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Reactivity of the Unsaturated Hydride $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ toward P-Donor Bidentate Ligands and Unsaturated N-Containing Organic Molecules

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The reactions of the 30-electron hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ with the bidentate P-donor ligands bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)methane (dmpm), and tetraethylpyrophosphite (tedip) lead to the electron-precise derivatives $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2(\mu\text{-}L_2)]$ (L_2 = dppm, dmpm, tedip), in which the bidentate ligand bridges the dimetal center. In the reaction with dppm, the tricarbonyl derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_3(\kappa^1\text{-dppm})]$ is also obtained as a minor byproduct. All of these compounds are obtained as mixtures of isomers, most of them interconverting in solution, and the structure of the major isomer of the tedip derivative was confirmed through an X-ray diffraction study (Mo−Mo = 3.2251(5) Å). The title unsaturated hydride reacts readily with isocyanides to give in good yield the insertion products $[Mo_2Cp_2(\mu\text{-}\eta,\kappa{:}\eta,\kappa\text{-HCNR})(\mu\text{-}PCy_2)(CO)_2]$ (R = *p*-tolyl, ^{t}Bu), having a 5e-donor formimidoyl ligand, as confirmed by an X-ray study of the ^{t}Bu compound. When R = *p*-tolyl, the addition derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2(CNR)_2]$ is also obtained as a minor product. Although the title hydride does not react with acetonitrile or simple diazo compounds, it reacts readily with benzyl azide ($PhCH_2N_3$) to give two 32-electron derivatives, the azavinylidene complex $[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$ (Mo−Mo = 2.632(1) Å) and the amido derivative $[Mo_2Cp_2\{\mu\text{-}NH(CH_2Ph)\}(\mu\text{-}PCy_2)(CO)_2]$, in a 2:1 ratio. The latter product can be obtained almost selectively by reaction of the triply bonded anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ with benzyl azide in the presence of H_2O as a source of protons. The solution structures of the new complexes are discussed on the basis of the solid-state X-ray studies and the IR and variable-temperature NMR (^{1}H, ^{31}P, ^{13}C) data, and the reaction pathways responsible for the formation of the new complexes are discussed on the basis of the available information.

Introduction

During our preliminary study of the reactivity of the 30-electron hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**), we found that this complex was quite reactive toward small electron-donor molecules under mild conditions as a result of its coordinative and electronic unsaturation.[1] For example, two molecules of CO are rapidly incorporated to the unsaturated dimetal center in **1** to yield the saturated tetracarbonyl $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$, previously synthesized by us through a more conventional route,[2] and rapid reaction also takes place with CN^{t}Bu, now to give the insertion product $[Mo_2Cp_2(\mu\text{-}HCN^tBu)(\mu\text{-}PCy_2)(CO)_2]$, having a bridging formimidoyl ligand.[1] In these reactions, the hydride complex behaves as a Lewis acid toward the incoming molecule, which is the electron donor, at least initially. However, the presence of the bridging hydride ligand allows for several possible further rearrangements of the incoming molecule, which may involve its insertion into the Mo−H bond (as in the above reaction), activation of E−H bonds (E = p-block element), H_2 elimination, etc., as shown by previous studies on the reactions of small molecules with compounds having unsaturated $M_2(\mu\text{-}H)_x$ centers, such as the neutral compounds $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[3] $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (L_2 = $Ph_2PCH_2PPh_2$ (dppm), $(EtO)_2POP(OEt)_2$ (tedip)),[4] $[Re_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$,[5] $[Re_2(\mu\text{-}H)_2(CO)_8]$,[6] and $[Ru_2Cp^*_2(\mu\text{-}H)_4]$ (Cp* = $\eta^5\text{-}C_5Me_5$)[7] or the cations $[Ru_2(\eta^6\text{-}C_6Me_6)_2(\mu\text{-}H)_3]^+$ [8] and $[Ir_2Cp^*_2(\mu\text{-dmpm})(\mu\text{-}H)_2]^{2+}$.[9] In all of the above compounds,

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[1] Alvarez, C. M.; Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2005**, *24*, 7.

[2] García, M. E.; Riera, V.; Ruiz, M. A.; Rueda, M. T.; Sáez, D. *Organometallics* **2002**, *21*, 5515.

[3] (a) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1. (b) Burgess, K. *Polyhedron* **1984**, *3*, 1175.

[4] See for example: (a) García-Alonso, F. J.; García-Sanz, M.; Riera, V.; Anillo-Abril, A.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1992**, *11*, 801. (b) García-Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1992**, *11*, 370. (c) García-Alonso, F. J.; García-Sanz, M.; Riera, V. *J. Organomet. Chem.* **1991**, *421*, C12. (d) Carreño, R.; Riera, V.; Ruiz, M. A. *J. Organomet. Chem.* **1991**, *419*, 163.

[5] (a) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171. (b) Prest, D. W.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2021.

[6] (a) Carlucci, L.; Proserpio, D. M.; D'Alfonso, G. *Organometallics* **1999**, *18*, 2091. (b) Carlucci, L.; Ciani, G.; von Gudenberg, D. W.; D'Alfonso, G. *J. Organomet. Chem.* **1997**, *534*, 233. (c) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 1101.

[7] See for example: (a) Takao, T.; Amako, M.; Suzuki, H. *Organometallics* **2003**, *22*, 3855. (b) Suzuki, H. *Eur. J. Inorg. Chem.* **2002**, 1009. (c) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2994. (d) Takao, T.; Amako, M.; Suzuki, H. *Organometallics* **2001**, *20*, 3406. (e) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3463. (f) Jones, W. D.; Chin, R. M.; Hoaglin, C. L. *Organometallics* **1999**, *18*, 1786. (g) Takao, T.; Yoshida, S.; Suzuki, H.; Tanaka, M. *Organometallics* **1995**, *14*, 3855. (h) Tada, K.; Oishi, M.; Suzuki, H. *Organometallics* **1996**, *15*, 2422. (i) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129. (j) Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, *5*, 283. (k) Omori, H.; Suzuki, H.; Take, Y.; Moro-oka, Y. *Organometallics* **1989**, *8*, 2270. (l) Suzuki, H.; Omori, H.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2579.

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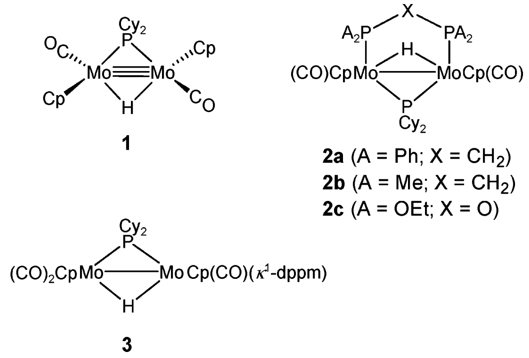
Chart 1



however, the number of hydride bridges at least matches the formal bond order based on the EAN rule, and there is no special coordinative unsaturation at the metal centers; hence, the incorporation of any donor molecule must modify the coordination mode of the bridging hydrides. In contrast, compound **1** displays just one hydride ligand over a formally triple intermetallic bond, and the molybdenum atoms are surrounded by one ligand fewer than usual (coordinative unsaturation). On the basis of these differences, we might anticipate some distinct behavior of compound **1** toward small donor molecules, in comparison to the aforementioned di- and polyhydride species (for instance, intramolecular dehydrogenation is no longer possible). In this paper we report the reactions of the unsaturated hydride **1** toward simple bidentate P-donors such as the diphosphines $R_2PCH_2PR_2$ (R = Ph (dppm), Me (dmpm)) and the diphosphite $(EtO)_2POP(OEt)_2$ (tedip) and the reactions of **1** with small organic molecules containing multiple C−N or N−N bonds, such as nitriles, isonitriles, diazo compounds, and azides. These reactions should give a measure of the real degree of unsaturation of the dimetal center in **1** and its ability for hydride transfer, respectively. Compound **1** is also quite reactive toward terminal and internal alkynes, and these results will be reported separately.

Results and Discussion

Reactions of 1 with Bidentate P-Donors. Since the diphosphines dppm and dmpm or the diphosphite tedip act usually as bridging 4e-donor ligands, it is expected that these molecules would coordinate easily to the unsaturated dimetal center in **1** in a bridging fashion, thus reducing the intermetallic bond order from 3 to 1. Isomerism, however, can arise if different relative positions of the ligands are possible, as happens to be the case.

Compound **1** reacts at room temperature with dppm in toluene to give the addition product $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2(\mu\text{-dppm})]$ (**2a**) in almost quantitative yield (Chart 1). This compound is obtained as a mixture of the two isomers **A** and **B** (Chart 2), which in solution are in equilibrium (see below; **A**/**B** = 9 in CD_2Cl_2 at 183 K). When this reaction is carried out in dichloromethane, compound **2a** is obtained along with small amounts of the tricarbonyl complex $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_3(\kappa^1\text{-dppm})]$ (**3**), which in solution also displays two isomers, **D** and **E** (Chart 3; **D**/**E** = 7 in C_6D_6 at 293 K). The reactions of **1** with dmpm and tedip proceed much more rapidly but give analogously the corresponding addition products $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2(\mu\text{-dmpm})]$ (**2b**) and $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2(\mu\text{-tedip})]$ (**2c**) in good yield. The dmpm compound seems to display a single isomer of type **A** in solution, although this was not confirmed by low-temperature NMR data. In contrast, the tedip compound exhibits three isomers in solution. Two of these isomers, **A** and **B**, are in fast equilibrium in solution (**A**/**B** = 3 in CD_2Cl_2 at 183 K) and are analogous to those found for the diphosphine compounds. The third isomer (**C**; Chart 2) does not seem to be in equilibrium with the other isomers and is obtained in a very low relative amount ((**A** + **B**)/**C** = 20).

Chart 2

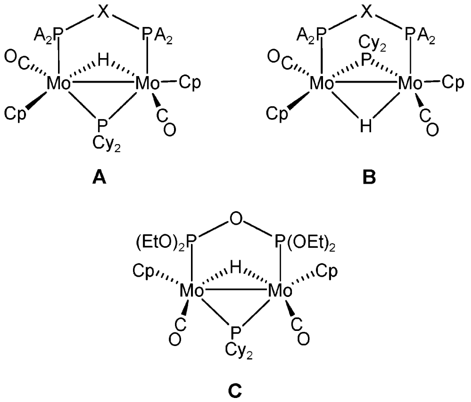


Chart 3

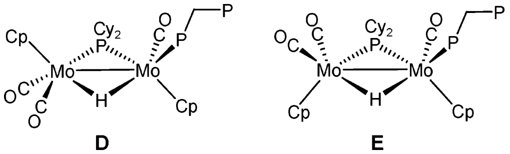


Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 2c

Mo(1)−Mo(2)	3.2251(5)	Mo(1)−P(1)	2.467(1)
Mo(1)−C(1)	1.909(4)	Mo(2)−P(1)	2.454(1)
Mo(2)−C(2)	1.923(5)	Mo(1)−P(2)	2.358(1)
Mo(1)−H(1)	1.90(6)	Mo(2)−P(3)	2.397(1)
Mo(2)−H(1)	1.84(6)		
O(1)−C(1)−Mo(1)	175.3(4)	C(2)−Mo(2)−Mo(1)	85.0(1)
O(2)−C(2)−Mo(2)	176.5(4)	P(3)−Mo(2)−P(1)	127.0(1)
Mo(1)−C(1)−Mo(2)	67.5(3)	P(2)−Mo(1)−P(1)	129.7(1)
Mo(1)−P(1)−Mo(2)	81.7(1)	Mo(1)−H(1)−Mo(2)	119(2)
C(1)−Mo(1)−Mo(2)	108.6(1)		

Structural Characterization of Compounds 2. The structure of compound **2c** (isomer **A**) was confirmed through a single-crystal X-ray diffraction study (Table 1 and Figure 1). The molecule displays two MoCp(CO) fragments in a transoid arrangement bridged by three ligands: hydride, diphosphite, and dicyclohexylphosphide. The intermetallic distance, 3.2215(5) Å, is comparable to those found for the related tri- and tetracarbonyl species $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_3L]$ (L = CO, PR_3),[10] ranging from 3.24 to 3.26 Å, thus fully consistent with the reduction of the intermetallic bond order, from 3 to 1. The tedip ligand is slightly twisted, so that the phosphorus atoms and the metal centers are not in the same plane. This could be a steric effect, since each of the phosphorus atoms is displaced away from the adjacent Cp ligand. A similar twist is observed in the

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[8] Tschan, M. J.-L.; Chérioux, F.; Karmazin-Brelot, L.; Süss-Fink, G. *Organometallics* **2005**, *24*, 1974.

