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Migration and Insertion Processes in the Reactions of the Hydrocarbyl-Bridged Unsaturated Complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$ (R = Me, CH_2Ph, Ph) with CO and NO

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The alkyl-bridged unsaturated complexes $[Mo_2Cp_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$ (R = Me, CH_2Ph) react readily with CO (1 atm) at room temperature or below, but the products are strongly dependent on the alkyl bridge. Thus the benzyl complex **1b** is selectively carbonylated to give the hydride derivative $[Mo_2Cp(\eta^5\text{-}C_5H_4CH_2Ph)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ [Mo−Mo = 3.217(1) Å], whereas the methyl complex gives first the acetyl-bridged complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(CO)_3]$, which then evolves to give up to three different products depending on the reaction conditions: the hydrides $[Mo_2Cp(\eta^5\text{-}C_5H_4R')(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (R′ = Me, C(O)Me) and the heptacarbonyl complex $[Mo_2Cp(\mu\text{-}PCy_2)(CO)_7]$ (Mo−Mo = 3.2120(3) Å), the latter requiring the displacement of a Cp ligand. The phenyl-bridged complex $[Mo_2Cp_2(\mu\text{-}Ph)(\mu\text{-}PCy_2)(CO)_2]$ requires higher CO pressures (ca. 3 atm) and temperatures (ca. 333 K) to be carbonylated at a reasonable rate, then yielding a mixture of the corresponding hydride $[Mo_2Cp(\eta^5\text{-}C_5H_4Ph)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ and the above heptacarbonyl complex. The title complexes also react readily with NO (2000 ppm in N_2) at room temperature, but the products obtained, again, strongly depend on the starting substrate. The methyl-bridged complex gives a mixture of two dinitrosyl derivatives having terminal methyl ($[Mo_2Cp_2(Me)(\mu\text{-}PCy_2)(CO)(NO)_2]$, Mo−Mo = 3.074(1) Å) or bridging acetyl ($[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(NO)_2]$, Mo−Mo = 2.9931(6) Å) ligands. The benzyl complex gives the analogous benzyl derivative ($[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$, Mo−Mo = 3.0993(4) Å) as major product, along with small amounts of the dicarbonyl $[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)_2(NO)_2]$ and the trinitrosyl complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$, the formation of the latter requiring the displacement of the benzyl ligand. Finally, the phenyl-bridged complex gives again the analogous phenyl derivative $[Mo_2Cp_2(Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$, but small amounts of dinitrosyl derivatives having terminal benzoyl, $[Mo_2Cp_2\{C(O)Ph\}(\mu\text{-}PCy_2)(CO)(NO)_2]$, bridging benzoyl, $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Ph\}(\mu\text{-}PCy_2)(NO)_2]$, and bridging phenyl ($[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}Ph\}(\mu\text{-}PCy_2)(NO)_2]$, Mo−Mo = 2.9753(5) Å)) ligands are now formed. The latter complex can be selectively generated through the photochemical decarbonylation of the major phenyl complex. In contrast, separate experiments revealed that all hydrocarbyl complexes of the type $[Mo_2Cp_2(R)(\mu\text{-}PCy_2)(CO)(NO)_2]$ rearrange thermally at ca. 343 K into the corresponding acyl isomers $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)R\}(\mu\text{-}PCy_2)(NO)_2]$.

Introduction

Recently we reported the preparation and a complete study of the structure and bonding of the unsaturated alkyl-bridged complexes $[Mo_2Cp_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$ [R = Me (**1a**), CH_2Ph (**1b**)], this revealing that in the solid state the alkyl ligands are involved in a very weak α-agostic interaction with the dimetal center. This interaction is retained in solution, but there the agostic forms **A** probably coexist with small amounts of the nonagostic forms **B**, computed to be only slightly more energetic (Chart 1).[1] Although in the agostic form the alkyl ligand formally behaves as a three-electron donor, but does it as a one-electron donor in the nonagostic form, the weakness of the C−H···Mo interaction in the former structure for compounds **1a**,**b** probably renders almost equivalent degrees of real unsaturation in both situations. Beyond the above formalisms, the dimetal center in these species is highly unsaturated, and we can more precisely describe the intermetallic interaction as being mainly composed of a tricentric (Mo_2C) and two bicentric (Mo_2) bonding interactions, the latter being of σ and π types. The latter implies the presence of low-lying metal-based empty orbitals, which should make these molecules highly reactive, thus providing a unique

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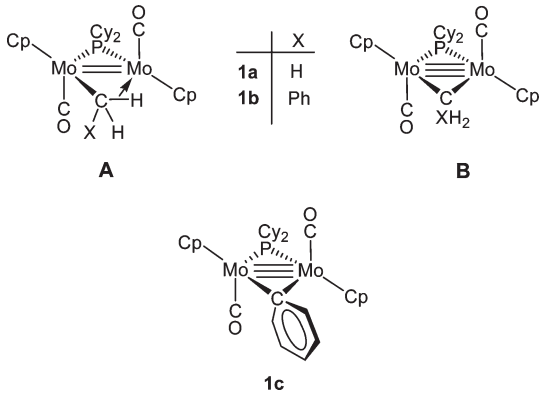
Chart 1



opportunity to examine at the molecular level the chemistry of bridging alkyl ligands at a highly unsaturated dimetal site. Alkyl-bridged complexes are species of general interest for several reasons: they serve as models both for intermediates in alkyl-transfer processes and for adsorbates in several heterogeneously catalyzed reactions such as the Fischer−Tropsch synthesis, and they are also implied as catalysts or precursors of the homogeneous catalysts used in the polymerization of olefins.[2,3] Although a large number of such binuclear complexes have been reported so far, only some of them display metal−metal bonds, these generally exhibiting an α-agostic interaction with one of the metal atoms. The reactivity reported so far for the alkyl bridges in the latter complexes includes the oxidative addition of the agostic C−H bond at trimetal centers,[4] rearrangement of the ligand to a terminal coordination mode,[5] deprotonation,[6] reductive elimination with other ligands,[7] and insertion of CO.[5b,c,8] Among all the alkyl-bridged complexes described so far, however, only a few of them display multiple intermetallic bonding,[9] and the reactivity of the latter unsaturated species has not been explored.

In a preliminary study on the chemical behavior of the methyl-bridged complex **1a** we found that, according to the expectations based on its electronic structure, this complex reacted readily with CO to remove both the agostic interaction and the multiple metal−metal bonding. However, an unexpected migration of the methyl ligand to yield methyl- and acetyl-substituted cyclopentadienyl ligands was also found to occur under mild conditions.[10] These are very unusual transformations; actually, the only close migratory transformations we can quote are the thermal decompositions above 373 K of the complexes $[MCpR(CO)_3]$ (M = Mo or W, R = Et, Ph, CH_2Ph) to give hexacarbonyl dimers of the type $[M_2Cp_2(CO)_6]$ having one or two η^5-C_5H_4R ligands.[11] Thus, we decided to study in more detail this migratory behavior at our unsaturated dimolybdenum centers. In this paper we report our full results on the reactions of the methyl- and benzyl-bridged complexes **1a**,**b** with CO and with NO. To check the influence of the agostic C−H···Mo interactions on the observed reactivity, we have also studied the phenyl-bridged complex $[Mo_2Cp_2(\mu\text{-R})(\mu\text{-PCy}_2)(CO)_2]$ (**1c**), a molecule having no agostic interactions with the metal center (Chart 1).[1a] As it will be shown below, the reactivity toward CO and NO of the agostic complexes **1a**,**b** is not very different from that of the nonagostic **1c**, and in all cases it involves easy migration of the hydrocarbyl ligand up to the cyclopentadienyl groups (carbonylation reactions), apart from other expected results, such as the disappearance of the agostic interactions and multiple metal−metal bonding.

Results and Discussion

Carbonylation of Compounds 1. The unsaturated complexes $[Mo_2Cp_2(\mu\text{-R})(\mu\text{-PCy}_2)(CO)_2]$ (**1a**−**c**) react readily with CO, but the products are strongly dependent on the hydrocarbyl bridge. Besides this, in no instance could the simple addition derivative of type $[Mo_2Cp_2(R)(\mu\text{-PCy}_2)(CO)_4]$ be obtained or even detected.

The benzyl complex **1b** reacts with CO (1 atm) at room temperature to give the hydride derivative $[Mo_2Cp(\eta^5\text{-}C_5H_4CH_2Ph)(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$ (**3b**), this implying a formal exchange between the benzyl ligand and a cyclopentadienylic hydrogen atom. In contrast, the methyl complex **1a** reacts with CO under comparable conditions to give a mixture of the acetyl-bridged complex $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-C(O)Me}\}(\mu\text{-PCy}_2)(CO)_3]$ (**2**), the methylcyclopentadienyl hydride complex $[Mo_2Cp(\eta^5\text{-}C_5H_4Me)(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$ (**3a**), the heptacarbonyl $[Mo_2Cp(\mu\text{-PCy}_2)(CO)_7]$ (**4**), and the acetylcyclopentadienyl hydride $[Mo_2Cp\{\eta^5\text{-}C_5H_4C(O)Me\}(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$ (**5**) (Chart 2), with their relative amounts being strongly dependent upon experimental conditions. Several separated experiments revealed that the acetyl-bridged complex **2** is the main precursor to all other species **3**−**5**. Thus, when **1a** is reacted with CO at 273 K for 5 h, complex **2** is obtained as the almost unique product. Compound **2**, in turn, can be transformed selectively into its isomer **3a** by just storing it in the solid state for 15 days.

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

compound	ν(X−O)[a]	δ(P)[b]
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(CO)_3]$ (**2**)[c]	1919 (s), 1864 (vs), 1816 (m, sh), 1583 (w)[c]	261.3,[d] 215.5,[d]
$[Mo_2Cp(\eta^5\text{-}C_5H_4Me)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**3a**)	1953 (m, sh), 1924 (vs), 1852 (s)	220.7[e]
$[Mo_2Cp(\eta^5\text{-}C_5H_4CH_2Ph)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**3b**)	1943 (m, sh), 1925 (vs), 1853 (s)	221.1
$[Mo_2Cp(\eta^5\text{-}C_5H_4Ph)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**3c**)	1943 (m, sh), 1926 (vs), 1854 (s)	229.5[e]
$[Mo_2Cp(\mu\text{-}PCy_2)(CO)_7]$ (**4**)	2067 (s), 1989 (w, sh), 1956 (vs), 1923 (s), 1856 (m)	259.9[e]
$[Mo_2Cp\{\eta^5\text{-}C_5H_4C(O)Me\}(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**5**)	1950 (m, sh), 1933 (vs), 1864 (s), 1678 (w)	224.6[e]
$[Mo_2Cp_2(Me)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6a**)	1972 (s), 1632 (s),[f] 1572 (vs)[f]	214.7
$[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6b**)	1977 (vs), 1636 (s),[f] 1570 (s)[f]	212.3
$[Mo_2Cp_2(Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6c**)	1979 (vs), 1635 (s),[f] 1579 (s)[f]	221.7
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(NO)_2]$ (**7a**)	1610 (m, sh),[f] 1578 (vs)[f]	224.7
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)CH_2Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**7b**)	1612 (m, sh),[f] 1578 (vs)[f]	224.9
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**7c**)	1614 (m, sh),[f] 1579 (vs)[f]	224.5[e]
$[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)_2(NO)_2]$ (**8**)	1906 (w), 1819 (vs), 1749 (m),[f] 1661(s)[f]	54.1[g]
$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ (**9**)	1589 (vs),[h] 1420 (m)[h]	219.4
$[Mo_2Cp_2\{C(O)Ph\}(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**10**)[i]	1980 (vs), 1640 (s),[f] 1576 (s)[f]	213.8[e]
$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**11**)	1612 (vs),[f] 1551 (w)[f]	224.9

[a] Recorded in dichloromethane solution, ν in cm^{-1}; X = C, N. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 (^{31}P) MHz, δ in ppm relative to external 85% aqueous H_3PO_4 (^{31}P). [c] *cis* and *trans* isomers coexist in solution. [d] Resonances for the averaged *cis* and *trans* isomers, recorded in toluene-d_8 at 290 K. When recorded at 213 K, four resonances, at 260.4 (*cis*-**2A**), 247.0 (*cis*-**2B**), 217.4 (*trans*-**2A**), and 211.5 (*trans*-**2B**), are observed. [e] Recorded in $CDCl_3$. [f] ν(N−O). [g] Recorded at 233 K. [h] Recorded in KBr disk. [i] Data estimated from the spectra of mixtures of compounds **7c** and **10**.

