a]	$R_1 = 0.0452$	$R_1 = 0.0886$	$R_1 = 0.0790$
	$wR_2 = 0.0526^b$	$wR_2 = 0.0776^c$	$wR_2 = 0.0898^d$
GOF	1.199	1.115	0.808
no. of restraints/params	0/449	1/727	126/577
$\Delta\rho$(max., min.), e Å^{-3}	1.362, −0.843	0.954, −1.140	0.665, −0.859

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0078$, $b = 8.1989$. [c] $a = 0.0040$, $b = 3.7660$. [d] $a = 0.0468$, $b = 0.0000$.

δ 167.5 (s, μ-P) ppm. ^{1}H NMR (C_6D_6): δ 5.13 (s, 10H, Cp), 4.28 (s, 1H, C_5H_4), 4.19 (s, 2H, C_5H_4), 4.13 (s, 1H, C_5H_4), 3.00−0.80 (m, 22H, Cy), 1.93 (s, 3H, CH_3), −15.82 (s, 1H, μ-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 244.4 (d, $J_{CP} = 12$, 2 × MoCO), 235.0, 233.4 (2 × s, 2 × MnCO), 97.5 (s, C^1-Cp′), 89.7 (s, 2 × Cp), 83.2, 82.1, 81.5, 81.3 (4 × s, C$^{2-5}$-Cp′), 51.4 (s, br, C^1-Cy), 33.9 (d, $J_{CP} = 3$, C^{2,6}-Cy), 33.1 (s, C^{6,2}-Cy), 28.5 (d, $J_{CP} = 12$, C^{3,5}-Cy), 28.2 (d, $J_{CP} = 10$, C^{5,3}-Cy), 26.6 (s, C^4-Cy), 14.2 (s, Me) ppm. ^{13}C{^{1}H} NMR (100.63 MHz, tol-d_8, 233 K, cyclopentadienyl region): δ 98.5 (s, C^1-Cp′), 91.1, 89.8 (2 × s, 2 × Cp), 84.0, 82.9, 81.9, 81.5 (4 × s, C$^{2-5}$-Cp′) ppm.

Preparation of [FeMoCp(μ-PCy$_2$)(CO)$_6$] (7). A toluene solution of compound **1** (0.040 g, 0.070 mmol) was stirred with [$Fe_2(CO)_9$] (0.035 g, 0.096 mmol) for 1 h to give a brown solution containing **7** as the major product. Solvents were then removed under vacuum, the residue was extracted with CH_2Cl_2−petroleum ether (1:4), and the extracts were chromatographed on alumina (activity II). Elution with the same mixture gave, after removal of solvents, compound **7** as an orange solid (0.026 g, 64%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a toluene solution of the complex at 253 K. Anal. Calcd for $C_{23}H_{27}FeMoO_6P$: C, 47.45; H, 4.67. Found: C, 47.36; H, 4.51. ^{31}P{^{1}H} NMR: δ 199.1 (s, μ-P) ppm. ^{1}H NMR: δ 5.26 (s, 5H, Cp), 2.80−0.80 (m, 22H, Cy) ppm.

Preparation of [CuMo$_2$ClCp$_2$(μ_3-H)(μ-PCy$_2$)(CO)$_2$] (8). CuCl (0.010 g, 0.101 mmol) was added to a toluene solution (10 mL) of compound **1** (0.030 g, 0.052 mmol), and the mixture was stirred for 1 h to give a brown solution. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (2 × 7 mL). Then, the brown solid was extracted with toluene (3 × 10 mL) and filtered through diatomaceous earth. Removal of solvent from the filtrate yielded compound **8** (0.031 mg, 81%) as a brown, microcrystalline solid. Anal. Calcd for $C_{24}H_{33}ClCuMo_2O_2P$: C, 42.68; H, 4.93. Found: C, 42.89; H, 5.37. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 230.8 (s, μ-P) ppm. ^{1}H NMR ($CDCl_3$): δ 5.29 (s, 10H, Cp), 2.60−1.00 (m, 22H, Cy), −6.71 (d, $J_{PH} = 4$, 1H, μ-H) ppm.

X-ray Structure Determination of Compound 5c. The X-ray intensity data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo Kα radiation at 120 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[42] 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,[42] and a multiscan absorption correction was applied with SADABS.[43] Using the program suite WinGX,[44] the structures were solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[45] All hydrogen atoms were located in the Fourier map, except for those of C(24) to C(29) of one of the cyclohexyl rings, which were geometrically located. All of them were given an overall isotropic thermal parameter. The final refinement on F^2 proceeded by full-matrix least-squares calculations using anisotropic thermal parameters for all the non-hydrogen atoms.

X-ray Structure Determination of Compound 6. Collection of data, structure solution, and refinements were done as described for **5c**. Two independent molecules are present in the asymmetric unit, without significant differences. All non-hydrogen atoms were refined anisotropically, except for C(44), which was persistently nonpositive definite. Most of the hydrogen atoms were found in the Fourier maps; however, because of the presence of two molecules in the asymmetric unit, in order to reduce the number of parameters to be refined, all hydrogen atoms were geometrically

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(42) *SMART & SAINT Software Reference Manuals,* Version 5.051 (Windows NT Version); Bruker Analytical X-ray Instruments: Madison WI, 1998.

(43) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996.

(44) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(45) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

positioned, except the bridging hydride ligands, which were located in the Fourier map and their positions refined. All of them were given an overall isotropic thermal parameter.

X-ray Structure Determination of Compound 7. Data were collected on a Philips PW1100 (Mo Kα radiation) single-crystal diffractometer. Details for the X-ray data collection are reported in Table 5. A correction for absorption was made [maximum and minimum value for the transmission coefficient was 1.000 and 0.821].[46] The structure was solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[45] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. Two independent but very similar molecules were present in the crystals.

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Supporting Information Available: Crystallographic data for the structural analysis of compounds **5c**, **6**, and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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