[9] Fujita, K.; Nakaguma, H.; Hanasaka, F.; Yamaguchi, R. *Organometallics* **2002**, *21*, 3749.

[10] (a) Alvarez, C. M.; Alvarez, M. A.; García-Vivó, D.; García, M. E.; Ruiz, M. A.; Sáez, D.; Falvello, L. R.; Soler, T.; Herson, P. *Dalton Trans.* **2004**, 4168. (b) Hartung, H.; Walther, B.; Baumeister, U.; Böttcher, H.-C.; Krug, A.; Rosche, F.; Jones, P. G. *Polyhedron* **1992**, *11*, 1563. (c) Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1083.

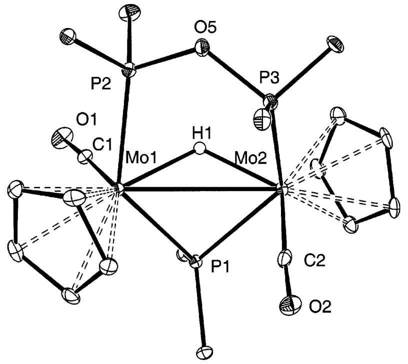
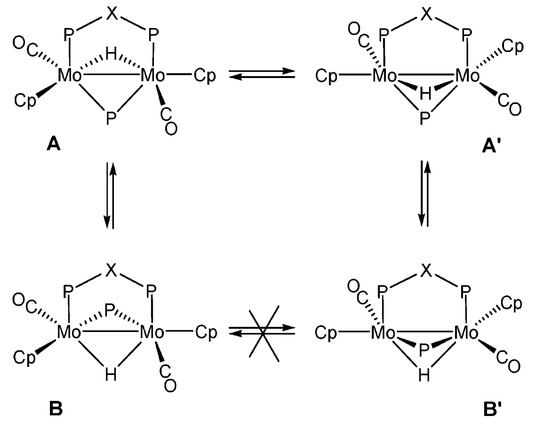


Figure 1. ORTEP diagram (30% probability) of compound **2c**, with H atoms, Cy rings, and Et groups omitted, except for the hydride ligand and the C^1 atoms of the Cy rings.

Scheme 1. Fluxional Process and Isomerization Equilibrium Proposed for Compounds 2a and 2c[a]



[a] Substituents on phosphorus are omitted for clarity.

tetracarbonyl derivative [$W_2Cp_2(CO)_4(\mu\text{-tedip})$],[11] where the Cp ligands are also placed in a transoid relative arrangement. In any case, the phosphide ligand is placed trans to the diphosphite bridge, in the average Mo_2P_2 plane. Finally, the centroids of the cyclopentadienyl rings, the carbonyls, and the hydride ligand are placed roughly in a plane perpendicular to the above one. The carbonyls are arranged in mutually transoid but quite inequivalent positions; one of them is placed cis to the hydride bridge and thus points away from the intermetallic vector (C(1)−Mo(1)−Mo(2) = 108.6(1)°), while the other carbonyl is placed trans to the hydride ligand and is slightly bent over the intermetallic bond (C(2)−Mo(2)−Mo(1) = 85.0(1)°). As a result, the coordination environment around Mo(2) is of the four-legged piano-stool type, whereas that around Mo(1) deviates strongly from that model. This structure can be related to that of the isoelectronic cation [$Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}I)(\mu\text{-}PPh_2)(CO)_2$]$^+$,[12] although in that case the presence of a bulky PPh_2 group (rather than the small hydride atom) in the plane of the carbonyls then induces a much more pronounced dissymmetry in the carbonyl ligands, with C−M−M angles of 120 and 77°, respectively.

The spectroscopic data collected for compounds **2a**−**c** in solution show that several isomers are present in solution, at least for the dppm and tedip compounds (Table 2 and Experimental Section). All of them exhibit C−O stretching bands at frequencies lower (by 40−70 cm^{-1}) than those of the hydride **1**,[13] as expected from the substantial increase in the electron density at the metal centers caused by the coordination of the bidentate P-donors. The IR spectra of the dppm and dmpm derivatives exhibit two bands with a pattern (medium and strong, in order of decreasing frequencies) indicative of the presence of two carbonyls in a transoid arrangement.[14] Indeed, this is what we would expect for a geometry such as that found in the solid state for **2c**, labeled by us as isomer **A**, in which the CO groups define an angle of ca. 160°. In fact, the solid-state IR spectrum of the crystals of **2c** (Nujol emulsion) displays two C−O stretching bands (1824 (s), 1791 (vs, br) cm^{-1}), consistent with this transoid arrangement of the CO ligands. However, the variable-temperature NMR data for **2a** (see Experimental Section) indicate that two interconverting isomers are present in solution. Thus, the ^{31}P NMR spectrum of **2a** at room temperature shows one set of averaged signals (Table 2) that, on lowering the temperature, gives the two sets attributed to isomers **A** and **B**.[15] The major isomer **A** presumably corresponds to the structure found for **2c** in the crystal: that is, with the carbonyls trans and cis, respectively, to the hydride bridge and the phosphorus ligands arranged mutually trans (Chart 2). This isomer is fluxional down to 183 K, presumably by displacement of the hydride ligand between both sides of the average Mo_2P_3 plane (**A** and **A′** in Scheme 1), then generating a false binary axis to yield equivalent P, Cp, or CO environments. This explains, for example, the fact that the hydride resonance at 183 K appears at −9.92 ppm (a position similar to those of conventional [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4$] complexes,[2,10a,c]) still as a doublet of triplets, with similar couplings (49 and 43 Hz) to all three P nuclei, in agreement with the cis arrangement of the hydride with respect to these atoms. The dmpm compound **2b** seems to exist in solution only in the form of the fluxional isomer **A**, since it exhibits sharp ^1H and ^{31}P NMR resonances at room temperature, the latter revealing a low coupling (J_{PP} = 10 Hz) between the phosphide and diphosphine P atoms, which is a characteristic feature of pairs of atoms in a trans arrangement in these types of cyclopentadienyl complexes.[16,17] In contrast, the minor isomer **B** in **2a** behaves as a rigid asymmetric molecule at low temperature and is proposed to be derived from the major isomer by just exchanging the positions of the hydride

Table 2. Selected IR[a] **and $^{31}P\{^1H\}$ NMR**[b] **Data for New Compounds**

compd	ν(CO)	$\delta(\mu\text{-P})$	$\delta(\mu\text{-P}_2)$
[$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2(\mu\text{-dppm})$] (**2a**)	1792 (m, sh), 1761 (vs)	162	64.3
[$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2(\mu\text{-dmpm})$] (**2b**)	1793 (m, sh), 1758 (vs)	160.9[c]	32.4[c]
[$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2(\mu\text{-tedip})$] (**2c**)	1842 (vw, sh), 1832 (w, sh), 1811 (m, sh), 1787 (vs)	149.5,[d] 201.8[e]	180.3,[d] 187.9[e]
[$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_3(\kappa^1\text{-dppm})$] (**3**)	1922 (vs), 1830 (s), 1792 (m)	196.5[f]	64.3, −23.8[f]
[$Mo_2Cp_2\{\mu\text{-}\eta:\kappa,\eta:\kappa\text{-HCN}(p\text{-tol})\}(\mu\text{-}PCy_2)(CO)_2$] (**4a**)	1853 (m, sh), 1836 (vs)	155.7	
[$Mo_2Cp_2\{\mu\text{-}\eta:\kappa,\eta:\kappa\text{-HCN}^t\text{Bu}\}(\mu\text{-}PCy_2)(CO)_2$] (**4b**)	1851 (m, sh), 1823 (vs)	155.2	
[$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)\{CN(p\text{-tol})\}_2(CO)_2$] (**5**)	2062 (w),[g] 2034 (w),[g] 1925 (s), 1840 (vs)	215.7[h]	
[$Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2$] (**6**)	1874 (m), 1842 (vs)	125.4[i]	
[$Mo_2Cp_2(\mu\text{-}NHCH_2Ph)(\mu\text{-}PCy_2)(CO)_2$] (**7**)	1843 (m, sh), 1813 (vs)	111.6[i]	

[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 and J in Hz. μ-P refers to the PCy_2 ligand and $\mu\text{-}P_2$ to the diphosphine or diphosphite ligand. [c] At 81.04 MHz, J_{PP} = 10 Hz. [d] Isomers **A** and **B** in C_6D_6. [e] Isomer **C**. [f] Isomer **D** in C_6D_6, J_{PCP}= 25 Hz. [g] ν(CN). [h] In $CDCl_3$ at 81.04 MHz. [i] At 162.01 MHz.

and phosphide bridges (Chart 2). A similar isomerism has been previously found by us in the cationic complexes $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_2(\mu\text{-}dppm)]^{2+}$ (R = R′ = Ph; R = H, R′ = Cy)[16] and $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]^{+}$ (M = Mo, W; X = SPh, I),[17] although these cations display terminal CO ligands parallel (as opposed to trans) to each other. In agreement with this proposal, the hydride resonance now exhibits quite different couplings to the three P atoms (δ −8.78 ppm, J_{HP} = 35, 48, and 65 Hz at 183 K). The rigid behavior of this isomer on the NMR time scale is not surprising, because a displacement of the bulky dicyclohexylphosphide ligand between both sides of the average Mo_2P_3 plane (**B** and **B′** in Scheme 1) could not possibly take place without severe rearrangements.