Chart 2

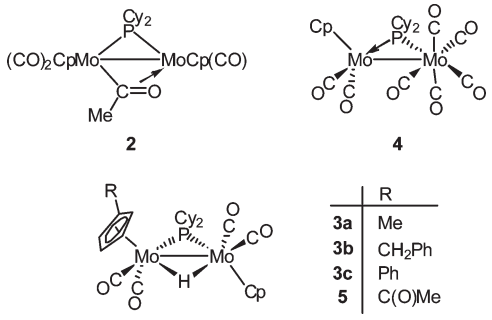
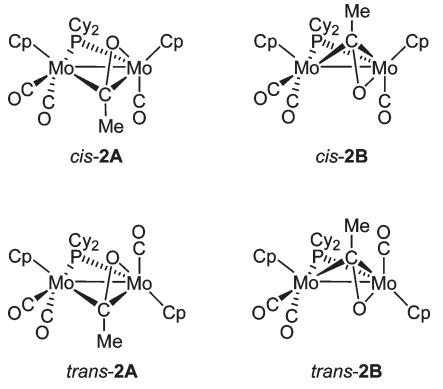


Chart 3



However, if a toluene solution of **2** is reacted with CO at room temperature, then the major species formed is the complex **5**, along with smaller amounts of compounds **3a** and **4**. Finally, an increase of the CO pressure (to ca. 3 atm) or the temperature in the above experiment causes a significant increase in the relative amount of the heptacarbonyl complex **4**.

The phenyl-bridged complex **1c** is less reactive toward CO (compared to the alkyl complexes **1a**,**b**) since it requires higher CO pressures (ca. 3 atm) and temperatures (ca. 333 K) to be carbonylated at a reasonable rate. Under these conditions, a mixture of the corresponding phenylcyclopentadienyl hydride $[Mo_2Cp(\eta^5\text{-}C_5H_4Ph)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (**3c**) and the heptacarbonyl complex **4** is obtained.

Solution Structure of the Tricarbonyl 2. The IR spectrum of **2** exhibits three strong to medium bands in the C−O stretching region of the carbonyl ligands (Table 1) and a weaker band at 1583 cm^{-1}, which is assigned to the C−O stretch of the acyl group. The relative intensities of the carbonyl bands are different from those computed using DFT methods for either the *cis* or the *trans* isomers of the isoelectronic carbyne complex $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_3]$,[12] but they can be interpreted as arising from a mixture of both types of isomers in similar amount. Actually, the NMR data to be discussed below indicate the presence of four interconverting isomers in solution for compound **2** (Chart 3).

The room-temperature ^1H NMR spectra of **2** suggest the presence of only two species in solution, with their relative proportion being solvent-dependent (1:1 in CD_2Cl_2; 2:1 in toluene-d_8) and both having separated resonances for the cyclopentadienyl ligands, as expected, while the high chemical shift of the methyl resonance (ca. 2.8 ppm in CD_2Cl_2) is consistent with the migration of the methyl ligand to a carbonyl, to yield an acetyl group. These isomers give rise to very differently deshielded ^{31}P NMR resonances, at 261 (major isomer in toluene) and 215 ppm (minor isomer). The chemical shift of the major isomer is similar to those of the isoelectronic tricarbonyl alkenyl complexes $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}HCC(p\text{-tol})H\}(\mu\text{-}PCy_2)(CO)_3]$ (δ_P = 251.2 ppm)[13a] and $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}HCCH_2\}(\mu\text{-}PCy_2)(CO)_3]$ (δ_P = 250.5 ppm),[13b] these complexes displaying a *cisoid* arrangement of the Cp ligands with respect to the average Mo_2P plane.[13b] Therefore, we identify the major isomer in **2** as that having a *cisoid* arrangement of the Cp ligands, and therefore assign the more shielded resonance to the corresponding *trans* isomer.

The room-temperature ^{31}P resonances of **2** are broad, but on lowering the temperature, they eventually split into two new ones with distinct intensities in each case (see Experimental Section), with their relative proportions being also solvent-dependent. We identify these resonances as arising from the four possible isomers derived from the different orientations of the bridging acyl ligand, assumed to have an alkenyl-like coordination geometry, as found for the dinitrosyl complex **7a** to be discussed later on. We have labeled in each case the major isomer as **A**, but the association of these

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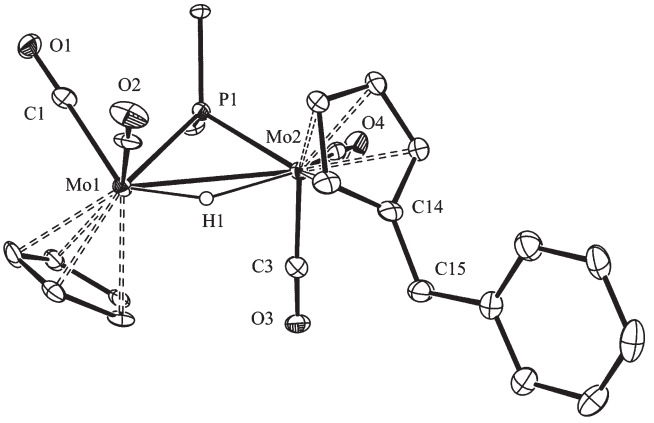

Figure 1. ORTEP diagram (30% probability) of compound **3b**, with Cy rings (except the C1 atoms) and H atoms (except the hydride ligand) omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3b

Mo(1)−Mo(2)	3.2172(8)	Mo(1)−P(1)−Mo(2)	82.0(1)
Mo(1)−P(1)	2.448(2)	Mo(1)−H(1)−Mo(2)	127(2)
Mo(2)−P(1)	2.454(2)	H(1)−Mo(1)−P(1)	77(2)
Mo(1)−H(1)	1.70(6)	H(1)−Mo(2)−P(1)	74(2)
Mo(2)−H(1)	1.90(6)	P(1)−Mo(1)−C(1)	75.0(2)
Mo(1)−C(1)	1.961(7)	P(1)−Mo(1)−C(2)	103.4(2)
Mo(1)−C(2)	1.950(7)	P(1)−Mo(2)−C(3)	102.7(2)
Mo(2)−C(3)	1.941(7)	P(1)−Mo(2)−C(4)	75.1(2)
Mo(2)−C(4)	1.971(7)		
C(14)−C(15)	1.491(9)		

isomers with the drawings in Chart 3 within each pair is arbitrary.

The $^{13}C\{^1H\}$ NMR spectrum for the absolute major isomer *cis*-**2A** displays a highly deshielded acyl resonance at 276 ppm, a chemical shift similar to those in complexes of the type $[MoCp\{C(O)R\}(CO)_2(PR'_3)]$.[14] Moreover, the carbonyl ligands give rise to three distinct resonances, with chemical shifts and P−C couplings comparable to those of the isoelectronic *cis*-$[Mo_2Cp_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(CO)_3]$[12] and *cis*-$[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-HCCRH}\}(\mu\text{-PCy}_2)(CO)_3]$.[13]

Solid-State and Solution Structure of Compounds 3 and 5. The molecule of compound **3b** (Figure 1 and Table 2) is built up from two $MoCp(CO)_2$ fragments placed in a *transoid* arrangement and bridged by phosphide and hydride ligands. This structure is comparable to those most commonly found for phosphide-hydride complexes of the type $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$[15,16] and thus needs no detailed comments. The most relevant feature is the presence of the benzyl group as a substituent in one cyclopentadienyl ring, with the corresponding C(14)−C(15) length of 1.493(9) Å being as expected for a single bond between sp^2 and sp^3 carbon atoms.[17]

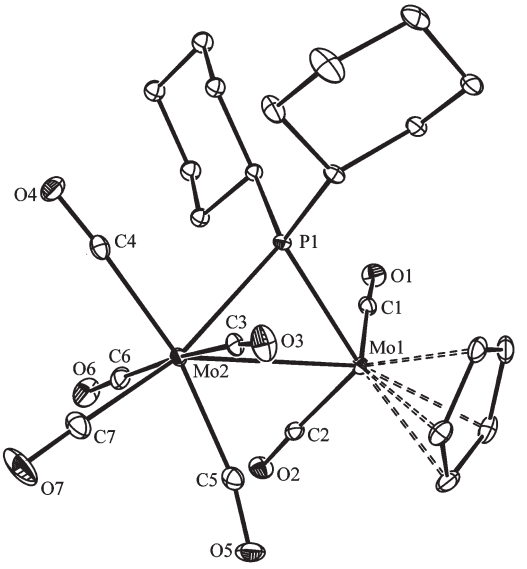

Figure 2. ORTEP diagram (30% probability) of compound **4** with H atoms omitted for clarity.

Spectroscopic data in solution for compounds **3** and **5** (Table 1 and Experimental Section) are similar to each other and comparable to those of similar complexes of the type $[M_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$ (M = Mo, W),[15,16,18,19] thus needing no detailed comments. We only note that, because of the presence of a substituent in one of the Cp rings and the asymmetry of the corresponding Mo center, all four CH groups in the substituted Cp ring are inequivalent and give rise to separated ^1H and ^{13}C NMR resonances. The same applies to the ^{13}C NMR resonances of the carbonyl ligands, which give rise to two doublets (C *cis* to P) and two singlets (C *trans* to P) as a result of their distinct P−C couplings. This is a well-known trend for mononuclear carbonyl complexes of the type $[MCpX(CO)_2(PR_3)]$ (M = Mo, W; X = halogen, alkyl, hydride, etc.), which systematically exhibit higher absolute values of J_{CP} for carbonyl ligands *cis* to the P atoms.[20] In the case of compound **5**, the presence of the acetyl group is revealed by the appearance of an IR band at 1678 cm^{-1} and of a quite deshielded $^{13}C\{^1H\}$ NMR resonance at 195.8 ppm, both of them in the usual region of acetyl substituents in organic compounds.

Solid-State and Solution Structure of Compound 4. The molecule of this heptacarbonyl complex (Figure 2 and Table 3) displays $Mo(CO)_5$ and $MoCp(CO)_2$ fragments bridged by a PCy_2 ligand. The first fragment adopts a pseudooctahedral geometry, with the sixth coordination position roughly pointing to the midpoint of the Mo(1)−P(1) bond, while the $MoCp(CO)_2$ fragment exhibits the common geometry found in complex **3b** and related species. The

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(16) (a) Petersen, J. L.; Dahl, L. F.; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *95*, 6610. (b) Jones, R. A.; Schawab, S. T.; Stuart, A. L.; Whittlesey, B. R.; Wright, T. C. *Polyhedron* **1985**, *4*, 1689. (c) Bridgeman, A. J.; Mays, M. J.; Woods, A. D. *Organometallics* **2001**, *20*, 2076.

(17) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993.

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(20) (a) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125. (b) Todd, L. J.; Wilkinson, J. L.; Hickley, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 4

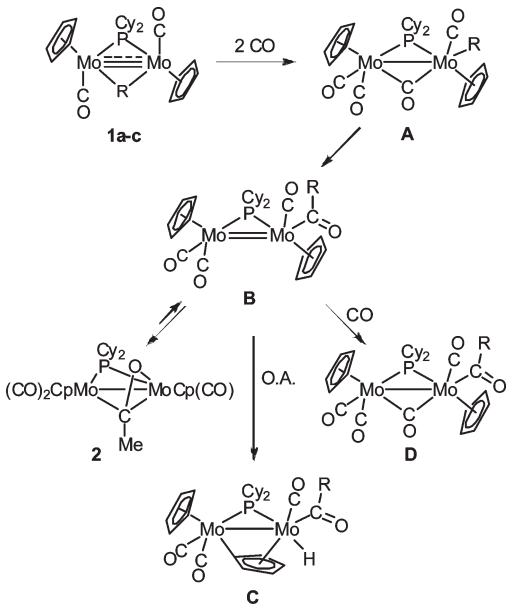
Mo(1)−Mo(2)	3.2120(3)	Mo(1)−P(1)−Mo(2)	80.9(1)
Mo(1)−P(1)	2.3964(6)	P(1)−Mo(1)−C(1)	82.1(1)
Mo(2)−P(1)	2.5520(6)	P(1)−Mo(1)−C(2)	110.1(1)
Mo(1)−C(1)	1.941(3)	P(1)−Mo(2)−C(7)	164.8(1)
Mo(1)−C(2)	1.967(3)	P(1)−Mo(2)−C(3)	88.3(1)
Mo(2)−C(3)	2.048(3)	P(1)−Mo(2)−C(6)	97.4(1)
Mo(2)−C(4)	2.065(3)	P(1)−Mo(2)−C(4)	80.8(1)
Mo(2)−C(5)	2.047(3)	P(1)−Mo(2)−C(5)	111.5(1)
Mo(2)−C(6)	2.068(3)	Mo(2)−Mo(1)−C(1)	117.4(1)
Mo(2)−C(7)	2.014(3)	Mo(2)−Mo(1)−C(2)	82.0(1)

intermetallic length in **4** (3.2120(3) Å) is comparable to that in **3b** and therefore consistent with the formulation of a single Mo−Mo bond for this molecule. Incidentally, this also implies that tricentric Mo_2H bonds (like those in the hydrides **3** and **5**) are not particularly elongated when compared to related bicentric Mo_2 bonds in this sort of complex. We finally note the strongly asymmetric coordination of the phosphide ligand, ca. 0.15 Å closer to the MoCp fragment, thus justifying an extreme description of the corresponding Mo−P bonds as of the single (P−Mo(2) = 2.5520(6) Å) and donor (P→Mo(1) = 2.3964(6) Å) types.