The situation in the solutions of the tedip compound **2c** is more complex. The IR spectrum in CH_2Cl_2 is different from those of the diphosphine compounds, since it exhibits weak additional C−O stretching bands at higher frequencies. This is due to the presence in solution of a third, very minor isomer (**C**) in addition to the isomers of type **A** and **B** discussed for **2a** (Chart 2), as confirmed by the NMR data.[15] Although not all resonances of isomer **C** could be identified, due to its low relative proportion, the data available are informative enough to conclude that this rigid isomer is not in equilibrium with the major isomers and most likely has a cis arrangement of its carbonyl ligands, as persistently found for the aforementioned cations $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_2(\mu\text{-}dppm)]^{2+}$ and $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]^{+}$. Evidence for this proposal comes from the presence of the noted additional C−O stretching bands at high frequency in the IR spectrum and the strong deshielding of the dicyclohexylphosphide P nucleus (ca. 50 ppm above the resonances of isomers **A** and **B**). These are the main spectroscopic differences found between cis and trans isomers in the dicarbonyl complexes $[M_2Cp_2(\mu\text{-}PR_2)_2(CO)_2]$ (M = Mo, W).[2,18]

Spectroscopic Characterization of Compound 3. The side product formed in the reaction of hydride **1** with dppm was satisfactorily characterized by IR and NMR spectroscopy, due to its similarity to the tricarbonyl derivatives $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3L]$ (L = P-donor ligand), previously prepared by Mays et al. through the photochemical reaction of the tetracarbonyl complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ with the corresponding ligand.[11c]

The IR spectrum of **3** in dichloromethane shows three C−O stretching bands similar to those reported for these tricarbonyl complexes. The room-temperature ^1H NMR spectrum in C_6D_6 reveals that compound **3** exhibits the two interconverting isomers **D** and **E** in solution (Chart 3). For the complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_3L]$ two isomers were also found in solution, with their ratios being dependent on the solvent and ligand L. These isomers were supposed to differ in the relative position (cis or trans) of L with respect to the bridging hydride.[10c] However, the hydride ligands in isomers **D** and **E** display similar couplings to the P nuclei, implying that the relative positions of the coordinated phosphorus atom of dppm and the hydride ligand are cis in both isomers (isomer **D**, δ −12.29 ppm, J_{PH} = 46, 42 Hz; isomer **E**, δ −11.95 ppm, J_{PH} = 49, 39 Hz). This is only possible by rotating the $Mo(CO)_2Cp$ moiety so as to yield a cis arrangement of both cyclopentadienyl groups. We must note that the first examples of related cis/trans isomerism in complexes of the type $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ have been reported only recently,[10a] although a similar isomerism was reported previously for isoelectronic thiolate-bridged species.[19] The ^{31}P NMR spectrum for the major isomer **D** in **3** (the corresponding resonance for the minor isomer **E** could not be identified) displays two doublets at 64.3 (κ^1 P) and −23.8 ppm (uncoordinated P atom), both resonances being in the range expected for a κ^1-dppm ligand on a dimolybdenum complex.[20] However, the P−P coupling between the free and coordinated P atoms of the diphosphine is anomalously low (25 Hz) in comparison to the usual values measured for related molybdenum complexes (ca. 80 Hz),[20] an observation for which we can give no satisfactory explanation at present. As for the phosphide ligand, it exhibits no coupling to the diphosphine P atoms (consistent with their mutual trans disposition) and appears at a relatively high chemical shift (196.5 ppm), in agreement with the presence of a single metal−metal bond in the molecule.[2]

Reactions of 1 with Isocyanides. Compounds having unsaturated $M_2(\mu\text{-}H)_x$ centers are usually reactive toward nitriles and isocyanides,[3,4a,5,7b,9] to give either addition or insertion derivatives. The insertion processes can lead to new 3e-donor bridging ligands such as azavinylidene (μ-N=CHR), iminoacyl (μ-η:κ-HNCR), formimidoyl (μ-η:κ-HCNR), or aminocarbyne (μ-CNHR). Thus, it is surprising that compound **1** does not react with neat acetonitrile or benzonitrile, even under refluxing conditions. In contrast, reaction with 1 equiv of isocyanides CNR (R = *p*-tol, ^{t}Bu) takes place rapidly at room temperature to give the formimidoyl complexes $[Mo_2Cp_2(\mu\text{-}\eta,\kappa:\eta,\kappa\text{-}HCNR)(\mu\text{-}PCy_2)(CO)_2]$ (R = *p*-tol (**4a**), ^{t}Bu (**4b**)), in which the formimidoyl ligand adopts an unusual 5e-donor coordination mode (μ-η,κ:η,κ) which renders an electron-precise dimetal center (see below). In addition, in the reaction with CN(*p*-tol), a small amount of the electron-precise diisocyanide derivative $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)\{CN(p\text{-}tol)\}_2(CO)_2]$ (**5**) is also formed.

Structural Characterization of Compounds 4. The structure of compound **4b** was confirmed through a single-crystal X-ray diffraction study (Figure 2).[1] The molecule displays two MoCp(CO) fragments in a transoid arrangement bridged by dicyclohexylphosphide and *tert*-butylformimidoyl ligands. The latter ligand is placed perpendicular to the dimetal centers, bonded through both its C- and N-donor atoms, in a η,κ:η,κ coordination mode. The arrangement of this ligand is such that the nitrogen atom is positioned roughly trans to the phosphide bridge (N−Mo−P = ca. 100°) and the C atom is placed cis to this group (C−Mo−P = ca. 80°), close to the approximate plane where the carbonyl ligands are placed. The geometry of **4b** might thus be related to that of the dicarbonyl complexes of type $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}Y)(\mu\text{-}Z)(CO)_2]$, having three bridging ligands, as discussed for **2a**, in which one of the bridges is close to the plane of the carbonyls and then renders quite different carbonyl

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(11) Alvarez, M. A.; Alvarez, C.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C. *Organometallics* **1997**, *16*, 2581.

(12) (a) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *375*, C23. (b) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *Organometallics* **1993**, *12*, 124.

(13) García, M. E.; Melón, S.; Ramos, A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983.

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

(15) A more detailed discussion of the low-temperature spectra of compounds **2a** and **2c**, including pictures of the $^{31}P\{^1H\}$ NMR spectra of **2c**, can be found in the Supporting Information.

(16) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.

(17) (a) Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A.; Vaissermann, J. *Organometallics* **2003**, *22*, 456. (b) Alvarez, M. A.; Anaya, Y.; García, M. E.; Ruiz, M. A. *Organometallics* **2004**, *23*, 3950.

(18) Alvarez, M. A.; García, M. E.; Martínez, M. E.; Ramos, A.; Ruiz, M. A.; Sáez, D.; Vaissermann, J. *Inorg. Chem.* **2006**, *45*, 6965.

(19) Schollhammer, P.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Girwood, S.-E. *J. Organomet. Chem.* **1995**, *486*, 183.

(20) (a) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *382*, 407. (b) García, G.; García, M. E.; Melón, S.; Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1997**, *16*, 624.

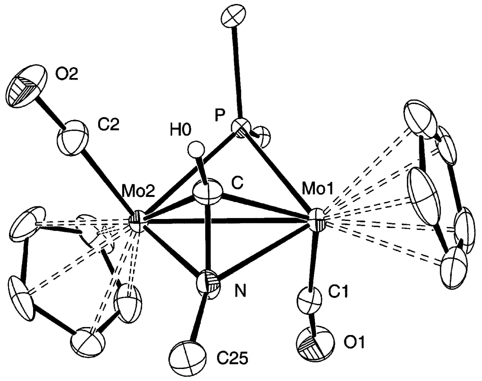

Figure 2. ORTEP diagram (30% probability) of compound **4b**,[1] with H atoms omitted, except the formimidoyl H atom, and Cy rings and ^{t}Bu groups omitted, except the corresponding C^1 atoms. Selected bond lengths (Å) and angles (deg): Mo(1)−Mo(2) = 2.883(2), Mo(1)−P = 2.416(2), Mo(2)−P = 2.436(2), Mo(1)−C(1) = 1.959(6), Mo(1)−C = 2.101(6), Mo(1)−N = 2.187(4), Mo(2)−C(2) = 1.914(6), Mo(2)−C = 2.115(6), Mo(2)−N = 2.157(4), C−N = 1.388(7); C(1)−Mo(1)−Mo(2) = 80.4(2), C(2)−Mo(2)−Mo(1) = 111.5(2), N−Mo(1)−P = 100.4(1), N−Mo(1)−P = 79.4(2).

environments, one (cis to that bridge) pointing away from the metal vector an the other one pointing toward the intermetallic region (C−Mo−Mo angles for **4b** are 80.4(2) and 111.5(2)°, respectively). The Mo−Mo distance is quite short, 2.883(2) Å, but it is still consistent with the presence of a single metal−metal bond by considering that two out of the three single-atom donors are of small covalent radii (C and N). For instance, the intermetallic lengths in related dimolybdenum compounds having three bridging thiolate ligands are even shorter, as found for the cations [Mo$_2$Cp$_2$(μ-SMe)$_3$(CO)$_2$]$^+$ (2.785 Å) and [Mo$_2$Cp*$_2$(μ-SMe)$_2$(μ-SH)(CO)$_2$]$^+$ (2.772(2) Å),[21] which are also electron-precise according to the EAN formalism.

The coordination mode of the formimidoyl ligand in **4b** is very unusual for a dinuclear species. In fact, we are only aware of one other example of a compound displaying a 5e-donor formimidoyl ligand across a dimetal center. This is the case of the tantalum derivative [Cl$_2$(κ^2-DTolF)Ta{μ-N(p-tol)}{μ-η,κ:η,κ-HCN(p-tol)}(κ^2-DTolF)$_2$] (DTolF$^-$ = N,N'-di-p-tolylformamidinate),[22] in which the formimidoyl ligand is generated after a C−N cleavage in a formamidinate group. A similar coordination mode is also found in the iminoacyl complex [W$_2$(η^5-C$_5$H$_4$^{i}Pr)$_2$Cl$_4$(μ-H)(μ-HNCEt)], obtained by protonation of a nitrile-bridged precursor.[23] In contrast, the coordination of a formimidoyl ligand as a 5e donor is well documented in some trinuclear clusters, such as [Os$_3$(μ-H)(μ_3-HCNPh)(CO)$_9$],[24] [Co$_3$Cp*$_3$(μ_2-H)(μ_3-HCN^{t}Bu)],[25] and the anion [Re$_3$(μ-H)$_3$(μ_3-HCNCy)(CO)$_9$]$^-$.[26] The C−N (formimidoyl) distance in **4b**, 1.388(7) Å, is significantly shorter than the average C−N single-bond distances in organic compounds (ca. 1.47 Å) but falls in the range found for the aforementioned 5e-donor formimidoyl and related iminoacyl complexes (Table 3). Moreover, this distance is clearly above the range found for the double C═N bonds present in 3e-donor formimidoyl ligands (μ-η:κ coordination mode, 1.21−1.32 Å).[24,26−28] In line with this description, the IR spectrum of a Nujol mull of **4b** displays a medium-intensity band at 1255 cm^{-1}, which we assign to the N−C stretch of the formimidoyl ligand. Taking into account that the range of stretching frequencies for single C−N bonds in aliphatic amines is 1220−1020 cm^{-1}, whereas that for double C═N bonds is 1690−1580 cm^{-1},[29] we then come also to the conclusion that the C−N interaction in the formimidoyl ligand of **4b** is close to a single bond.

Table 3. C−N Distances in Compounds with 5e-Donor Formimidoyl Ligands

compd	d_{CN}/Å
[Mo$_2$Cp$_2$(μ-η,κ:η,κ-HCN^{t}Bu)(μ−PCy$_2$)(CO)$_2$] (**4b**)	1.388(7)
[Cl$_2$(κ^2-DTolF)Ta{μ-N(p-tol)}{μ-η,κ:η,κ-HCN(p-tol)}-Ta(κ^2-DTolF)$_2$]	1.43(1)[22]
[W$_2$(η^5-C$_5$H$_4$^{i}Pr)$_2$Cl$_4$(μ-Cl)(μ-η,κ:η,κ-HNCEt)]	1.405(8)[23]
[Os$_3$(μ-H)(μ_3-HCNPh)(CO)$_9$]	1.415(1)[24]
[Co$_3$Cp*$_3$(μ-H)(μ_3-HCN^{t}Bu)]	1.346(7)[25]
[Re$_3$(μ-H)$_3$(μ_3-HCNCy)(CO)$_9$]$^-$	1.29(1)[26]

The above description of the formimidoyl ligand in **4b** as a 5e donor is further supported by the C−Mo (ca. 2.11 Å) and N−Mo (ca. 2.17 Å) distances, which are comparable to the reference values for single bonds between these atoms. For example, we find only slightly shorter Mo−N distances in related dimolybdenum derivatives displaying strongly bound 3e-donor nitrogen bridges, such as the azavinylidene complexes [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-κ:κ-NC(Me)CH$_2$CN}] (ca. 2.10 Å)[30] and [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-κ:κ-NCHMe)] (ca. 2.08 Å)[31] or the ketenimine complexes of the type [Mo$_2$Cp$_2$(CO)$_4$(μ-κ:κ,η-RNC═CR'$_2$)] (Mo−N = ca. 2.06−2.19 Å).[32] As for the Mo−C lengths, these are comparable, for example, to the corresponding lengths in related complexes having bridging carbonyl ligands over short intermetallic bonds, such as [Mo$_2$Cp$_2$(μ-PPh$_2$)$_2$(μ-CO)][33] and [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-COEt)(μ-CO)][13] (Mo−C distances ca. 2.10 Å).

Spectroscopic data recorded in solution for compounds **4** (Table 2 and Experimental Section) are fully consistent with the structure of **4b** found in the crystal. Thus, the IR spectrum for these complexes shows two C−O stretching bands with the typical pattern of *trans*-dicarbonyls defining angles between CO groups close to 180°,[14] while their ^{31}P NMR spectra exhibit a resonance at ca. 155 ppm, a position comparable to those of the phosphide resonances in the trans isomers of the electron-precise hydrides **2a**−**c**. The ^{1}H NMR spectra for compounds **4** exhibit in each case two cyclopentadienyl resonances, as expected, while the H atom of the formimidoyl ligand appears at ca. 4 ppm with a small P−H coupling (ca. 2 Hz). These chemical shifts are significantly lower than those found previ-

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[21] Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178−180*, 203.

[22] Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1997**, *36*, 896.

[23] (a) Feng, Q.; Ferrer, M.; Green, M. L. H.; McGowan, P. C.; Mountford, P.; Mtetwa, V. S. B. *J. Chem. Soc., Chem. Commun.* **1991**, 552. (b) Feng, Q.; Ferrer, M.; Green, M. L. H.; Mountford, P.; Mtetwa, V. S. B. *J. Chem. Soc., Dalton Trans.* **1992**, 1205.

[24] Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

[25] (a) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L.; Gavney, J. A., Jr. *J. Chem. Soc., Chem. Commun.* **1993**, 1692. (b) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L.; Hayasi, R. K.; Gavney, J. A., Jr. *Organometallics* **1994**, *13*, 4720.

[26] Beringhelli, T.; D'Alfonso, G.; Minoja, A.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1991**, *10*, 3131.

[27] Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Moret, M.; Sironi, A. *J. Organomet. Chem.* **1990**, *399*, 291.

[28] Hogarth, G.; Lavender, M. H.; Shukri, K. *Organometallics* **1995**, *14*, 2325.

[29] Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*, 2nd ed.; Methuen: London, 1958.

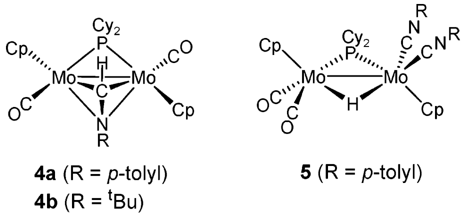
[30] Schollhammer, P.; Pichon, M.; Muir, K. W.; Pétillon, F. Y.; Pichon, R.; Talarmin, J. *Eur. J. Inorg. Chem.* **1999**, 221.

[31] Schollhammer, P.; Cabon, N.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Chem. Commun.* **2000**, 2137.

[32] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 3603.

[33] Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

Chart 4

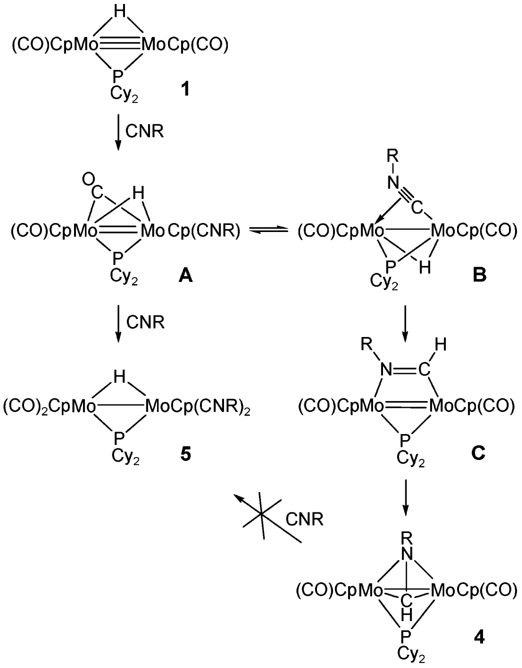


ously for compounds having 5e-donor (μ_3-η,κ:η,κ or μ_2-η,κ:η,κ)[22−26] or even 3e-donor (μ_2-η:κ)[5b,26,28,34] formimidoyl ligands, ranging from 7 to 11 ppm. In the aforementioned tantalum derivative having a μ_2-η,κ:η,κ-formimidoyl ligand, the corresponding proton resonance was not unambiguously assigned but was located in the aromatic region (7−9 ppm).[22] We interpret this spectroscopic feature of compounds **4** as an indication of strong coordination of the formimidoyl ligand, rendering a pseudotetrahedral environment (sp^3 hybridation) at the bridging C atom. In agreement with this, the ^{13}C NMR resonance for the formimidoyl CH atom appears quite shielded (δ ca. 60 ppm), in comparison to previously reported formimidoyl bridges: for example, ca. 155 ppm for the tricobalt clusters [$Co_3Cp^*_3(\mu$-H)(μ_3-HCNCR$_3$)] (R$_3$ = Me$_3$, Me$_2$Et).[25]

Spectroscopic Characterization of Compound 5. As mentioned above, compound **5** is obtained as a minor product in the reaction of the hydride **1** with *p*-tolyl isocyanide. The IR spectrum of **5** shows two pairs of stretching bands in the 2200−1600 cm^{-1} region. The weaker and more energetic bands at 2062 and 2034 cm^{-1} are due to the C−N stretches of the isocyanide ligands, whereas the intense bands at 1925 (s) and 1840 (vs) cm^{-1} clearly correspond mainly to the C−O stretches of the carbonyl ligands. The large separation (85 cm^{-1}) and relative intensities of the latter bands suggest that both CO ligands are bound to the same metal center. Although no suitable crystals of **5** could be grown to check the full conformational details, it is likely that the cyclopentadienyl ligands are placed in a transoid arrangement (Chart 4), as found for most complexes of the type [$M_2Cp_2(\mu$-H)(μ-PRR′)(CO)$_{4-n}$L$_n$] (M = Mo, W; L = 2e-donor ligand).[2,10] In agreement with this proposal, the ^{31}P NMR spectrum of **5** exhibits a resonance at 215.7 ppm, very close to the chemical shift measured for the parent tetracarbonyl [$Mo_2Cp_2(\mu$-H)(μ-PCy$_2$)(CO)$_4$] (218.8 ppm).[2] The ^{1}H spectrum of **5** displays two resonances for the inequivalent Cp groups, consistent with the presence of two isocyanide ligands bound to the same metal center. The hydride resonance appears as a doublet at −13.32 ppm, with relatively large P−H coupling (J_{PH} = 35 Hz), these data being similar to the corresponding data measured for the related complexes [$Mo_2Cp_2(\mu$-H)(μ-PRR′)(CO)$_3$L] (L = CO, P-donor ligand).[2,10] Unexpectedly, the inequivalent *p*-tolyl groups display just one methyl resonance, which could be due to an accidental degeneracy or to the presence of a fluxional process (not investigated) similar to those detected for the parent tetracarbonyls [$Mo_2Cp_2(\mu$-H)(μ-PRR′)(CO)$_4$].[2,10]

Reaction Pathways for the Isocyanide Addition to Compound 1. Compound **5** is the result of a double addition of the isocyanide ligand to the triply bonded hydride **1**, this leading to the full saturation of the dimetal center, as observed in the reaction with CO to give [$Mo_2Cp_2(\mu$-H)(μ-PCy$_2$)(CO)$_4$].[1] However, this obviously must occur in a stepwise manner and in competition with the main pathway, requiring just a single molecule of isocyanide and leading to the insertion products **4**. Although we have detected no intermediates in these reactions, we can rationalize the experimental results, as depicted in Scheme 2. The reaction would start with the coordination of a CNR molecule to one of the metal atoms, this possibly implying the displacement of a CO ligand into a bridging position, to yield the unsaturated intermediate **A** that might reach electronic saturation in two different ways. The obvious way would be the incorporation of a second molecule of ligand, to give the diisocyanide complex **5**. However, on the basis of the product distribution, we conclude that this is a slow process, at least at low ligand concentrations. Alternatively, intermediate **A** would reach electronic saturation by a change in the coordination of its isocyanide ligand, from the terminal to the σ,π-bonded bridging mode (**B**). This type of coordination has been observed as a result of the addition of isocyanides to the triply bonded complexes [$M_2Cp_2(CO)_2L_2$] (M = Mo, W; L$_2$ = (CO)$_2$,[35a] dppm,[35b,20b]) or to the unsaturated dihydrides [$Mn_2(\mu$-H)$_2$(CO)$_6$(μ-L$_2$)] (L$_2$ = dppm, tedip).[4a] Intermediate **B** now could experience more easily the migration of the hydride ligand to the isocyanide carbon atom (compared to a terminal ligand), to give the unsaturated intermediate **C** having a formimidoyl ligand coordinated in a 3e-donor (μ-η:κ) mode. The unsaturation of the metal center would now induce the final rearrangement of this ligand, to adopt the 5e-donor (μ-η,κ:η,κ) coordination mode that ensures the electronic saturation in the major products **4**. As for the structure of compound **5**, it should be noted that the second isocyanide molecule is incorporated at the metal center already having a coordinated isocyanide ligand, which is unexpected on steric grounds. The observed regioselectivity, then, can be interpreted as a thermodynamic preference that could be related to the principle of symbiosis.[36] We finally note that a separate experiment proved that **4b** does not react with a second equivalent of isocyanide under mild conditions, this

Scheme 2. Reaction Pathways Proposed for the Formation of Compounds 4 and 5



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[34] Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.