The spectroscopic data in solution for **4** (Table 1 and Experimental Section) are in full agreement with the structure found in the crystal. Thus its IR spectrum exhibits five C−O stretching bands, with the three most energetic bands being characteristic of $Mo(CO)_5$ fragments.[21] The $^{13}C\{^1H\}$ NMR spectra, however, reveal the presence of dynamic effects in solution, since at room temperature they exhibit only four different carbonyl resonances. The two more deshielded resonances [241.0 (d, J_{CP} = 22) and 234.7 ppm (s)] have chemical shifts and P−C couplings comparable to those observed for the hydride compounds **3** and **5** and are thus safely assigned to the $MoCp(CO)_2$ fragment. The most shielded resonance (209.1 ppm, J_{CP} = 14) can be assigned to the carbonyl *trans* to phosphorus in the $Mo(CO)_5$ fragment, by comparison with the data of compounds of the type $[Mo(CO)_5(PR_3)]$.[22] Finally, the intense resonance at 210.1 ppm must correspond to the average resonance of the four equatorial carbonyls of the $Mo(CO)_5$ fragment. Indeed, on lowering the temperature, this resonance eventually splits into four different resonances. A rotational movement of the $Mo(CO)_5$ fragment around the Mo−CO(axial) axis can easily account for this positional exchange.

Reaction Pathways in the Carbonylation of Compounds 1. The reactions of compounds **1a−c** with CO share many common features and are thus likely to proceed through analogous pathways, even if not all possible compounds have been identified for all three starting substrates. For instance, the acyl intermediate **2** has been detected only in the reactions of the methyl complex, although it is likely to be formed also for the benzyl and phenyl complexes, whereas the heptacarbonyl compound **4** is formed in significant amounts only for the methyl and phenyl complexes, in the latter case surely because of the more forcing conditions necessary to take the reaction to completion in a reasonable time. Notably, in all cases the activation of a C−H bond of a cyclopentadienyl ligand, as required to form complexes **3** and **5**, is the prevalent process, even under the mild reaction conditions being used. In previous work on the activation of Cp ligands at Mo_2 and W_2 substrates we have shown that the coordinative unsaturation of the dimetal center can induce reversible oxidative addition of the cyclopentadienyl C−H bonds to give hydride cyclopentadienylidene derivatives.[23] As shown below, we can propose sensible elemental steps that can lead to the coordinative situation in which the necessary C−H bond cleavage step can take place.

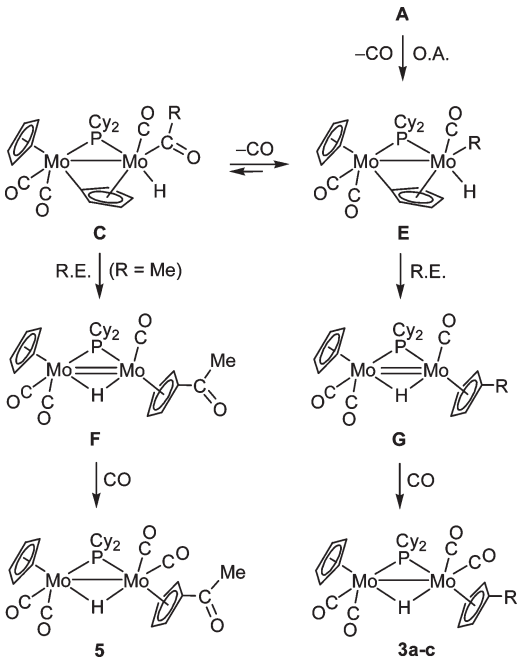
Scheme 1. Initial Reaction Pathways in the Carbonylation of Compounds 1a−c (O.A. = oxidative addition)



By considering the unsaturation of the complexes **1a−c**, it is very likely that the reaction is initiated by a rapid uptake of two CO molecules to give an electron-precise tetracarbonyl intermediate **A** having a terminal hydrocarbyl ligand (Scheme 1), thus paralleling the carbonylation reaction of the isoelectronic stannyl-bridged complex $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}SnPh_3)(CO)_2]$.[24] The intermediates **A** could next evolve by insertion of CO in the Mo−C(hydrocarbyl) bond at the more crowded Mo center, to give the acyl derivatives **B**. This is a well-known reaction of mononuclear alkyl and aryl carbonyl complexes of the transition metals.[25] The intermediates **B**, however, are electronically and coordinatively unsaturated, and they would then evolve at least in three different ways. In the absence of additional CO, this unsaturation might be removed in two ways: either by rearrangement of the acyl ligand, from terminal to a bridging position, to give compound **2** (the fastest process for the methyl complex), or through the oxidative addition of a C−H bond of a Cp ligand, to give the corresponding hydride cyclopentadienylidene intermediates **C** (not detected), thus paralleling the formation of the hydride complexes $[M_2Cp(\mu\text{-}\kappa^1\text{:}\eta^5\text{-}C_5H_4)(\mu\text{-}H)(CO)_3(\mu\text{-}A_2PXPA_2)]$ (M = Mo, W; X = CH_2, O; A = Ph, OEt).[23a] In the presence of enough CO, however, the intermediates **B** would just evolve to give the electron-precise intermediates **D**, thought to be the precursors of the heptacarbonyl complex **4**, as discussed below.

(21) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, U.K., 1975.
(22) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, U.K., 1981.
(23) (a) Alvarez, M. A.; Alvarez, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 2581, and references therein. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1324.
(24) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2006**, *25*, 5374.
(25) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John Wiley & Sons: New York, 1994.

Scheme 2. Proposed Reaction Pathways to the Hydride Complexes 3a and 5 (R.E. = reductive elimination)

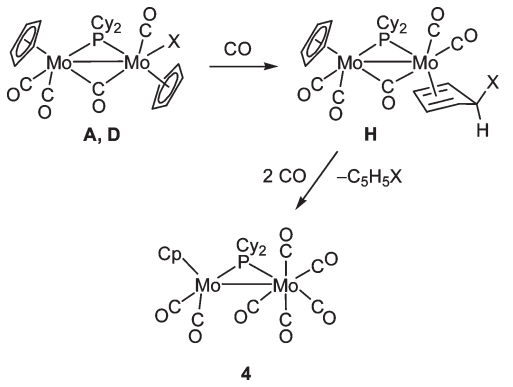


The formation of compound **5** can be justified as a result of a reductive elimination between the acyl and cyclopentadienylidene ligands in the intermediate **C** when R = Me, this giving first an unsaturated tricarbonyl intermediate **F** that would finally accept another CO molecule (Scheme 2). The formation of compounds **3a**−**c** might proceed analogously, but requires a deinsertion process of CO from **C** to give a related complex **E** having an hydrocarbyl (instead of acyl) terminal ligand. This is not unlikely, because the carbonylation of alkyl or aryl complexes to give the corresponding acyl derivatives is often a reversible process.[25] Additionally, we cannot exclude that the intermediates **E** would directly come from **A** after decarbonylation and C−H bond cleavage steps.

Finally, the formation of the heptacarbonyl **4**, which is favored under pressure of CO, can be rationalized as a further reaction of the corresponding intermediates **A** or **D** with CO (Scheme 3), this forcing the migration of the hydrocarbyl or acyl groups to the Cp ligand to give pentacarbonyl intermediates **H** having a η^4-cyclopentadiene ligand, which would finally be displaced by two additional CO molecules to give compound **4**. Although the migration of an alkyl or aryl ligand to a metal-bound Cp ligand is a rare process, it has been observed occasionally. For instance, the phenyl complex $[VCp_2Ph]$ reacts in this way with CO to give the phenylcyclopentadiene derivative $[VCp(\eta^4\text{-}C_5H_5Ph)(CO)_2]$, although the related methyl and benzyl complexes give only the more common acyl derivatives $[VCp_2\{C(O)R\}(CO)]$.[26]

Reactions of Compounds 1a−c with NO. Nitrogen monoxide is a remarkable molecule able to strongly bind to transition metal atoms in both high and low oxidation states,

Scheme 3. Proposed Reaction Pathway Leading to Compound 4 (X = R, C(O)Me)



thus giving rise to a wide variety of coordination and organometallic complexes exhibiting a rich chemistry.[27,28] It was thus expected that NO would readily react with the unsaturated complexes **1a**−**c** under mild conditions, although, this ligand being an odd-electron molecule, different insertion or migration processes of the hydrocarbyl groups might be thus induced.

Diluted NO (2000 ppm in N_2) is indeed able to react smoothly with the methyl complex **1a** in toluene at room temperature to give a 1:2 mixture of two dinitrosyl derivatives, the methyl complex $[Mo_2Cp_2(CH_3)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6a**) and its acyl-bridged isomer $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(NO)_2]$ (**7a**). Under similar conditions, the benzyl complex **1b** gives the benzyl derivative $[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6b**) as major product, along with small amounts of the dicarbonyl $[Mo_2Cp_2(CH_2Ph)(\mu\text{-}PCy_2)(CO)_2(NO)_2]$ (**8**) and the trinitrosyl $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}NO)(NO)_2]$ (**9**) (Chart 4). Finally, the phenyl-bridged complex gives again the hydrocarbyl derivative $[Mo_2Cp_2(Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6c**) as major product, but now small amounts are obtained of dinitrosyl derivatives having terminal benzoyl, $[Mo_2Cp_2\{C(O)CPh\}(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**10**), bridging benzoyl, $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**7c**), or bridging phenyl ligands, $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**11**) (Chart 4). The latter can be selectively generated through the photochemical decarbonylation of the major product **6c** (Scheme 4). In contrast, separated experiments revealed that all hydrocarbyl complexes of type **6** rearrange thermally at ca. 343 K into the corresponding acyl-bridged isomers **7**. We note that the benzoyl complex **10** can be decarbonylated thermally or photochemically to give the benzoyl-bridged derivative **7c**, but the latter does not transform into **11** even after extended photolysis. Thus it seems that, once formed, the benzoyl ligands in these dinitrosyl substrates do not experience deinsertion of CO easily.

Solid-State and Solution Structure of Compounds 6. The molecular structures of **6a** and **6b** (Figures 3 and 4, and Table 4) are similar to each other and display *transoid* MoCp(R)(NO) and MoCp(CO)(NO) fragments bridged by a PCy_2 ligand. The intermetallic separations of ca. 3.07 and 3.10 Å, respectively, are consistent with the formulation of single metal−metal bonds for these 34-electron complexes and are comparable to that measured in the related dinitrosyl complex $[Mo_2Cp^*_2(\mu\text{-}PHPh)_2(NO)_2]$ [3.099(2) Å],[29] as they are the M−N and N−O bond lengths. The phosphide ligand

(26) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 516.

(27) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., 1992.

(28) (a) Hayton, T. W.; Legzdins, P.; Sharp, W. B. *Chem. Rev.* **2002**, *102*, 935. (b) Ford, P. C.; Lorkovic, I. M. *Chem. Rev.* **2002**, *102*, 993. (c) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293. (d) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(29) Legzdins, P.; Ross, K. J.; Sayers, S. F.; Rettig, S. J. *Organometallics* **1997**, *16*, 190.