[35] (a) Curtis, M. D. *Polyhedron* **1987**, *6*, 759 and references therein. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L R.; Bois, C. *Organometallics* **1997**, *16*, 354.

[36] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper and Row: New York, 1993; Chapter 12, p 518.

showing the irreversible character of the insertion process leading to the formimidoyl complexes **4**.

Reaction of 1 toward Diazo Compounds and Organic Azides. The diazo compounds N_2CR_2 are well-known to be the precursors of "CR_2" fragments after dinitrogen elimination, being quite reactive toward unsaturated organic and organometallic compounds. In fact, addition of N_2CH_2 to unsaturated complexes having doubly bonded $M_2(\mu\text{-}H)_2$ units has been shown previously to result in the insertion of a methylene fragment into a M−H bond to give the corresponding alkyl-bridged "$M_2(\mu\text{-}H)(\mu\text{-}CH_3)$" derivatives, often exhibiting C−H−M agostic interactions.[6a,37] Surprisingly, the unsaturated hydride **1** seems to just induce the decomposition of the diazoalkanes N_2CHR (R = H, $SiMe_3$), since no new organometallic products were detected in these reactions, even when one of the expected products, the methyl complex $[Mo_2Cp_2(\mu\text{-}CH_3)(\mu\text{-}PCy_2)(CO)_2]$, has been previously prepared by us through an independent route and has a good thermal stability.[13]

Organic azides (RN_3) often undergo reactions with transition-metal complexes in which dinitrogen can be also extruded, thus yielding new imido (M−NR) derivatives.[38] However, the reactions with unsaturated hydride complexes can be more difficult to anticipate. For instance, the reactions of azides with the unsaturated triosmium cluster $[Os_3((\mu\text{-}H)_2(CO)_{10}]$ have been studied in detail and shown to yield μ_3-NR, μ_2-NHR, μ_2-κ^1:κ^1-HNNNR, or even μ_2-N═CHR′ derivatives, depending on the nature of the substituent R and reaction conditions.[3] Taking all these precedents into account, it was of interest to examine the behavior of the triply bonded hydride **1** toward an organic azide. In fact, compound **1** reacts smoothly (2.5 h) at room temperature with an excess of benzyl azide to give a mixture of two distinct products: the azavinylidene $[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$ (**6**) and the amido derivative $[Mo_2Cp_2\{\mu\text{-}NH(CH_2Ph)\}(\mu\text{-}PCy_2)(CO)_2]$ (**7**) (**6**/**7** = 2). During our attempts to find alternative routes to the above compounds and to better understand the reaction pathways under operation (see below), we found out that the above compounds could be also prepared by reaction of the azide with the unsaturated anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$, but now the relative proportions were dramatically reversed (**6**/**7** = 0.05). Both products could be isolated using low-temperature chromatographic techniques, and a separate experiment indicated that compound **7** in solution does not transform (by dehydrogenation) into **6** at room temperature or even in refluxing toluene, in which case only a generalized decomposition was observed.

Structural Characterization of Compounds 6 and 7. A single-crystal X-ray diffraction study was performed on compound **6**. The molecule displays two MoCp(CO) fragments in a transoid arrangement and bridging dicyclohexylphosphide and azabenzylidene ligands (Figure 3). The intermetallic distance is very short, 2.632(1) Å (Table 4), and therefore consistent with the formulation of a Mo═Mo double bond for this complex on the basis of the EAN rule. That intermetallic separation is even shorter than those measured in the related 32-electron complexes *trans*-$[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (2.716(1) Å)[33] and *trans*-$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(CN^tBu)_2]BF_4$ (2.6550(5) Å).[39] This shortening effect, however, can be attributed to the fact that nitrogen has a covalent radius smaller than those of carbon or phosphorus. As for the Mo−N distances, 2.062(6) and 2.084(6) Å, these are similar to those found for other dimolybdenum compounds having an azavinylidene bridge, in the range 2.03−2.12 Å.[30,31,40] The same applies to the C−N distance (1.278(9) Å), falling in the range observed for the mentioned compounds (1.23−1.38 Å) and being indicative of the presence of a double C═N bond, as expected. In agreement with this, the angles N(1)−C(13)−H(13) and N(1)−C(13)−C(14), 121.4(7) and 125.4(7)°, respectively, are very close to the theoretical 120° expected for an sp^2-hybridized C(13) atom, while the N(19), C(13), H(13), C(14), and Mo atoms are all essentially in the same plane. This imposes some steric pressure on the metal center, as the phenyl substituent at the azavinylidene carbon points toward the cyclopentadienyl ring on the Mo(2) atom. This is partially relieved by a slight rotation of that MoCp(CO) moiety, resulting in distinct CO environments, with the carbonyl on Mo(2) pointing away from the metal center (Mo−Mo−C = 94.9(2)°) and that on Mo(1) pointing toward the intermetallic region (Mo−Mo−C = 78.8(3)°).

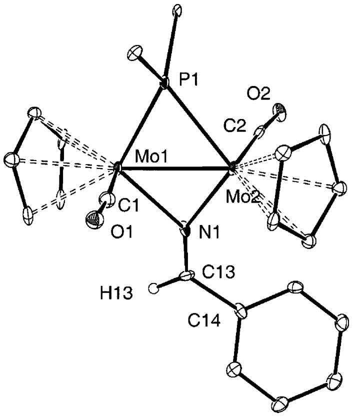

Figure 3. ORTEP diagram (30% probability) of compound **6**, with H atoms omitted, except the azavinylidene H atom, and Cy rings and ^{t}Bu groups omitted, except the corresponding C^1 atoms.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Mo(1)−Mo(2)	2.632(1)	Mo(1)−P(1)	2.380(2)
Mo(1)−N(1)	2.062(6)	Mo(2)−P(1)	2.388(2)
Mo(2)−N(1)	2.084(6)	Mo(1)−C(1)	1.925(9)
N(1)−C(13)	1.278(9)	Mo(2)−C(2)	1.949(9)
C(13)−H(13)	0.960(8)		
Mo(1)−N(1)−Mo(2)	78.8(2)	N(1)−C(13)−H(13)	121.4(8)
Mo(1)−P(1)−Mo(2)	67.02(6)	C(14)−C(13)−H(13)	113.0(7)
Mo(1)−N(1)−C(13)	134.6(6)	C(1)−Mo(1)−Mo(2)	78.8(3)
Mo(2)−N(1)−C(13)	146.5(6)	C(2)−Mo(2)−Mo(1)	94.9(2)
N(1)−C(13)−C(14)	125.4(7)		

The spectroscopic data in solution for compound **6** (Table 2 and Experimental Section) are fully consistent with its solid-state structure. First, the IR spectrum in CH_2Cl_2 shows two C−O stretching bands with the characteristic pattern of *trans*-dicarbonyls already found in compounds **2** and **4**. However, its ^{31}P NMR spectrum now displays a resonance considerably more shielded than those in the electron-precise complexes **2** and **4**. Actually, its chemical shift (125.4 ppm) falls in the range found for the related 32-electron compounds *trans*-$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}X)(CO)_2]$ (X = 3e-donor ligand),[2,13] all of them formally displaying a Mo═Mo double bond. The ^1H and ^{13}C NMR spectra of **6** confirm the absence of symmetry elements in the molecule derived from the presence of the rigid and intrinsically asymmetric azaphenylvinylidene ligand, this explaining the

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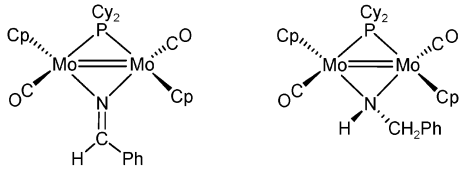
[37] (a) Beringhelli, T.; D'Alfonso, G.; Panigati, M.; Porta, F.; Mercandelli, P.; Moret, M.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 2307. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[38] Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

[39] Alvarez, C. M.; Alvarez, M. A.; Garcia, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2005**, *24*, 4122.

[40] (a) Cabon, N.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Dalton Trans.* **2004**, 2708. (b) Herrmann, W. A.; Bell, L. K.; Ziegler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39.

Chart 5



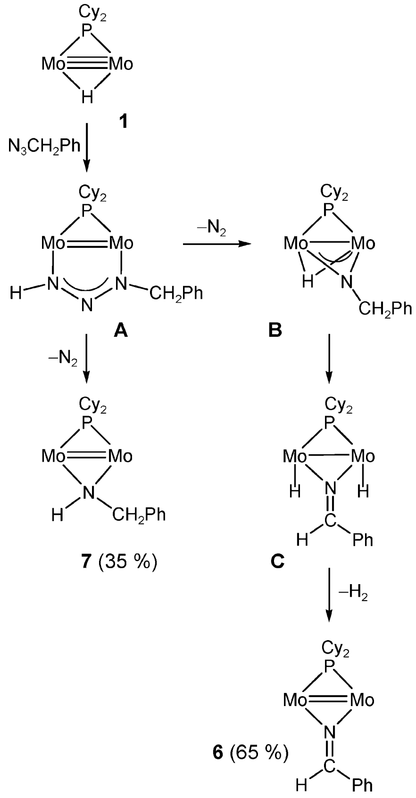
6 **7**

appearance of independent resonances for the Cp and carbonyl groups, and the presence of 12 ^{13}C cyclohexyl resonances. The azavinylidene ligand gives rise to highly deshielded ^{1}H (9.83 ppm) and ^{13}C NMR (168.7 ppm) resonances, both of them in the ranges expected for these sorts of ligands.[4a,41]

As for compound **7**, the spectroscopic data collected in solution are informative enough to support the proposed structure (Chart 5), even when no suitable crystals could be grown for an X-ray diffraction study. In fact, these data are very similar to those of **6** (Table 2 and Experimental Section) except for the nitrogenated ligand. Thus, a *trans*-dicarbonyl geometry and the presence of a 3e-donor bridge (in addition to the dicyclohexylphosphide bridge, then yielding a 32-electron count) is far from doubt. The presence of a benzylamido bridge is revealed by the appearance in the ^{1}H NMR spectrum of two resonances (4.95 and 3.64 ppm) corresponding to a pair of diastereotopic methylenic protons ($\mathrm{C}\mathit{H}_2\mathrm{Ph}$), and a third one, somewhat broad, corresponding to the N-bound proton (5.51 ppm). All other spectroscopic data are similar to those of **6** and then needs no further discussion.

Reaction Pathways in the Formation of Compounds 6 and 7. Although no intermediates were detected in the reactions leading to complexes **6** and **7**, the experimental data available and the studies previously carried out on the reactions of organic azides with unsaturated metal complexes allow us to make a reasonable proposal to explain the observed facts (Scheme 3). Most likely, the reaction of **1** with the azide starts with the coordination of the ligand to the dimetal center followed by rapid insertion in the Mo−H bond, to give an intermediate species with the bridging triazenido ligand μ-κ^1:κ^1-HNNNCH$_2$Ph (**A** in Scheme 3). Stable complexes of the latter type have been prepared by reaction of the unsaturated cluster $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ with alkyl azides.[42] At this stage, two distinct pathways must be proposed to account for the formation of compounds **6** and **7**. In the first place, intermediate **A** could spontaneously evolve N_2 with a simultaneous 1,3-H atom shift to give the amide complex **7.** This is remarkable, since the mentioned triazenido osmium complexes require prolonged heating at 85 °C to experience a similar denitrogenation reaction, which in that case yields μ_3-imido clusters.[42] However, in the case of azides having electron-withdrawing substituents, reactions with $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ yielded directly μ_2-amido complexes (no triazenido intermediates detected), although prolonged heating at 60 °C was still required. It seems therefore that compound **1** induces denitrogenation processes on the azide molecules more easily than the triosmium dihydride.