Scheme 4. Thermal and Photochemical Evolution of Compounds 6

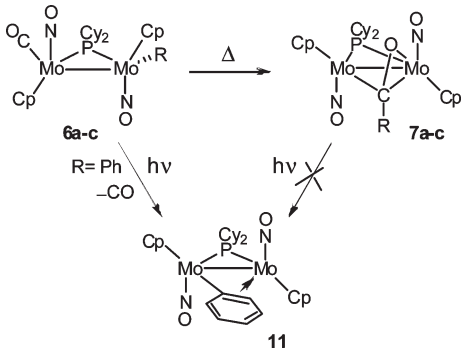
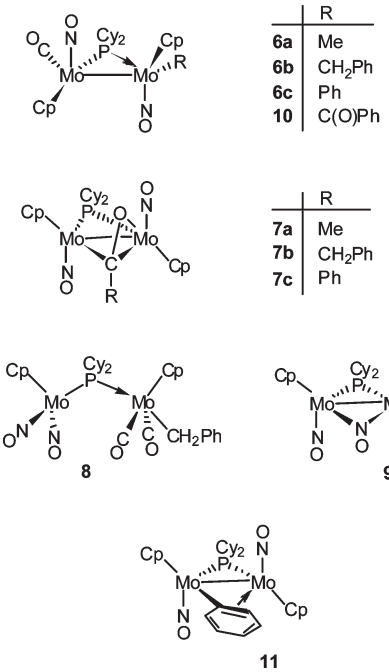


Chart 4



is expectedly bound in a significantly asymmetric way, closer (by ca. 0.1 Å) to the electron-poorer metal atom, so we might again represent the corresponding interactions as single (P−Mo ca. 2.50 Å) and donor (P→Mo ca. 2.40 Å) bonds, thus achieving an 18-electron configuration at each metal center. The hydrocarbyl ligands display Mo−C lengths of 2.205(8) and 2.272(3) Å, respectively, which suggest a strong binding of these groups to the metal atoms since, for instance, the methyl complexes of the type $[MoL(CO)_3Me]$ (L = substituted η^5-Cp ligand) display Mo−C lengths of ca. 2.30 Å.[30]

The spectroscopic data in solution for compounds **6a−c** (Table 1 and Experimental Section) are similar to each other and consistent with the structures just discussed. They all exhibit a strong C−O stretching band at ca. 1975 cm^{-1} in the region of terminal carbonyls and two strong bands at ca. 1635 and 1575 cm^{-1}, consistent with the presence of two terminal nitrosyl ligands in each case. The fact that the relative intensities of both N−O stretching bands are similar in all cases is somewhat unexpected considering that the relative positioning of these ligands is of a *transoid* type, but this can be attributed to the coupling of the C−O and N−O stretches, with it increasing the intensity of the symmetrical stretch.

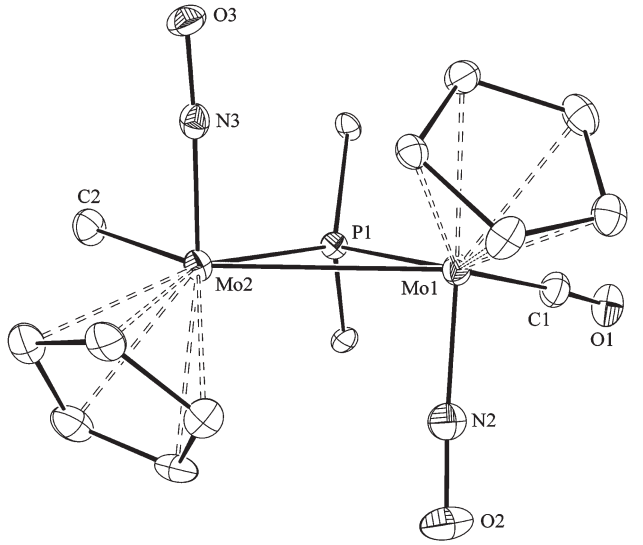


Figure 3. ORTEP diagram (30% probability) of compound **6a**, with Cy rings (except the C1 atoms) and H atoms omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

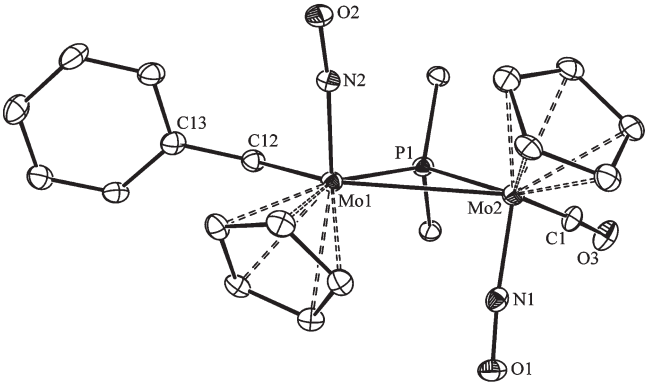
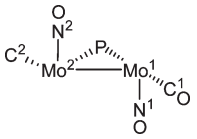


Figure 4. ORTEP diagram (30% probability) of compound **6b**, with Cy rings (except the C1 atoms) and H atoms omitted for clarity.

The $^{31}P\{^1H\}$ NMR spectra of compounds **6** display a resonance at ca. 215 ppm, not far from those of the hydrides **3** and all other complexes with a single metal−metal bond reported in this work (Table 1). The ^1H and ^{13}C NMR spectra display the expected resonances derived from the presence of inequivalent Cp and Cy groups, in addition to those corresponding to the metal-bound hydrocarbyl group in each case and deserve no special comments. We note only that the phenyl complex **6c** gives rise to five (^1H) and six (^{13}C) different resonances in the normal aromatic region. From this we conclude that there is a severe steric crowding in the molecule preventing the Ph ring from free rotation around the Mo−C bond. In line with this, an inspection of the crystal structure of compounds **6a** and **6b** reveals a close proximity between some of the methyl (or benzyl) and cyclohexyl H atoms.

(30) (a) Zhao, J.; Santos, A. M.; Herdtweck, E.; Kühn, F. E. *J. Mol. Catal. A* **2004**, *222*, 265. (b) Körnich, J.; Haubold, S.; He, J.; Reimelt, O.; Heck, J. *J. Organomet. Chem.* **1999**, *584*, 329. (c) El Mouatassim, B.; Elamouri, H.; Vaissermann, J.; Jaouen, G. *Organometallics* **1995**, *14*, 3296. (d) Rogers, R. D.; Atwood, J. L.; Rausch, M. D.; Macomber, D. W. *J. Chem. Crystallogr.* **1990**, *20*, 555.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 6a and 6b



	6a	6b
Mo(1)−Mo(2)	3.074(1)	3.0993(4)
Mo(1)−P	2.502(2)	2.513(1)
Mo(2)−P	2.401(2)	2.402(1)
Mo(1)−N(1)	1.794(6)	1.797(3)
Mo(2)−N(2)	1.760(6)	1.775(3)
Mo(1)−C(1)	1.991(7)	1.976(4)
Mo(2)−C(2)	2.205(8)	2.272(3)
Mo(1)−P−Mo(2)	77.6(1)	78.2(1)
Mo(1)−Mo(2)−N(2)	89.8(2)	94.3(1)
Mo(1)−Mo(2)−C(2)	136.7(2)	133.8(1)
Mo(2)−Mo(1)−N(1)	87.4(2)	85.3(1)
Mo(2)−Mo(1)−C(1)	126.2(2)	122.9(1)
P−Mo(1)−C(1)	78.0(2)	76.8(1)
P−Mo(1)−N(1)	97.9(2)	99.8(1)
P−Mo(2)−C(2)	84.5(2)	81.3(1)
P−Mo(2)−N(2)	96.1(2)	97.5(1)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 7a

Mo(1)−Mo(2)	2.9931(6)	Mo(1)−P(1)−Mo(2)	75.6(1)
Mo(1)−P(1)	2.473(1)	Mo(1)−Mo(2)−N(2)	116.2(2)
Mo(2)−P(1)	2.411(1)	Mo(2)−Mo(1)−N(1)	87.3(1)
Mo(1)−N(1)	1.775(5)	Mo(1)−N(1)−O(1)	169.7(4)
Mo(2)−N(2)	1.770(5)	Mo(2)−N(2)−O(2)	173.4(5)
Mo(1)−C(1)	2.345(5)	Mo(1)−O(3)−C(1)	82.9(3)
Mo(1)−O(3)	2.111(3)	Mo(2)−C(1)−O(3)	120.5(4)
Mo(2)−C(1)	2.068(5)	Mo(2)−C(1)−C(2)	124.6(4)
C(1)−O(3)	1.313(6)	O(3)−C(1)−C(2)	114.6(5)
N(1)−O(1)	1.219(6)	P(1)−Mo(1)−C(1)	89.3(1)
N(2)−O(2)	1.216(6)	P(1)−Mo(2)−C(1)	98.0(1)
C(1)−C(2)	1.512(8)		

Solid-State and Solution Structure of Compounds 7. The molecular structure of the acetyl-bridged complex **7a** (Figure 5 and Table 5) exhibits two MoCp(NO) fragments arranged in a *transoid* manner and bridged by phosphide and acyl ligands. The intermetallic length of 2.9931(6) Å is shorter than that in **6** yet consistent with the formulation of a single bond for this 34-electron complex. The acyl ligand bridges the dimetal center in an alkenyl-like (κ^1:η^2) mode characterized by relatively short Mo−C(bridgehead) distances to *both* metal atoms.[13] Thus the Mo(2)−C(1) distance of 2.068(5) Å is substantially shorter than those in "normal" terminal acyl complexes (ca. 2.26 Å for compounds of the type [MoCp{C(O)R}(CO)$_2$(PR$_3$)]),[14b,c] while the Mo(1)−C(1) length of 2.345(1) Å is only slightly longer than these reference values. On the other hand, the C(1)−O(3) length of 1.313(6) Å has a value intermediate between the reference values for double and single C−O bonds involving sp^2 carbon atoms (cf. 1.19 Å for aldehydes and 1.33 Å for enols),[31] but closer to the upper limit, thus suggesting a strong π-coordination of the double C═O bond to the Mo(1) atom. We note that the alkenyl-like coordination of the acyl ligand in **7a** is very different from that of the acyl ligands obtained by CO insertion in agostic methyl ligands bridging late transition metals, usually adopting a κ^1:κ^1 coordination mode, which leaves the O atom within the M$_2$C plane.[8a] In contrast, the O atom of the acyl ligand in **7a** is well above the Mo$_2$C plane, and this in fact causes a significant distortion in the nitrosyl ligands, with one of them pointing away from the dimetal center, surely to avoid unfavorable repulsions with the methyl group (Mo−Mo−NO = 113.2(2)°), while the second nitrosyl remains almost normal to the intermetallic vector (Mo−Mo−NO = 87.3(1)°).

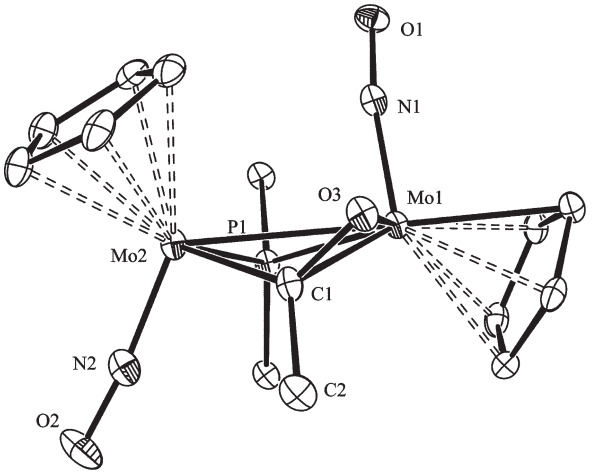


Figure 5. ORTEP diagram (30% probability) of compound **7a**, with Cy rings (except the C1 atoms) and H atoms omitted for clarity.

The spectroscopic data in solution for compounds **7a**−**c** (Table 1 and Experimental Section) are similar to each other and consistent with the solid-state structure of **7a** just discussed. The IR spectra of these complexes exhibit N−O stretching bands at ca. 1610 and 1580 cm^{-1} with medium and strong intensities, respectively, thus indicating the retention in solution of the *transoid* arrangement of the nitrosyl ligands. The ^{1}H NMR spectra exhibit two cyclopentadienyl resonances in each case, as expected, and the methyl resonance of **7a** appears at 2.65 ppm, a chemical shift comparable to that in compound **2**. Finally, the acyl group gives rise in all cases to a characteristically deshielded ^{13}C NMR resonance at ca. 270 ppm, a chemical shift also comparable to that of the corresponding resonance in the acetyl-bridged complex **2** (276.0 ppm for the isomer *cis*-**2A**).

Solution Structure of Compounds 8−10. The IR spectrum of compound **8** exhibits two C−O stretching bands of weak and strong intensities at 1906 and 1819 cm^{-1} and two N−O stretching bands of medium and strong intensities at 1749 and 1661 cm^{-1}, respectively (Table 1). The C−O bands are comparable to those of *trans*-dicarbonyl complexes of the type [MoCp(R)(CO)$_2$(PR$_3$)],[32] whereas the N−O bands are similar to those exhibited by the mononuclear complexes [MoCp(NO)$_2$X] (X = Me, Et, Ph, iBu, Cl).[33] In addition, the phosphide ligand gives rise to an abnormally shielded resonance at 54.1 ppm, an effect observed for dialkyl- and diarylphosphide ligands bridging metal atoms without metal−metal bonds.[34] All this strongly supports the formulation

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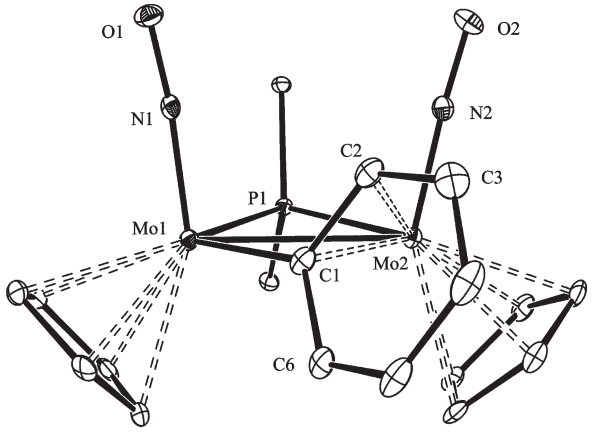


Figure 6. ORTEP diagram (30% probability) of compound **11**, with Cy rings (except the C1 atoms) and H atoms omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

of **8** as made up of a *trans*-$MoCp(CH_2Ph)(CO)_2(PCy_2)$ fragment bound through its P atom to a $MoCp(NO)_2$ fragment (Chart 4). In agreement with this, the CO ligands and the CH_2 protons of the benzyl group give rise to a single NMR resonance in each case.

When recorded in dichloromethane solution, the IR spectrum of compound **9** displays two bands, at 1625 and 1587 cm^{-1}, of weak and strong intensities, respectively, these being comparable to those of compounds **7** and therefore suggestive of the presence of two terminal nitrosyls in a *transoid* arrangement. In addition, a third band at lower frequency (1420 cm^{-1}) can be detected when recording the IR spectrum in a KBr disk, which indicates the presence of a bridging nitrosyl ligand.[35] Moreover, the inequivalence of the diastereotopic pairs of cyclohexyl carbon atoms gives an independent confirmation of the *transoid* arrangement of the MoCp(NO) fragments of the molecule. Finally, a mass spectrum showed the molecular ion, thus providing further support for the composition proposed for this compound.

As for compound **10** we note that, although we were not able to isolate it as a pure material, the available spectroscopic data for this complex suggest a structure comparable to those of the carbonyldinitrosyl complexes **6**, but having a terminal benzoyl ligand. This is confirmed by the appearance of a strongly deshielded resonance at 278.9 ppm in its ^{13}C NMR spectrum, which can be safely assigned to the metal-bound carbon atom.

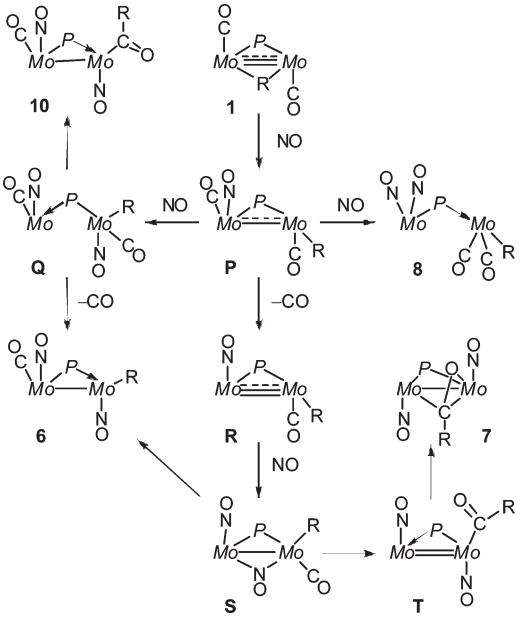
Solid-State and Solution Structure of Compound 11. The crystals of the phenyl-bridged complex **11** have two independent molecules in the unit cell with comparable geometries (Figure 6 and Table 6). This complex exhibits two MoCp(NO) fragments in an almost eclipsed conformation and bridged by PCy_2 and phenyl ligands. The nitrosyl ligands are almost parallel to each other and essentially perpendicular to the Mo_2P plane, and the intermetallic lengths of 2.9753(5) and 3.0403(5) Å in the two independent molecules are comparable to those measured in compounds **6a**,**b** or **7a** and consistent with the formulation of a single Mo−Mo bond for this molecule. This requires the phenyl ligand to be acting as a three-electron donor group, which is consistent with its coordination to the dimetal center, that being of the alkenyl (μ-κ^1:η^2) type, so that the *ipso* carbon of the ring is strongly bound to one molybdenum atom (Mo(1)−C(1) = 2.150(4) Å in the molecule of Figure 6), while the *ipso* and *ortho* carbons are involved in a π-bonding interaction with the second Mo atom (Mo(2)−C(1) = 2.372(4) and Mo(2)−C(2) = 2.514(2) Å). As a result, the bond involved in this interaction (C(1)−C(2) = 1.423(6) Å) is elongated with respect to the reference values of unperturbed aromatic rings (ca. 1.37 Å). A comparable effect has been found in the heterometallic complex [$RuIrCp^*_2(\mu$-H)(μ-κ^1:η^2-Ph)(μ-PPh_2)] (C−C = 1.404(8) Å).[36] We also note that the π-bonding interaction with the metal has a localizing effect of the π-bonding within the aromatic ring (short−long sequence in the C−C lengths), with a maximum difference of ca. 0.07 Å for adjacent C−C bonds.

The spectroscopic data in solution for **11** are consistent with the retention of the solid-state structure also in solution. Thus its IR spectrum exhibits two N−O stretching bands at 1612 and 1551 cm^{-1}, with strong and weak intensities, respectively, which is indicative of a *cisoid* arrangement of the nitrosyl ligands in solution. As for the phenyl ligand, it

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound 11

Mo(1)−Mo(2)	2.9753(5)	Mo(1)−P(1)−Mo(2)	75.9(1)
Mo(1)−P(1)	2.395(1)	N(1)−Mo(1)−Mo(2)	97.4(1)
Mo(2)−P(1)	2.441(1)	N(2)−Mo(2)−Mo(1)	103.8(1)
Mo(1)−C(1)	2.150(4)	Mo(1)−C(1)−Mo(2)	82.1(1)
Mo(2)−C(1)	2.372(4)	Mo(1)−C(1)−C(2)	121.9(3)
Mo(2)−C(2)	2.514(4)	C(2)−C(1)−C(6)	113.7(4)
Mo(1)−N(1)	1.773(3)	Mo(1)−N(1)−O(1)	173.7(3)
Mo(2)−N(2)	1.780(3)	Mo(2)−N(2)−O(2)	176.2(3)
C(1)−C(2)	1.423(6)	P(1)−Mo(1)−C(1)	104.8(1)
C(2)−C(3)	1.424(6)	P(1)−Mo(2)−C(2)	112.7(1)
C(3)−C(4)	1.368(6)		
C(4)−C(5)	1.416(6)		
C(5)−C(6)	1.369(6)		
C(6)−C(1)	1.442(5)		

Scheme 5. Reaction Pathways in the Nitrosylation of Compounds 1a−c (*Mo* = MoCp; *P* = PCy_2)



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exhibits five inequivalent proton resonances, with one of them being considerably shielded (5.95 ppm), which is consistent with the π-coordination of the *ipso* and *ortho* carbons of the ring to the second metal atom. We note that this shielding is also characteristic of μ-κ^1:η^2-alkenyl ligands[13] and that a similar shielding was observed in the spectrum of the above phenyl-bridged RuIr complex when recorded in THF-d_8 solution at 153 K. This heterometallic complex also exhibited rapid rotation of the phenyl ring at room temperature involving the exchange between coordinated and uncoordinated *ortho* positions. In the case of compound **11** this does not take place at a significant rate even at room temperature. However, another dynamic process must necessarily occur, since the Cp ligands give rise to a single resonance at 5.14 ppm in spite of their inequivalence. Although we have not investigated this in detail, it is very likely that the phenyl ring experiences a fast movement similar to the windshield wiper movement characteristic of μ-κ^1:η^2-alkenyl ligands, first proposed by Shapley et al.[13a,37] This movement would render equivalent environments for both molybdenum centers while maintaining the individual chemical environments of each carbon and hydrogen site of the phenyl ring.

Pathways in the Nitrosylation Reactions of Compounds 1a−c. The reactions of the unsaturated compounds **1** with NO are of only moderate selectivity, although they bear some analogies. Moreover, even when some of the products are related by decarbonylation or isomerization processes actually occurring at ca. 343 K (i.e., **10** → **7c** or **6a−c** → **7a−c**) or under photochemical activation (i.e., **6c** → **11**), the very fact that they all are formed at room temperature indicates that there are separated pathways leading to each of them. Besides this, we can guess that some of these products might be formed through more than a single pathway. Thus we will not attempt to justify the different products formed in each case, but just outline sensible steps accounting for their presence in the corresponding reaction mixtures (Scheme 5).

The coordination of the first NO molecule to the unsaturated complexes **1** would generate an unstable paramagnetic intermediate **P** rapidly reacting with a second NO molecule to remove its unpaired electron. This is a well-known behavior of mononuclear organometallic radicals,[38] and we have shown previously that binuclear radicals like the neutral $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$[39] or the cationic ones $[Mo_2Cp_2(\mu\text{-}A_2PXPA_2)(\mu\text{-}CO)_2(CO)_2]^+$ also react rapidly with NO under mild conditions.[40] The second NO molecule should preferably bind the more deficient MoR(CO) center, but this would force the insertion or removal of CO in order to reduce the subsequent steric crowding at that metal center in the resulting intermediate **Q**: insertion of CO into the Mo−R bond would give compound **10**, whereas decarbonylation would lead to compounds **6**. On the other hand, the alternative coordination of the second NO molecule to the Mo(NO)(CO) fragment would at least force a shift of the carbonyl ligand to the other metal center, thus leading to compounds like **8**, only formed for the benzyl substrate, perhaps for steric reasons. Finally, the room-temperature formation of the acyl-bridged complexes **7a** and **7c** could be justified by assuming a third possible evolution of the initial intermediate **P**: a simple decarbonylation to give a second paramagnetic intermediate **R**. Indeed it is known that mononuclear radicals experience very fast decarbonylation processes under mild conditions,[38] and we have also shown that binuclear radicals lose CO molecules readily at room temperature.[40,41] The incorporation of the second molecule to the intermediate **R** would give a dinitrosyl intermediate **S** having different coordination numbers at both metal centers. This difference could be then removed in two possible ways, either by carbonyl transfer between metal centers, this leading to compounds **6**, or by insertion of CO into the Mo−R bond followed by rearrangement of the resulting acyl ligand from terminal to a bridging position, thus explaining the room-temperature formation of compounds **7**.

Concluding Remarks

The electronic and coordinative unsaturation of the hydrocarbyl-bridged complexes $[Mo_2Cp_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$ (**1a−c**) (R = Me, CH_2Ph, Ph) facilitates the multiple uptake of simple donor molecules such as CO or NO under mild conditions, this invariably implying the displacement of the hydrocarbyl group to a terminal position at an early stage of the reaction. As a result, few differences are observed between the behavior of the agostic methyl or benzyl complexes **1a**,**b** and the nonagostic phenyl-bridged complex **1c**. The carbonylation reactions are thought to involve in the early stages the reversible insertion of CO into the Mo−C(hydrocarbyl) bonds to yield acyl-bridged intermediates, which then invariably evolve so that the hydrocarbyl groups eventually reach the cyclopentadienyl ligands, either by direct migration (to give a substituted cyclopentadiene easily displaced by CO) or through the coupling with a cyclopentadienylidene ligand, in turn derived from a C−H bond cleavage reaction. The latter route is dominant in all cases and gives the hydride derivatives of general formula $[Mo_2Cp(\eta^5\text{-}C_5H_4R')(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (R′ = Me, C(O)Me, CH_2Ph, Ph).

The reactions of compounds **1a−c** with NO also imply the displacement of the hydrocarbyl groups to a terminal position, and the insertion of CO into Mo−C(hydrocarbyl) bonds to yield acyl derivatives is again one of the relevant processes taking place, but now the resulting products of all these elemental steps are thermally stable and no migration or any other sort of coupling of the hydrocarbyl ligand with the cyclopentadienyl groups is observed under mild or even forcing conditions.