Scheme 3. Reaction Pathways Operative in the Reactions of 1 with PhCH$_2$N$_3$[a]



[a] Mo ≡ MoCp(CO).

Alternatively, denitrogenation of the intermediate **A** might occur with transfer of the H atom to the metal, to give the imido−hydride intermediate **B**. The latter could then evolve through a β-elimination of hydrogen from the benzyl group to give the dihydride derivative **C**, which, after an irreversible reductive elimination of dihydrogen, would give the azavinylidene **6**. The unstable nature of the electron-precise imido intermediate **B** is unexpected, both because it is an electron-precise complex and also because organic azides have been often used in the preparation of organometallic imido complexes. Very likely, the irreversible elimination of dihydrogen is the thermodynamic driving force for this reaction to proceed. The reaction of the unsaturated hydride **1** with benzyl azide seems to be the first example of a reaction of an organometallic compound with an azide to lead directly to an azavinylidene derivative. The closest precedent to this behavior is found in the triosmium azavinylidene $[\mathrm{Os_3}(\mu\text{-H})\{\mu\text{-N{=}C(CH_3)Ph}\}(\mathrm{CO})_{10}]$, formed by reaction of $[\mathrm{Os_3}(\mu\text{-H})_2(\mathrm{CO})_{10}]$ with $\mathrm{N_3C({=}CH_2)Ph}$ and further thermolysis of the corresponding triazenido derivative.[42] However, the mechanism in that case is different, since it does not involve the loss of hydrogen. In fact, the dehydrogenative route leading to **6** represents an unusual route to azavinylidene ligands, more commonly prepared by insertion of nitriles into M−H bonds[4a,5b,7h,40a,41b] or nucleophilic attack at coordinated nitriles.[30,31,40a] The chemical behavior of **1** toward organic azides is also different from that found for the unsaturated dimanganese complexes $[\mathrm{Mn_2}(\mu\text{-H})_2(\mathrm{CO})_6(\mu\text{-L}_2)]$, which react with $\mathrm{N_3SiMe_3}$ to yield the corresponding μ_2-azido derivatives,[4c] this implying the loss of H and $\mathrm{SiMe_3}$ radicals but no denitrogenation.

To account for the inverse product distribution found in the reactions of the anion $[\mathrm{Mo_2Cp_2}(\mu\text{-PCy_2})(\mu\text{-CO})_2]^-$ with benzyl azide in the presence of water, we must first note that no significant reaction takes place under rigorously anhydrous conditions and that the above anion does not react itself with water. Thus, we propose that the anion would be in a left-shifted equilibrium with two addition products, in which the azide

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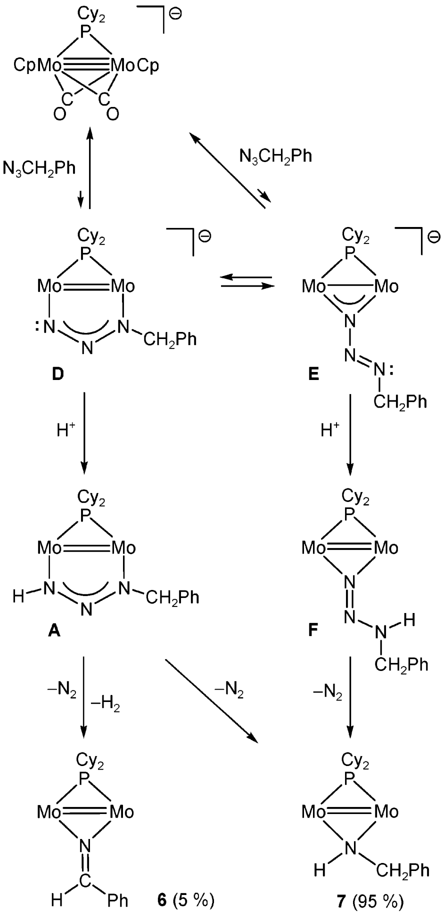
(41) See for example: (a) Dönnecke, D.; Halbauer, K.; Imhof, W. *J. Organomet. Chem.* **2004**, *689*, 2707. (b) Zippel, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429. (c) He, Z.; Neibecker, D.; Lugan, N.; Mathieu, R. *Organometallics* **1992**, *11*, 817.

(42) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2085.

Scheme 4. Reaction Pathways Operative in the Reactions of the Anion [$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2$]$^-$ with $PhCH_2N_3$ in the Presence of H_2O[a]



[a] Mo ≡ MoCp(CO), except for the starting complex.

molecule bridges the dimetal center through either two N atoms or just one N atom (**D** and **E** in Scheme 4). There are some precedents in support of these intermediates. For example, the anionic intermediates [$Fe_2(\mu\text{-}\kappa{:}\kappa\text{-}N_3Ar)(\mu\text{-}SR)(CO)_6$]$^-$ related to **D** have been proposed in the reactions of [$Fe_2(\mu\text{-}SR)(\mu\text{-}CO)(CO)_6$]$^-$ with ArN_3,[43] and there are also examples of dinuclear compounds having an azide ligand bridging the metal centers by only one N atom, as is the case for the stable complexes [$IrZrCpCp^*(\mu\text{-}N^tBu)(\mu\text{-}N_3Ph)$][44] and the dipalladium derivative [$Pd_2Cl_2(dppm)_2(\mu\text{-}\kappa^1\text{-}N_3SO_2Ar)$] (Ar = 2,4,6-$C_6H_2$-(^{i}Pr)$_3$).[45] The presence of water causes the reaction with our dimolybdenum anion to proceed rapidly. Thus, the next step would involve the protonation of intermediates **D** and **E** at N atoms. In the first case, the triazenido intermediate **A** would likely be obtained, identical with that formed from the hydride **1**. This intermediate, therefore, would evolve as discussed previously to give a mixture of compounds **6** and **7** in a 2:1 ratio. Since the experimental ratio of products in this reaction is 1:20, then this triazenido route must be of marginal significance. The dominant route, surely based on more favorable kinetics, would start with protonation at the γ-nitrogen of intermediate **E**, to give the aminodiazenide intermediate **F**, which, upon denitrogenation, would finally give the amido complex **7**. The γ-nitrogen atom of an N-bound organic azide is expected to be quite basic. In fact, in the reactions of the triply bonded [$Mo_2Cp_2(CO)_4$] with aryl azides, a second equivalent of azide binds to the dimetal center, as proposed for **E**, while its γ-nitrogen attacks the carbon atom of a CO ligand to finally give the dicarbonyl [$Mo_2Cp_2(CO)_2(NAr)\{\mu\text{-}\kappa{:}\kappa,\eta\text{-}N_3(CO)Ar\}$],[46] and a similar behavior was observed in the reactions of PhN_3 with the triosmium clusters [$Os_3(CO)_{10}(NCR)_2$] (R = Me, Ph).[47] In the case of intermediate **E**, this basicity must be even more pronounced due to its anionic nature.

Concluding Remarks. In this paper we have shown that the unsaturated hydride [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (**1**) does behave as a complex having a triple intermetallic bond, which is then able to incorporate 2e-donor atoms without compulsory opening of the hydride bridge, as illustrated by the reactions with the bidentate P-donors dppm, dmpm, and tedip. Transfer of the hydride atom to the entering molecule, however, can take place easily, as revealed by the reactions with isocyanides and benzyl azide. In the first case, the hydride transfer generates a formimidoyl ligand which adopts the unusual $\mu_2\text{-}\kappa,\eta{:}\kappa,\eta$ coordination mode (5e donor) in order to achieve the electronic saturation of the dimetal center. The behavior of **1** toward benzyl azide is different from that reported previously for other complexes having unsaturated $M_2(\mu\text{-}H)_x$ centers toward organic azides in two aspects. In the first place, loss of N_2 takes place much more easily at our dimolybdenum system, this occurring at room temperature. Moreover, dehydrogenation between the hydride and the benzyl substituent can also occur. It is proposed that loss of N_2 can take place in two different ways, one leading to the amido derivative [$Mo_2Cp_2\{\mu\text{-}NH(CH_2Ph)\}(\mu\text{-}PCy_2)(CO)_2$] and the other one leading, after dehydrogenation, to the azavinylidene complex [$Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2$].

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.[48] The compounds [$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2$]$^-$, ($Li^+$ salt) and [$Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2$] (**1**) were prepared as described previously,[13] 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 65−70 °C. Chromatographic separations were carried out using jacketed columns cooled by tap water. 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. IR stretching frequencies of CO ligands were measured either in solution (using CaF_2 windows) or in Nujol mulls (using NaCl windows) and are referred to as ν(CO). 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. In the NMR spectra, “fq” stands for “false quartet” and “*J*ap” stands for “apparent coupling constant”.

Reaction of Compound 1 with Bis(diphenylphosphino)methane (dppm). Compound **1** (0.040 g, 0.068 mmol) and dppm

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(43) Wang, Z.-X.; Miao, S.-B.; Zhou, Z.-Y.; Zhou, X.-G. *J. Organomet. Chem.* **2000**, *601*, 87.

(44) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 653.

(45) Besenyei, G.; Párkányi, L.; Foch, I.; Simándi, L. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 956.

(46) Curtis, M. D.; D’Errico, J. J.; Butler, W. M. *Organometallics* **1987**, *6*, 2151.

(47) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2119.

(48) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, U.K., 2003.

(0.029 g, 0.073 mmol) were stirred in CH_2Cl_2 (10 mL) for 2 h at room temperature to obtain an orange reddish solution. Solvent was then removed under vacuum, and the residue was extracted with dichloromethane−petroleum ether (1:4). The extracts were then chromatographed on an alumina column. Elution with the latter mixture gave an orange fraction yielding, after removal of solvents, the hydride complex $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_3(\kappa^1\text{-dppm})]$ (**3**) as an orange solid (0.006 g, 9%), shown (by NMR) to be an equilibrium mixture of the two isomers **D** and **E** (**D**/**E** = 7 at 290 K). Elution with dichloromethane−petroleum ether (1:1) gave another orange fraction, yielding, after removal of solvents, compound **2a** as an orange solid (0.053 g, 81%), also shown (by NMR) to be an equilibrium mixture of the two isomers **A** and **B** (**A**/**B** = 9 at 183 K). Compound **2a** can be also prepared quantitatively by carrying out the reaction in toluene (10 mL, 2 h) at room temperature; under these conditions, no traces of **3** were detected. Anal. Calcd for $C_{49}H_{55}Mo_2O_2P_3$ (**2a**): C, 61.26; H, 5.77. Found: C, 61.21; H, 6.11. Spectroscopic data for **2a** are as follows. $^{31}P\{^1H\}$ NMR: δ 162.0 (s, br, μ-PCy$_2$), 64.3 (s, br, 2P, μ-dppm). $^{31}P\{^1H\}$ NMR (162.00 MHz, 233 K): δ 161.4 (s, br, μ-PCy$_2$), 64.3 (s, br, 2P, μ-dppm). ^1H NMR: δ 7.70−6.90 (m, 20H, Ph), 4.57 (s, br, 10H, Cp), 3.53 (s, br, 2H, CH$_2$), 2.60−1.10 (m, 22H, Cy), −9.63 (s, br, 1H, μ-H). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 246.8 (m, CO), 143.1 (AA′X, $|J_{CP} + J_{CP'}| = 36$, C^1 Ph), 135.8 (AA′X, $|J_{CP} + J_{CP'}| = 45$, C^1 Ph), 134.9, 131.4 (2 × s, C^2 Ph), 130.2, 129.1 (2 × s, C^4 Ph), 128.4, 128.2 (2 × s, C^3 Ph), 88.8 (s, Cp), 52.3 (s, br, C^1-Cy), 40.1 (t, $J_{CP} = 23$, PCH$_2$), 36.7 (s, C^{2,6} Cy), 34.9 (d, $J_{CP} = 2.6$, C^{6,2} Cy), 29.4 (d, $J_{CP} = 10$, C^{3,5} Cy), 29.1 (d, $J_{CP} = 9$, C^{5,3}-Cy), 27.3 (s, C^4 Cy). Low-temperature data for **2a** are as follows. Isomer **A**: $^{31}P\{^1H\}$ NMR (162.00 MHz, 174 K) δ 162.9 (s, μ-PCy$_2$), 64.8 (s, br, 2P, μ-dppm); ^1H NMR (400.13 MHz, 183 K) δ 8.00−6.50 (m, Ph, 20H), 4.56 (s, 10H, Cp), 3.47 (s, br, 2H, CH$_2$), 3.00−1.00 (m, 22H, Cy), −9.92 (dt, $J_{PH} = 49$, 43, 1H, μ-H). Isomer **B**: $^{31}P\{^1H\}$ NMR (162.00 MHz, 198 K) δ 153.1 (s, br, μ-PCy$_2$), 70.6 (s, br, 1P, μ-dppm), 57.7 (s, br, 1P, μ-dppm); $^{31}P\{^1H\}$ NMR (162.00 MHz, 183 K) δ 153.1 (s, μ-PCy$_2$), 70.6 (d, $J_{PP} = 93$, 1P, μ-dppm), 57.5 (d, $J_{PP} = 93$, 1P, μ-dppm); ^1H NMR (400.13 MHz, 183 K) δ 4.79 (s, 5H, Cp), −8.78 (ddd, $J_{PH} = 35$, 48, 65, 1H, μ-H) ppm; other resonances for this isomer were masked by those of the major isomer. Spectroscopic data for **3** are as follows. Isomer **D**: $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ 196.5 (s, μ-PCy$_2$), 64.3 (d, $J_{PP} = 25$, Mo−*P*-C−P), −23.8 (d, $J_{PP} = 25$, Mo−P−C-*P*); ^1H NMR (C$_6$D$_6$) δ 8.15−6.80 (m, 20H, Ph), 4.60, 4.51 (2 × s, 2 × 5H, 2 × Cp), 3.62, (ABMX, $J_{HH} = 16$, $J_{PH} = 3$, 3, 1H, CH$_2$), 3.46 (ABMX, $J_{HH} = 16$, $J_{PH} = 9$, 0, 1H, CH$_2$), 3.10−0.90 (m, 22H, Cy), −12.29 (dd, $J_{PH} = 42$, 46, 1H, μ-H). Isomer **E**: ^1H NMR (C$_6$D$_6$) δ 4.79, 4.71 (2 × s, 2 × 5H, 2 × Cp), −11.95 (dd, J_{PH}= 39, 49, 1H, μ-H) ppm; other resonances for this isomer were masked by those of the major isomer.

Preparation of $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2(\mu\text{-dmpm})]$ (2b). Compound **1** (0.030 g, 0.052 mmol) and dmpm (12 μL, 0.074 mmol) were stirred in toluene (10 mL) for 2 min to obtain an orange solution. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (2 × 5 mL). Removal of solvents under vacuum gave compound **2b** (0.030 g, 81%) as an orange microcrystalline powder. Anal. Calcd for $C_{29}H_{47}Mo_2O_2P_3$: C, 48.89; H, 6.65. Found: C, 48.81; H, 6.31. $^{31}P\{^1H\}$ NMR (81.04 MHz): δ 160.9 (t, $J_{PP} = 10$, μ-PCy$_2$), 32.4 (d, $J_{PP} = 10$, 2P, μ-dmpm). ^1H NMR (200.13 MHz): δ 4.89 (d, $J_{PH} = 0.5$, 10H, Cp), 2.40−1.10 (m, 22H, Cy), 2.07 (t, $J_{PH} = 8$, 2H, CH$_2$), 1.57 (AA′X$_3$X′$_3$, $|J_{PH} + J_{P'H}| = 12$, 6H, CH$_3$), 1.42 (AA′X$_3$X′$_3$, $|J_{PH} + J_{P'H}| = 18$, 6H, CH$_3$), −11.49 (dt, $J_{PH} = 57$, 41, 1H, μ-H) ppm.

Preparation of $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_2(\mu\text{-tedip})]$ (2c). Compound **1** (0.033 g, 0.055 mmol) and tedip (15 μL, 0.061 mmol) were stirred in toluene (10 mL) for 5 min to obtain an orange reddish solution. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (3 mL) at 273 K to give compound **2c** as an orange solid (0.043 g, 93%), shown (by NMR) to be an equilibrium mixture of isomers **A**−**C** (**A**/**B** = 3 at 183 K, (**A** + **B**)/**C** = 20 at 290 K). The crystals of isomer **A** 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 $C_{32}H_{53}O_7P_3Mo_2$: C, 46.05; H, 6.40. Found: C, 45.55; H, 5.97. IR ν(CO) (Nujol mull/orange crystals of isomer **A**): 1824 (s), 1791 (vs, br) cm^{-1}. Spectroscopic data for isomers **A** and **B** are as follows. $^{31}P\{^1H\}$ NMR (C$_6$D$_6$, **A** and **B**): δ 180.3 (s, 2P, μ-tedip), 149.5 (s, μ-PCy$_2$) ppm. $^{31}P\{^1H\}$ NMR (290 K, **A** and **B**): δ 178.5 (s, br, 2P, μ-tedip), 149.8 (s, br, μ-PCy$_2$). $^{31}P\{^1H\}$ NMR (183 K, **A**:**B** ≈ 3): δ 185.6, 174.8 (2 × d, $J_{PP} \approx 95$, μ-tedip, **B**), 181.0 (s, 2P, μ-tedip, **A**), 156.5 (s, μ-PCy$_2$, **A**), 147.0 (s, μ-PCy$_2$, **B**). ^1H NMR (C$_6$D$_6$, **A** and **B**): δ 5.20 (s, 10H, Cp), 4.15−3.70 (m, 4 × 2H, OCH$_2$), 2.60−1.20 (m, 22H, Cy), 1.12 (t, $J_{PH} = 7$, 6H, CH$_3$), 1.04 (t, $J_{PH} = 7$, 6H, CH$_3$), −9.85 (dt, $J_{PH} = 62$, 50, μ-H, 1H) ppm. ^1H NMR (290 K, **A** and **B**): δ 5.02 (s, br, 10H, Cp), 4.20−3.80 (m, 4 × 2H, OCH$_2$), 2.60−1.20 (m, 22H, Cy), 1.33 (t, $J_{PH} = 7$, 6H, CH$_3$), 1.24 (t, $J_{PH} = 7$, 6H, CH$_3$), −10.25 (s, br, 1H, μ-H). ^1H NMR (223 K, **A** and **B**): δ 5.02 (s, 10H, Cp), −10.55 (dt, $J_{PH} = 59$, 48, 1H, μ-H). ^1H NMR (183 K): δ 5.16, (s, br, 5H, Cp, **B**), 4.99 (s, br, 10H, Cp, **A**), −10.74 (fq, $J_{PH} = 50$, 1H, μ-H, **A**). One cyclopentadienyl and the hydride resonance for isomer **B** were obscured by those of the major isomer. $^{13}C\{^1H\}$ NMR (298 K, **A** and **B**): δ 245.7 (AA′MX, fq, $J_{CP} = 13$, $|J_{CP} + J_{CP'}| = 25$, CO), 88.0 (s, Cp), 61.8 (AA′X, $|J_{CP} + J_{CP'}| = 10$, OCH$_2$), 61.3 (AA′X, $|J_{CP} + J_{CP'}| = 4$, OCH$_2$), 50.0 (d, $J_{CP} = 8$, C^1-Cy), 35.6 (d, $J_{CP} = 4$, C^{2,6}-Cy), 34.6 (d, $J_{CP} = 4$, C^{6,2} Cy), 29.1 (d, $J_{CP} = 11$, C^{3,5} Cy), 28.6 (d, $J_{CP} = 10$, C^{5,3} Cy), 27.0 (d, $J_{CP} = 2$, C^4 Cy), 16.4 (AA′X, $|J_{CP} + J_{CP'}| = 6$, CH$_3$), 16.1 (AA′X, $|J_{CP} + J_{CP'}| = 7$, CH$_3$). $^{13}C\{^1H\}$ NMR (183 K, Cp region): δ 89.6, 86.8 (2 × s, Cp, **B**), 88.0 (s, 2 × Cp, **A**) ppm. Spectroscopic data for isomer **C** are as follows. ^1H NMR: δ 4.94, (s, 10H, Cp), −12.58 (td, $J_{PH} = 41$, 34, 1H, μ-H); other resonances obscured by those of the major isomers. $^{31}P\{^1H\}$ NMR: δ 201.8 (s, μ-PCy$_2$), 186.5 (s, 2P, μ-tedip). $^{31}P\{^1H\}$ NMR (243 K): δ 201.9 (s, μ-PCy$_2$), 187.9 (s, 2P, μ-tedip).