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

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prior to use.[42] Petroleum ether refers to that fraction distilling in the range 338−343 K. The compounds $[Mo_2Cp_2(\mu\text{-}R)(\mu\text{-}PCy_2)(CO)_2]$ [R = Me (**1a**), CH_2Ph (**1b**), Ph (**1c**)] were prepared as described previously.[1] Photochemical experiments were performed using jacketed Pyrex Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp (Applied Photophysics) placed ca. 1 cm away from the Schlenk tube was used for these experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K). 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. All other reagents were obtained from the usual commercial suppliers and used as received. IR stretching frequencies were measured in solution, Nujol mulls, or KBr and are referred to as ν(solvent), ν(Nujol), or ν(KBr), respectively. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13 (^{1}H), 162.01 ($^{31}P\{^1H\}$), or 100.63 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 (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz.

Preparation of $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Me\}(\mu\text{-}PCy_2)(CO)_3]$ (2). A solution of compound **1a** (0.060 g, 0.102 mmol) in toluene (4 mL) was stirred under a CO atmosphere for 5 h at 273 K to give an orange solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:4) yielded an orange fraction. Removal of solvents under vacuum from the latter fraction gave compound **2** as an orange microcrystalline solid (0.050 g, 76%). In solution, this product was shown (by ^{1}H or ^{31}P NMR spectroscopy) to be a mixture of four isomers, with their equilibrium ratios being both solvent- and temperature-dependent. Interconversion within the pairs *cis*-**2A**/*cis*-**2B** and *trans*-**2A**/*trans*-**2B** is fast on the NMR time scale at room temperature. The average *cis*/*trans* ratios at room temperature are 1:1 in CD_2Cl_2 and 2:1 in toluene-d_8. At 213 K, the overall *cis*/*trans* ratios are 2:1 both in CD_2Cl_2 and in toluene-d_8. At this temperature, the ratios *cis*-**2A**/*cis*-**2B** are 3:1 in CD_2Cl_2 and 10:1 in toluene-d_8, while the ratios *trans*-**2A**/*trans*-**2B** are 2:1 in CD_2Cl_2 and 1:1 in toluene-d_8. Anal. Calcd for $C_{27}H_{35}Mo_2O_4P$: C, 50.17; H, 5.46. Found: C, 49.89; H, 5.50. *Spectroscopic data for cis*-**2** (average resonances): $^{31}P\{^1H\}$ NMR: δ 263.8 (s, br). ^{1}H NMR: δ 5.34 (s, 5H, Cp), 5.01 (s, br, 5H, Cp), 2.78 (s, 3H, Me), 2.36−0.64 (m, 22H, Cy). ^{1}H NMR (toluene-d_8): δ 4.86 (s, 5H, Cp), 4.72 (s, br, 5H, Cp), 2.15 (s, 3H, Me), 2.58−0.76 (m, 22H, Cy). *Spectroscopic data for cis*-**2A**: $^{31}P\{^1H\}$ NMR (213 K): δ 263.6 (s). ^{1}H NMR (213 K): δ 5.38 (s, 5H, Cp), 4.91 (d, J_{PH} = 2, 5H, Cp), 2.90 (s, 3H, Me), 3.02−0.47 (m, 22H, Cy). ^{1}H NMR (toluene-d_8, 213 K): δ 4.71 (s, 5H, Cp), 4.57 (s, 5H, Cp), 2.03 (s, 3H, Me), 3.28−0.58 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (toluene-d_8, 213 K): δ 276.0 [s, *C*(O)Me], 241.2 (d, J_{CP} = 18, CO), 238.8 (d, J_{CP} = 25, CO), 237 (s, CO), 91.9, 89.2 (2s, Cp), 43.7 [s, br, C^1(Cy)], 42.2 [d, J_{CP} = 18, C^1(Cy)], 35.5 [s, C^2(Cy)], 32.3 (s, Me), 31.3, 30.2, 29.5 [3s, C^2(Cy)], 29.0−27.3 [m, C^3(Cy)], 26.2, 26.1 [2s, C^4(Cy)]. *Spectroscopic data for cis*-**2B**: $^{31}P\{^1H\}$ NMR (213 K): δ 250.4 (s). ^{1}H NMR (213 K): δ 5.42 (s, 5H, Cp), 5.06 (s, 5H, Cp), 2.85 (s, 3H, Me), 3.02−0.47 (m, 22H, Cy). ^{1}H NMR (toluene-d_8, 213 K): δ 4.78 (s, 5H, Cp), 3.28−0.58 (m, 22H, Cy), other resonances of minor isomer *cis*-**2B** were masked by those of the major isomer. *Spectroscopic data for trans*-**2** (average resonances): $^{31}P\{^1H\}$ NMR: δ 216.9 (s). ^{1}H NMR: δ 5.30, 5.21 (2s, 2 × 5H, Cp), 2.78 (s, 3H, Me), 2.36−0.64 (m, 22H, Cy). ^{1}H NMR (toluene-d_8): δ 4.93, 4.85 (2s, 2 × 5H, Cp), 2.62−0.76 (m, 22H, Cy), the resonance of the Me group of isomer *trans*-**2** was masked by those of the major isomer *cis*-**2**. *Spectroscopic data for trans*-**2A**: $^{31}P\{^1H\}$ NMR (213 K): δ 219.9 (s). ^{1}H NMR (213 K): δ 5.43 (d, J_{PH} = 2, 5H, Cp), 5.16 (s, 5H, Cp), 2.84 (s, 3H, Me), 3.02−0.47 (m, 22H, Cy). ^{1}H NMR (toluene-d_8, 213 K): δ 4.86 (s, br, 5H, Cp), 4.70 (s, 5H, Cp), 3.28−0.58 (m, 22H, Cy), the resonance of the Me group of isomer *trans*-**2A** was masked by those of the major isomer. *Spectroscopic data for trans*-**2B**: $^{31}P\{^1H\}$ NMR: δ 213.8 (s). ^{1}H NMR (213 K): 3.02−0.47 (m, 22H, Cy), other resonances of minor isomer *trans*-**2B** were masked by those of the major isomers. ^{1}H NMR (toluene-d_8, 213 K): δ 4.86, 4.35 (2s, br, 2 × 5H, Cp), 3.28−0.58 (m, 22H, Cy), the resonance of the Me group of isomer *trans*-**2B** was masked by those of the major isomers.

Preparation of $[Mo_2Cp(\eta^5\text{-}C_5H_4Me)(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (3a). A solid sample of compound **2** (0.050 g, 0.077 mmol) was stored at 253 K for 15 days under a nitrogen atmosphere, whereupon it was transformed almost selectively into the tetracarbonyl complex **3a**. The residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:10) yielded an orange fraction. Removal of solvents under vacuum from the latter fraction gave compound **3a** as an orange microcrystalline solid (0.040 g, 80%). Anal. Calcd for $C_{27}H_{35}Mo_2O_4P$: C, 50.17; H, 5.46. Found: C, 49.89; H, 5.35. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 5.37 (m, 1H, C_5H_4), 5.32 (s, 5H, Cp), 5.17, 5.04, 4.93 (3m, 3 × 1H, C_5H_4), 2.27 (s, 3H, Me), 2.73−1.03 (m, 22H, Cy), −13.18 (d, J_{CP} = 35, 1H, μ-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 213 K): δ 245.8 (d, J_{CP} = 27, CO), 245.0 (d, J_{CP} = 25, CO), 236.7, 236.6 (2s, CO), 108.2 [s, $C^1(C_5H_4)$], 92.8 (s, C_5H_4), 90.5 (s, Cp), 90.3, 90.0, 88.5 (3s, C_5H_4), 40.1 [m, $2C^1$(Cy)], 31.4 [s, $2C^2$(Cy)], 29.8, 29.3 [2s, C^2(Cy)], 28.0−26.9 [m, C^3, C^4(Cy)], 15.4 (s, Me).

Preparation of $[Mo_2Cp\{\eta^5\text{-}C_5H_4C(O)Me\}(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (5). A solution of compound **2** (0.050 g, 0.077 mmol) in toluene (4 mL) was stirred under a CO atmosphere at room temperature for 2 h to give an orange solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with petroleum ether yielded a pink fraction. Removal of solvents under vacuum from the latter fraction gave compound $[Mo_2Cp(\mu\text{-}PCy_2)(CO)_7]$ (**4**) as a pink microcrystalline solid (0.005 g, 14%). Elution with dichloromethane−petroleum ether (1:10) yielded an orange fraction, which yielded analogously compound **3a** as an orange microcrystalline solid (0.005 g, 10%). Elution with dichloromethane−petroleum ether (1:3) yielded an orange fraction, which gave analogously compound **5** as an orange microcrystalline solid (0.035 g, 67%). The crystals of **4** used in the X-ray study were grown by the slow evaporation at room temperature of a concentrated solution of the complex in petroleum ether. *Data for* **4**: Anal. Calcd for $C_{24}H_{27}Mo_2O_7P$: C, 44.33; H, 4.18. Found: C, 43.92; H, 4.05. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 5.28 (s, 5H, Cp), 2.73−1.03 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 241.0 (d, J_{CP} = 22, CO), 234.7 (s, CO), 210.1 (s, br, 4CO), 209.1 (d, J_{CP} = 14, CO), 93.0 (s, Cp), 55.3 [d, J_{CP} = 13, C^1(Cy)], 48.4 [d, J_{CP} = 15, C^1(Cy)], 35.6 [d, J_{CP} = 5, C^2(Cy)], 34.8 [s, C^2(Cy)], 33.8 [d, J_{CP} = 4, C^2(Cy)], 33.4 [s, C^2(Cy)], 28.6 [d, J_{CP} = 10, $2C^3$(Cy)], 28.2 [d, J_{CP} = 10, C^3(Cy)], 28.0 [d, J_{CP} = 14, C^3(Cy)], 26.5 [s, $2C^4$(Cy)]. $^{13}C\{^1H\}$ NMR (213 K): δ 241.5 (d, J_{CP} = 22, CO), 235.6, 227.1, 227.0 (3s, CO), 209.1 (s, br, CO), 203.6, 201.5 (2s, CO). *Data for* **5**: Anal. Calcd for $C_{28}H_{35}Mo_2O_5P$: C, 49.86; H, 5.23. Found: C, 49.59; H, 5.35. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 6.03, 5.81, 5.37 (3m, 3 × 1H, C_5H_4), 5.32 (s, 5H, Cp), 5.08 (m, 1H, C_5H_4), 2.50 (s, 3H, Me), 2.71−0.02 (m, 22H, Cy), −13.31 (d, J_{PH} = 35, 1H, μ-H). $^{13}C\{^1H\}$ NMR (213 K): δ 243.0, 242.3 (2d, J_{CP} = 27, CO), 236.0, 233.8 (2s, CO), 195.8 [s, C(O)Me], 98.7 (s, C_5H_4), 98.0 [s, $C^1(C_5H_4)$], 93.2, 92.8 (2s, C_5H_4), 90.8 (s, Cp), 88.0 (s, C_5H_4), 40.6 [d, J_{CP} = 18, C^1(Cy)], 39.4 [d, J_{CP} = 16, C^1(Cy)], 31.8 [s, $2C^2$-(Cy)], 30.1, 29.0 [2s, C^2(Cy)], 28.0, 27.8 [2d, J_{CP} = 9, C^3(Cy)],

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

27.3 (s, Me), 27.2 [d, J_{CP} = 16, C^3(Cy)], 27.1 [d, J_{CP} = 14, C^3-(Cy)], 26.9, 26.7 [2s, C^4(Cy)].

Preparation of [$Mo_2Cp(\eta^5$-$C_5H_4CH_2Ph)(\mu$-H)(μ-PCy_2)$(CO)_4$] (3b). A solution of compound **1b** (0.050 g, 0.075 mmol) in toluene (4 mL) was stirred under a CO atmosphere at room temperature for 2 h to give an orange solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:8) yielded an orange fraction. Removal of solvents under vacuum from the latter fraction gave compound **3b** as an orange microcrystalline solid (0.044 g, 81%). The crystals used in the X-ray study were grown by the slow diffusion of petroleum ether into a THF solution of the complex at 273 K. Anal. Calcd for $C_{33}H_{39}Mo_2O_4P$: C, 54.86; H, 5.44. Found: C, 54.80; H, 5.46. ^{1}H NMR (300.09 MHz): δ 7.36−7.24 (m, 5H, Ph), 5.41 (m, 2H, C_5H_4), 5.34 (s, 5H, Cp), 5.07, 5.00 (2m, 2 × 1H, C_5H_4), 3.91 (s, 2H, CH_2), 2.72−1.11 (m, 22H, Cy), −13.12 (d, J_{PH} = 35, 1H, μ-H). $^{13}C\{^1H\}$ NMR (213 K): δ 244.9 (d, J_{CP} = 26, CO), 244.3 (d, J_{CP} = 25, CO), 235.8, 235.7 (2s, CO), 140.8 [s, C^1(Ph)], 128.2 [s, C^3(Ph)], 127.9 [s, C^2(Ph)], 126.0 [s, C^4(Ph)], 110.6 [s, $C^1(C_5H_4)$], 91.6, 90.5 (2s, C_5H_4), 89.8 (s, Cp), 88.6, 88.0 (2s, C_5H_4), 39.2, 39.1 [2d, J_{CP} = 15, C^1(Cy)], 35.2 (s, CH_2), 30.4 [s, $2C^2$(Cy)], 28.9, 28.6 [2s, C^2(Cy)], 27.0 [s, br $2C^3$(Cy)], 26.4 [d, J_{CP} = 10, $2C^3$(Cy)], 26.1 [s, $2C^4$(Cy)].

Preparation of [$Mo_2Cp(\eta^5$-$C_5H_4Ph)(\mu$-H)(μ-PCy_2)$(CO)_4$] (3c). A solution of compound **1c** (0.025 g, 0.038 mmol) in toluene (4 mL) was placed in a bulb equipped with a Young's valve. The bulb was cooled at 77 K, evacuated under vacuum, and then refilled with CO. The valve was then closed, and the solution was allowed to reach room temperate and further stirred at 333 K for 40 h. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with petroleum ether yielded a pink fraction. Removal of solvents under vacuum from the latter fraction gave compound [$Mo_2Cp(\mu$-$PCy_2)(CO)_7$] (**4**) as a pink microcrystalline solid (0.005 g, 28%). Elution with dichloromethane−petroleum ether (1:10) yielded an orange fraction, which gave analogously compound **3c** as an orange microcrystalline solid (0.015 g, 56%). *Data for* **3c**: Anal. Calcd for $C_{32}H_{37}Mo_2O_4P$: C, 54.25; H, 5.26. Found: C, 54.60; H, 5.46. ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 2H, Ph), 7.39 (m, 2H, Ph), 7.29 (m, 1H, Ph), 5.90 (m, 2H, C_5H_4), 5.32, 5.27 (2m, 2 × 1H, C_5H_4), 5.14 (s, 5H, Cp), 2.80−0.88 (m, 22H, Cy), −13.13 (d, J_{PH} = 35, 1H, μ-H).

Reaction of Compound 1a with NO. A solution of compound **1a** (0.030 g, 0.051 mmol) in toluene (4 mL) was stirred at room temperature while gently bubbling NO (2000 ppm in N_2) through the solution for 4 h to give a yellow solution shown (by NMR) to be a mixture of compounds [$Mo_2Cp_2(Me)(\mu$-$PCy_2)(CO)(NO)_2$] (**6a**) and [$Mo_2Cp_2\{\mu$-κ^1:η^2-C(O)Me$\}(\mu$-$PCy_2)(NO)_2$] (**7a**) in a 1:2 ratio. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:5) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound **6a** as a yellow microcrystalline solid (0.010 g, 31%). Elution with dichloromethane−petroleum ether (1:2) yielded a second yellow fraction, which gave analogously compound **7a** as an orange microcrystalline solid (0.020 g, 62%). The crystals of **6a** used in the X-ray study were grown by the slow diffusion at 253 K of a layer of petroleum ether into a saturated solution of the complex in dichloromethane. The crystals of **7a** used in the X-ray study were grown by the slow diffusion of petroleum ether into a toluene solution of the complex at 253 K. *Data for* **6a**: Anal. Calcd for $C_{24}H_{35}Mo_2N_2O_3P$: C, 46.31; H, 5.67; N, 4.50. Found: C, 46.42; H, 5.69; N, 4.51. IR ν(Nujol): 1972 (vs), 1651 (s), 1584 (s) cm^{-1}. ^{1}H NMR: δ 5.60, 5.55 (2s, 2 × 5H, Cp), 2.41−0.36 (m, 22H, Cy), 0.56 (d, J_{PH} = 7, 3H, Mo−Me). *Data for* **7a**: Anal. Calcd for $C_{31}H_{43}Mo_2N_2O_3P$ (**7a**·C_7H_8): C, 52.11; H, 6.07; N, 3.92. Found: C, 51.73; H, 5.69; N, 4.15. ^{1}H NMR: δ 5.58, 5.26 (2s, 2 × 5H, Cp), 2.65 (d, J_{PH} = 1, 3H, C(O)Me), 2.22−1.20 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 274.8 [d, J_{CP} = 6, μ-*C*(O)Me], 99.0, 95.9 (2s, Cp), 49.3 [d, J_{CP} = 13, C^1(Cy)], 41.7 [d, J_{CP} = 16, C^1(Cy)], 42.4 (s, Me), 35.7 [s, C^2(Cy)], 35.3 [d, J_{CP} = 3, C^2(Cy)], 35.1, 34.6 [2d, J_{CP} = 4, C^2(Cy)], 28.8 [d, J_{CP} = 13, C^3(Cy)], 28.7 [d, J_{CP} = 11, C^3(Cy)], 28.6 [d, J_{CP} = 13, C^3(Cy)], 28.5 [d, J_{CP} = 10, C^3(Cy)], 26.6, 26.5 [2s, C^4(Cy)].

Preparation of [$Mo_2Cp_2\{\mu$-κ^1:η^2-C(O)Me$\}(\mu$-$PCy_2)(NO)_2$] (7a). A toluene solution (4 mL) of compounds **6a** and **7a** was prepared "in situ" as described above from compound **1a** (0.030 g, 0.051 mmol), and this mixture was stirred at 333 K for 2 h to give a yellow solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:2) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound **7a** as a yellow microcrystalline solid (0.027 g, 84%).

Reaction of Compound 1b with NO. A solution of compound **1b** (0.060 g, 0.090 mmol) in toluene (4 mL) was stirred at room temperature while gently bubbling NO (2000 ppm in N_2) through the solution for 1 h to give a green solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:8) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound [$Mo_2Cp_2(CH_2Ph)(\mu$-$PCy_2)(CO)_2(NO)_2$] (**8**) as a yellow microcrystalline, quite air-sensitive solid (0.010 g, 15%). Elution with dichloromethane−petroleum ether (1:6) yielded a yellow fraction, which gave analogously compound [Mo_2Cp_2-$(CH_2Ph)(\mu$-$PCy_2)(CO)(NO)_2$] (**6b**) as a yellow microcrystalline solid (0.040 g, 65%). Elution with dichloromethane−petroleum ether (1:3) yielded a blue fraction, which gave analogously compound [$Mo_2Cp_2(\mu$-$PCy_2)(\mu$-$NO)(NO)_2$] (**9**) as a blue microcrystalline, quite air-sensitive solid (0.005 g, 9%). The crystals of **6b** used in the X-ray study were grown by the slow diffusion of petroleum ether into a dichloromethane solution of the complex at 253 K. *Data for* **6b**: Anal. Calcd for $C_{30}H_{39}Mo_2N_2O_3P$: C, 51.59; H, 5.63; N, 4.01. Found: C, 51.50; H, 6.04; N, 3.62. IR ν(Nujol): 1970 (vs), 1640 (s), 1579 (s) cm^{-1}. ^{1}H NMR: δ 7.23−7.18 (m, 4H, Ph), 6.93 (m, 1H, Ph), 5.62, 5.22 (2s, 2 × 5H, Cp), 3.65 (t, J_{PH} = J_{HH} = 9, 1H, $MoCH_2$), 2.46 (dd, J_{HH} = 9, J_{PH} = 4, 1H, $MoCH_2$), 2.81−0.37 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 229.5 (d, J_{CP} = 17, CO), 156.7 [d, J_{CP} = 3, C^1(Ph)], 128.0 [s, C^3(Ph), C^2(Ph)], 122.2 [s, C^4(Ph)], 100.6, 95.1 (2s, Cp), 42.5, 41.7 [2d, J_{CP} = 13, C^1(Cy)], 33.2 [d, J_{CP} = 6, C^2(Cy)], 31.6 [s, $2C^2$(Cy)], 31.2 [s, C^2(Cy)], 28.2 [d, J_{CP} = 10, C^3(Cy)], 28.1 [d, J_{CP} = 9, C^3(Cy)], 27.9, 27.8 [2d, J_{CP} = 13, C^3(Cy)], 26.8, 26.7 [2s, C^4(Cy)], 14.6 (d, J_{CP} = 13, $MoCH_2$). *Spectroscopic data for* **8**: ^{1}H NMR: δ 7.25 [d, J_{HH} = 7, 2H, H^2(Ph)], 7.06 [ft, J_{HH} = 7, 2H, H^3(Ph)], 6.83 [ft, J_{HH} = 7, 1H, H^4(Ph)], 5.62 (s, br, 5H, Cp), 4.89 (s, 5H, Cp), 2.62 (d, J_{PH} = 1, 2H, $MoCH_2$), 2.10−1.17 (m, 22H, Cy). ^{1}H NMR (233 K): δ 7.25 [d, J_{HH} = 7, 2H, H^2(Ph)], 7.09 [ft, J_{HH} = 7, 2H, H^3(Ph)], 6.86 [ft, J_{HH} = 7, 1H, H^4(Ph)], 5.55, 4.92 (2s, 2 × 5H, Cp), 2.61 (s, 2H, CH_2), 2.50−1.21 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (233 K): δ 247.7 (s, br, CO), 153.1 [s, C^1(Ph)], 127.4, 127.3 [2s, C^3(Ph), C^2(Ph)], 122.4 [s, C^4(Ph)], 103.7, 93.0 (2s, Cp), 46.0 [s, br, C^1(Cy)], 32.9, 32.8 [2s, C^2(Cy)], 28.3 [d, J_{CP} = 14, C^3(Cy)], 28.2 [d, J_{CP} = 9, C^3(Cy)], 26.7 [s, C^4(Cy)], 7.06 (d, J_{CP} = 7, $MoCH_2$). *Spectroscopic data for* **9**: $\nu(CH_2Cl_2)$: 1625 (w, sh), 1587 (vs) cm^{-1}. ^{1}H NMR (300.13 MHz): δ 5.63 (s, 10H, Cp), 2.39−1.26 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 99.7 (s, Cp), 48.0 [d, J_{CP} = 15, C^1(Cy)], 39.4 [d, J_{CP} = 3, C^2(Cy)], 34.6 [d, J_{CP} = 4, C^2(Cy)], 28.8, 28.4 [2d, J_{CP} = 12, C^3(Cy)], 26.5 [s, C^4(Cy)]. SIMS (*m*/*z*): 609.00 (M^+), 579.01 (M^+ − NO), 351.87 (M^+ − 2 NO, PCy_2).

Preparation of $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)CH_2Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (7b). A toluene solution of compound **6b** (0.020 g, 0.029 mmol) was stirred for 2 h at 343 K to give a yellow solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:3) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound **7b** as a yellow microcrystalline solid (0.015 g, 75%). Anal. Calcd for $C_{30}H_{39}Mo_2N_2O_3P$: C, 51.59; H, 5.63; N, 4.01. Found: C, 51.26; H, 5.61; N, 3.86. ^{1}H NMR ($CDCl_3$): δ 7.59−7.25 (m, 5H, Ph), 5.58, 4.92 (2s, 2 × 5H, Cp), 4.86, 3.15 (2d, J_{HH} = 11, 2 × 1H, CH_2), 2.40−1.10 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 271.6 [d, J_{CP} = 5, μ-*C*(O)CH_2Ph], 140.1 [s, C^1(Ph)], 130.4, 128.6 [2s, C^3(Ph), C^2(Ph)], 126.5 [s, C^4(Ph)], 98.6, 95.8 (2s, Cp), 61.3 (s, CH_2), 49.4 [d, J_{CP} = 12, C^1(Cy)], 47.5 [d, J_{CP} = 15, C^1(Cy)], 35.6 [s, $2C^2$(Cy)], 35.2, 34.7 [2d, J_{CP} = 5, C^2(Cy)], 28.8 [d, J_{CP} = 13, C^3(Cy)], 28.7, 28.6 [2d, J_{CP} = 12, C^3(Cy)], 28.5 [d, J_{CP} = 11, C^3(Cy)], 26.6, 26.5 [2s, C^4(Cy)].