Reaction of Compound 1 with *p*-Tolyl Isocyanide. Compound **1** (0.035 g, 0.061 mmol) was stirred with CN(*p*-tolyl) (1.5 mL of a 0.05 M solution in petroleum ether, 0.075 mmol) for 1 min in dichloromethane (10 mL) to give a yellow-orange solution. Solvent was then removed under vacuum, the residue extracted with dichloromethane−petroleum ether (1:4), and the extract chromatographed on an alumina column (activity IV). Elution with the latter mixture gave two yellow-orange fractions which gave, after removal of solvents, the compounds $[Mo_2Cp_2\{\mu\text{-HCN}(p\text{-tol})\}(\mu\text{-PCy}_2)(CO)_2]$ (**4a**, 0.032 g, 75%) and $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)\{CN(p\text{-tol})\}_2(CO)_2]$ (**5**, 0.004 g, 7%), respectively, both as yellow-orange solids. Spectroscopic data for **4a** are as follows. ^1H NMR: δ 6.91, 6.74 (AB, $J_{HH} = 8$, 4H, C$_6$H$_4$), 5.25, 5.06 (2 × s, 2 × 5H, Cp), 3.91 (d, $J_{PH} = 2$, 1H, CHN), 2.80−0.80 (m, Cy, 22H), 2.22 (s, CH$_3$, 3H). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 242.8 (d, $J_{CP} = 10$, CO), 238.2 (d, $J_{CP} = 8$, CO), 153.4 (s, C^1 *p*-tol), 132.7 (s, C^4 *p*-tol), 129.7 (s, C^2 *p*-tol), 123.4 (s, C^3 *p*-tol), 93.6, 89.1 (2 × s, Cp), 60.9 (d, $J_{CP} = 35$, CHN), 49.6 (d, $J_{CP} = 15$, C^1 Cy), 41.5 (d, $J_{CP} = 8$, C^1 Cy), 35.9, 35.4 (2 × s, C^{2,6} Cy), 34.4 (d, $J_{CP} = 4$, C^{2,6} Cy), 32.7 (s, C^{2,6} Cy), 28.8, 28.1 (2 × d, $J_{CP} = 11$, C^{3,5} Cy), 28.5 (d, $J_{CP} = 14$, C^{3,5}-Cy), 28.4 (d, $J_{CP} = 9$, C^{3,5} Cy), 26.8, 26.7 (2 × s, C^4 Cy), 20.9 (s, CH$_3$). Spectroscopic data for **5** are as follows. ^1H NMR (CDCl$_3$, 200.13 MHz): δ 7.17 (d, $J_{HH} = 8$, 2H, C$_6$H$_4$), 7.07 (d, $J_{HH} = 8$, 2H, C$_6$H$_4$), 5.33 (s, br, 5H, Cp), 5.24 (s, 5H, Cp), 2.50−1.00 (m, Cy, 22H), 2.37 (s, 6H, CH$_3$), −13.32 (d, $J_{PH} = 35$, 1H, μ-H).

Preparation of $[Mo_2Cp_2(\mu\text{-HCN}^t\text{Bu})(\mu\text{-PCy}_2)(CO)_2]$ (4b). Compound **1** (0.040 g, 0.069 mmol) in dichloromethane (10 mL) was stirred with CN^{t}Bu (1.5 mL of a 0.05 M solution in petroleum ether, 0.075 mmol) for 1 min to give a yellow solution. Solvent was then removed under vacuum, the residue dissolved in dichloromethane–petroleum ether (1:4), and this solution chromatographed on an alumina column (activity IV) at 15 °C. Elution with the same solvent mixture gave a yellow fraction. Removal of solvents from the latter fraction yielded compound **4b** as a yellow microcrystalline solid (0.042 g, 92%). The crystals used in the X-ray study were grown by slow diffusion of a layer of petroleum ether into a diethyl ether solution of the complex at 253 K. Anal. Calcd for $C_{29}H_{42}Mo_2NO_2P$: C, 52.81; H, 6.42; N, 2.12. Found: C, 52.24; H, 6.21; N, 1.90. ^1H NMR: δ 5.32, 5.27 (2 × s, 2 × 5H, Cp), 3.72 (d, J_{HP} = 1.5 Hz, 1H, HCN), 2.30–1.10 (m, 22H, Cy), 0.90 (s, 9H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 242.1 (d, J_{CP} = 9, CO), 238.2 (d, J_{CP} = 8, CO), 92.3, 88.2 (2 × s, Cp), 63.6 (d, J_{CP} = 33, HCN), 54.0 (s, C^1 ^{t}Bu), 49.3 (d, J_{CP} = 13, C^1- Cy), 44.8 (d, J_{CP} = 8, C^1 Cy), 35.9, 34.4, 33.6 (3 × s, $C^{2,6}$ Cy), 34.1 (d, J_{CP} = 4, $C^{2,6}$ Cy), 31.0 (s, C^2 ^{t}Bu), 28.9–28.1 (4 × d, $C^{3,5}$ Cy), 26.9, 26.6 (2 × s, C^4 Cy).

Reaction of Compound 1 with Benzyl Azide. Compound **1** (0.045 g, 0.078 mmol) and benzyl azide (60 μL, 0.45 mmol) were stirred in toluene (10 mL) for 2.5 h to obtain a dark green solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:9), and the extract was chromatographed on an alumina column (activity IV) at 233 K. Elution with the latter mixture gave two green fractions. Removal of solvents from the first fraction yielded $[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$ (**6**) as a green solid (0.032 g, 62%), and removal of solvents from the second fraction yielded $[Mo_2Cp_2(\mu\text{-}NHCH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$ (**7**), also as a green solid (0.017 g, 32%, see below). The crystals of compound **6** 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 $C_{31}H_{38}Mo_2NO_2P$: C, 54.80; H, 5.64; N, 2.06. Found: C, 54.46; H, 5.74; N, 1.94. ^1H NMR (400.13 MHz): δ 9.83 (s, 1H, CH), 7.60, 7.46, 7.27 (AA′BB′X, 5H, C_6H_5), 5.40 (s, 5H, Cp), 5.17 (d, J_{PH} = 0.5, 5H, Cp), 2.50–1.10 (m, Cy, 22H). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 253.1 (d, J_{PC} = 12, CO), 247.1 (d, J_{PC} = 14, CO), 168.7 (s, CH), 140.4 (s, C^1 Ph), 128.2, 127.3 (2 × s, $C^{2,3}$ Ph), 127.8 (s, C^4 Ph), 92.0, 91.5 (2 × s, Cp), 49.5 (d, J_{PC} = 20, C^1 Cy), 45.2 (d, J_{PC}= 18, C^1 Cy), 35.3 (d, J_{PC}= 2, $C^{2,6}$ Cy), 35.1 (s, $C^{2,6}$ Cy), 34.5 (d, J_{PC} = 4, $C^{2,6}$ Cy), 33.1 (s, $C^{2,6}$ Cy), 28.8–28.3 (4 × d, 4 × $C^{3,5}$ Cy), 26.7, 26.5 (2 × s, 2 × C^4 Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}NHCH_2Ph)(\mu\text{-}PCy_2)(CO)_2]$ (7). Distilled water (8 μL, 0.44 mmol) was added to a solution of the salt $Li[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]$ (ca. 0.05 mmol) and an excess of benzyl azide (50 μL, 0.37 mmol) in THF (10 mL). The mixture was stirred for 10 min to give a green brownish solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:9), and the extract was chromatographed on an alumina column (activity IV) at 233 K. Elution with the latter mixture gave a tiny pale green band containing a small amount of **6**, and then a green fraction. Removal of solvents from the latter fraction yielded compound **7** as a green solid (0.030 g, 88%). Anal. Calcd for $C_{31}H_{40}Mo_2NO_2P$: C, 54.63; H, 5.92; N, 2.06. Found: C, 54.31; H, 5.82; N, 1.99. ^1H NMR (400.13 MHz): δ 7.45–7.30 (m, 5H, C_6H_5), 5.51 (dd, br, J_{HH} = 5, 10, 1H, NH), 5.36 (s, 5H, Cp), 4.95 (dd, J_{HH} = 5, 13, 1H, CH), 4.84 (s, 5H, Cp), 3.64 (dd, J_{HH} = 10, 13, CH), 2.30–1.10 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 254.2 (d, J_{PC} = 14, CO), 251.7 (d, J_{PC} = 15, CO), 144.5 (s, C^1 Ph), 128.7 (s, $C^{2,3}$ Ph), 127.2 (s, C^4 Ph), 89.9, 89.8 (2 × s, Cp), 73.8 (d, J_{PC} = 8, CH_2), 48.1 (d, J_{PC} = 18, C^1 Cy), 46.1 (d, J_{PC} = 17, C^1 Cy), 34.7, 34.6 (2 × d, J_{PC} = 3, 2 × $C^{2,6}$ Cy), 34.6, 34.2 (2 × s, J_{PC} = 3, 2 × $C^{2,6}$ Cy), 28.8–28.4 (4 × d, 4 × $C^{3,5}$ Cy), 26.7 (s, 2 × C^4 Cy).

X-ray Structure Determination of Compound 2c. The X-ray intensity data for **2c** 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 of reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. The software SMART[49] 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,[49] and a multiscan absorption correction was applied with SADABS.[50] Using the program suite WinGX,[51] the structures were solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[52] A two-site disorder was found to be present in one of the ethoxy groups of the bridging ligand (C27 and C28); the occupancy factors given (0.65 and 0.35) provided satisfactory refinement. All non-hydrogen atoms were refined anisotropically, except those involved in the disorder, which were refined isotropically because they were persistently nonpositive definites. All hydrogen atoms were located in the Fourier map and refined, except those of the disordered ethoxy group, which were geometrically located. All of them were given an overall isotropic thermal parameter.

Table 5. Crystal Data for Compounds 2c and 6

	2c	6
mol formula	$C_{32}H_{53}Mo_2O_7P_3$	$C_{31}H_{38}Mo_2NO_2P$
mol wt	834.53	679.47
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
radiation (λ, Å)	0.710 73	0.710 73
a, Å	10.351(2)	9.270(2)
b, Å	10.879(2)	10.598(2)
c, Å	17.308(2)	28.384(5)
α, deg	91.151(2)	90
β, deg	98.372(2)	90
γ, deg	111.963(2)	90
V, Å^3	1782.4(4)	2788.3(9)
Z	2	4
calcd density, g cm^{-3}	1.555	1.619
abs coeff, mm^{-1}	0.882	0.986
temp, K	120	100
θ range, deg	2.03–28.33	1.43–26.45
index ranges (h, k, l)	−13, +13; −14, +14; −23, +23	−11, +11; 0, 13; 0, 35
no. of rflns collected	43 690	23 736
no. of indep rflns (R_{int})	8675 (0.0782)	5754 (0.0972)
no. of rflns with $I > 2\sigma(I)$	5937	4314
R indexes (data with $I > 2\sigma(I)$)[a]	R1 = 0.0414, wR2 = 0.0694[b]	R1 = 0.0560, wR2 = 0.1252[c]
R indexes (all data)[a]	R1 = 0.0871, wR2 = 0.0825[b]	R1 = 0.0820, wR2 = 0.1366[c]
GOF	1.109	0.996
no. of restraints/params	3/589	0/300
$\Delta\rho$(max, min), e Å^{-3}	0.877, −0.820	1.090, −1.597

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] a = 0.0000, b = 5.4849. [c] a = 0.0786, b = 0.0000.

X-ray Structure Determination of Compound 6. Collection of data, structure solution, and refinements were done as described for **2c**, except for the data collection temperature for **6** (100 K). All non-hydrogen atoms were refined by full-matrix least squares using anisotropic thermal parameters, except for C(1), O(1), C(3), and C(7) atoms, as their temperature factors were persistently nonpositive definites. All hydrogen atoms were fixed at calculated geometric positions in the last least-squares refinements, except for H(13), which was located in the Fourier map; however, fixing of the positional parameters for this atom was also necessary to obtain a convenient convergence. All hydrogen atoms were given an overall isotropic thermal parameter. Crystal data for **2c** and **6** are given in Table 5.

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

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

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

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

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Supporting Information Available: CIF files giving crystallographic data for the structural analysis of compounds **2c** and **6** and text and figures giving a more detailed discussion of the low-temperature spectra of compounds **2a** and **2c**, including the ^{31}P-{^{1}H} NMR spectra of **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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