Reaction of Compound 1c with NO. A solution of compound **1c** (0.040 g, 0.061 mmol) in toluene (40 mL) was stirred while gently bubbling NO (2000 ppm in N_2) through the solution for 16 h to give an orange solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:4) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound $[Mo_2Cp_2(Ph)(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**6c**) as a yellow microcrystalline solid (0.020 g, 48%). Elution with dichloromethane−petroleum ether (1:2) yielded a yellow fraction, which gave analogously a mixture of the compounds $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (**7c**) and $[Mo_2Cp_2\{C(O)Ph\}(\mu\text{-}PCy_2)(CO)(NO)_2]$ (**10**) as a yellow microcrystalline solid (ratio **7c**:**10** ca. 5:3), which could not be further purified. Finally, elution with dichloromethane−petroleum ether (1:1) yielded an orange fraction, which gave analogously compound $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\eta^2\text{-}Ph)(\mu\text{-}PCy_2)(NO)_2]$ (**11**) as an orange microcrystalline solid (0.010 g, 25%). The crystals of compound **11** used in the X-ray were grown by slow diffusion of petroleum ether into a dichloromethane solution of the complex at 253 K. *Data for* **6c**: Anal. Calcd for $C_{29}H_{37}Mo_2N_2O_3P$: C, 50.89; H, 5.45; N, 4.09. Found: C, 50.80; H, 5.55; N, 3.92. ^{1}H NMR ($CDCl_3$): δ 7.44 [br, 2H, H^2(Ph)], 7.02 [ft, J_{HH} = 7, 2H, H^3(Ph)], 6.83 [ft, J_{HH} = 7, 1H, H^4(Ph)], 5.65, 5.62 (2s, 2 × 5H, Cp), 2.51−0.64 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (233 K): δ 230.6 (d, J_{CP} = 17, CO), 162.0 [d, J_{CP} = 11, C^1(Ph)], 143.9, 142.0 [2s, C^2(Ph)], 127.7, 125.7 [2s, C^3(Ph)], 122.3 [s, C^4(Ph)], 100.7, 95.2 (2s, Cp), 44.7 [d, J_{CP} = 17, C^1(Cy)], 40.2 [d, J_{CP} = 12, C^1(Cy)], 32.2 [s, C^2(Cy)], 31.2 [d, J_{CP} = 4, C^2(Cy)], 31.1 [d, J_{CP} = 5, C^2(Cy)], 28.7 [s, C^2(Cy)], 27.9 [d, J_{CP} = 9, C^3(Cy)], 27.2 [d, J_{CP} = 10, C^3(Cy)], 27.5 [d, J_{CP} = 14, C^3(Cy)], 27.4 [d, J_{CP} = 11, C^3(Cy)], 26.4, 26.1 [2s, C^4(Cy)]. *Data for* **7c**: Anal. Calcd for $C_{29}H_{37}Mo_2N_2O_3P$: C, 50.89; H, 5.45; N, 4.09. Found: C, 50.75; H, 5.33; N, 4.15. ^{1}H NMR ($CDCl_3$): δ 7.84 [m, 2H, H^2(Ph)], 7.42−7.17 (m, 3H, Ph), 5.39, 5.31 (2s, 2 × 5H, Cp), 2.35−1.26 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (233 K): δ 266.5 [d, J_{CP} = 4, C(O)Ph], 150.6 [s, C^1(Ph)], 130.1 [s, C^4(Ph)], 128.4, 127.0 [2s, C^3(Ph), C^2(Ph)], 99.1, 96.0 (2s, Cp), 52.0 [d, J_{CP} =10, C^1(Cy)], 42.8 [d, J_{CP} = 16, C^1(Cy)], 36.6 [s, C^2(Cy)], 35.7 [d, J_{CP} = 3, C^2(Cy)], 35.0, 34.1 [2s, C^2(Cy)], 28.7 [d, J_{CP} = 15, C^3(Cy)], 28.6 [d, J_{CP} = 11, $2C^3$(Cy)], 28.3 [d, J_{CP} = 10, C^3(Cy)], 26.48, 26.46 [2s, C^4(Cy)]. *Spectroscopic data for* **10**: ^{1}H NMR ($CDCl_3$): δ 7.64 [m, 2H, H^2(Ph)], 7.42−7.17 (m, 3H, Ph), 5.70, 5.61 (2s, 2 × 5H, Cp), 2.35−1.26 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (233 K): δ 278.9 [d, J_{CP} = 11, C(O)Ph], 228.5 (d, J_{CP} = 17, CO), 155.0 [s, C^1(Ph)], 129.4 [s, C^4(Ph)], 127.0, 125.6 [2s, C^3(Ph), C^2(Ph)], 100.9, 95.0 (2s, Cp), 42.0, 40.6 [2d, J_{CP} =15, C^1(Cy)], 34.1 [s, C^2(Cy)], 32.9 [d, J_{CP} = 4, C^2(Cy)], 30.1 [s, $2C^2$(Cy)], 29.1−27.5 [m, C^3(Cy)], 26.4, 26.2 [2s, C^4(Cy)]. *Data for* **11**: Anal. Calcd for $C_{28}H_{37}Mo_2N_2O_2P$: C, 51.23; H, 5.68; N, 4.27. Found: C, 50.99; H, 5.58; N, 4.14. ^{1}H NMR ($CDCl_3$): δ 7.64 (ft, J_{HH} = 8, 1H, Ph), 7.18 (ft, J_{HH} = 8, 1H, Ph), 6.80 (d, J_{HH} = 8, 1H, Ph), 6.43 (ft, J_{HH} = 8, 1H, Ph), 5.95 (d, J_{HH} = 8, 1H, Ph), 5.14 (s, 10H, Cp), 2.39−1.26 (m, 22H, Cy).

Preparation of $[Mo_2Cp_2\{\mu\text{-}\kappa^1\text{:}\eta^2\text{-}C(O)Ph\}(\mu\text{-}PCy_2)(NO)_2]$ (7c). *Method A*: A toluene solution of compound **6c** (0.020 g, 0.029 mmol) was stirred for 1.5 h at 343 K to give a yellow solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:2) yielded a yellow fraction. Removal of solvents under vacuum from the latter fraction gave compound **7c** as a yellow microcrystalline solid (0.015 g, 75%). *Method B*: The crude mixture of compounds **6c**, **7c**, **10**, and **11** obtained as described above from compound **1c** (0.040 g, 0.046 mmol) and NO was further stirred for 1 h in refluxing toluene to give a yellow solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:2) yielded a yellow fraction, which gave analogously compound **7c** as a yellow microcrystalline solid (0.029 g, 70%).

Preparation of $[Mo_2Cp_2(\mu\text{-}\kappa^1\text{:}\eta^2\text{-}Ph)(\mu\text{-}PCy_2)(NO)_2]$ (11). A toluene solution of compound **6c** (0.020 g, 0.029 mmol) was irradiated with UV−visible light at 285 K for 15 min to give an orange solution. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane and chromatographed through an alumina column (activity IV) at 288 K. Elution with dichloromethane−petroleum ether (1:1) yielded an orange fraction. Removal of solvents under vacuum from the latter fraction gave compound **11** as an orange microcrystalline solid (0.015 g, 79%).

X-ray Structure Determination of Compounds 3b and 11. The X-ray intensity data were collected on Smart-CCD-1000 (**3b**) and Kappa-Appex-II (**11**) Bruker diffractometers using graphite-monochromated Mo Kα radiation. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in three sets of 30 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART[43] was used for collecting frames of data, indexing reflections, and determining lattice parameters for **3b**, and the software APEX[44] was used for collecting frames with the omega/phi scan measurement method for **11**. The collected frames were then processed for integration by the software SAINT,[43] and a multiscan absorption correction was applied with SADABS.[45] Using the program suite WinGX,[46] the structure was solved by Patterson interpretation and phase expansion (**3b**) or direct methods (**11**) and refined with full-matrix least-squares on F^2 with SHELXL97.[47] All non-hydrogen atoms were refined anisotropically. In the case of compound **3b** two independent molecules were found in the asymmetric unit, and three reflections had to be omitted in order to avoid inadequate anisotropic parameters in C(53). Most of the hydrogen atoms could be located in the Fourier map in the last least-squares refinements, but in order to avoid a low reflections/parameters ratio, all them except the hydride ligands were fixed at calculated geometric positions. As for the hydride ligands, the H(2) atom could be located in the Fourier maps, while for H(1) possible positions were investigated by a potential energy minima search using the program HYDEX.[48]

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Table 7. Crystal Data for New Compounds

	3b	**4**	**6a**	**6b**	**7a·C_7H_8**	**11**
mol formula	$C_{33}H_{39}Mo_2O_4P$	$C_{24}H_{27}Mo_2O_7P$	$C_{24}H_{35}Mo_2N_2O_3P$	$C_{30}H_{39}Mo_2N_2O_3P$	$C_{31}H_{43}Mo_2N_2O_3P$	$C_{28}H_{37}Mo_2N_2O_2P$
mol wt	722.49	650.31	622.39	698.48	714.52	656.45
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$Pca2_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
radiation (λ, Å)	0.71073	0.71073	1.54184	1.54184	1.54184	0.71073
a, Å	13.403(2)	15.2107(3)	9.903(5)	9.10550(10)	8.7525(3)	14.7493(8)
b, Å	15.504(3)	11.5579(2)	27.514(5)	33.0473(3)	12.2232(3)	19.0347(11)
c, Å	15.517(3)	17.7653(4)	17.963(5)	9.75290(10)	14.5532(5)	18.8952(8)
α, deg	84.337(3)	90	90.000(5)	90	87.328(3)	90
β, deg	72.189(3)	125.1440(10)	90.000(5)	105.342(2)	75.793(3)	93.055(2)
γ, deg	83.307(3)	90	90.000(5)	90	82.829(2)	90
V, Å^3	3042.2(9)	2553.87(9)	4894(3)	2830.18(5)	1497.32(8)	5297.3(5)
Z	4	4	8	4	2	8
calcd density, g cm^{-3}	1.577	1.691	1.689	1.639	1.585	1.644
absorp coeff, mm^{-1}	0.913	1.085	9.238	8.065	7.634	1.036
temperature, K	120(2)	100(2)	100(2)	100(2)	100(2)	100.0(1)
θ range, deg	1.38−26.43	2.25−25.35	3.21−73.87	4.89−73.91	3.13−73⊡71	1.38−26.02
index ranges (h, k, l)	−15, 16;−19, 19; 0, 19	−18, 17;−13, 0; −21, 16	−11, 10;−33, 26; −22, 20	−10, 11;−39, 40; −10, 11	−10, 10;−14, 15; −17, 17	−18, 18;−0, 23; 0, 23
no. of reflns collected	32 980	23 604	17 200	15 257	14 309	40 199
no. of indep reflns (R_{int})	12 335 (0.0579)	4670 (0.0304)	8162 (0.0229)	5368 (0.0355)	5692 (0.0289)	10 434 (0.0573)
no. of reflns with $I > 2\sigma(I)$	7844	4283	7604	4464	4984	8126
R indexes [data with $I > 2\sigma(I)$][a]	$R_1 = 0.0479$	$R_1 = 0.0194$	$R_1 = 0.0372$	$R_1 = 0.0332$	$R_1 = 0.0372$	$R_1 = 0.0359$
	$wR_2 = 0.1109$[b]	$wR_2 = 0.0649$[c]	$wR_2 = 0.0958$[d]	$wR_2 = 0.084$[e]	$wR_2 = 0.1007$[f]	$wR_2 = 0.0706$[g]
R indexes (all data)[a]	$R_1 = 0.0898$	$R_1 = 0.0255$	$R_1 = 0.0403$	$R_1 = 0.0422$	$R_1 = 0.0462$	$R_1 = 0.0545$
	$wR_2 = 0.1392$[b]	$wR_2 = 0.0756$[c]	$wR_2 = 0.0979$[d]	$wR_2 = 0.0882$[e]	$wR_2 = 0.1035$[f]	$wR_2 = 0.0778$[g]
GOF	1.166	1.284	1.053	0.999	1.246	1.029
no. of restraints/ params	0/728	0/301	1/580	0/343	0/418	0/639
$\Delta\rho$ (max., min.), e Å^{-3}	1.274, −1.714	0.641, −0.834	1.683, −0.772	0.732, −1.185	0.715, −0.684	0.815, −0.677

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0470, b = 5.2766$. [c] $a = 0.0387, b = 0.9114$. [d] $a = 0.0516, b = 14.2617$. [e] $a = 0.0628, b = 0$. [f] $a = 0, b = 10.4207$. [g] $a = 0.0212, b = 9.4585$.

Only one minimum was found around the Mo(1)−Mo(2) bond, and therefore it was assigned to H(1). All hydrogen atoms were refined isotropically. Compound **11** was also found to crystallize with two independent molecules in the asymmetric unit. All hydrogen atoms were geometrically placed and refined using a riding model, except for H(2) and H(2B), which were located in the Fourier maps and refined isotropically. The final refinements on F^2 proceeded by full-matrix least-squares calculations in all cases. Further details of the data collection and refinements are given in Table 7.

X-ray Structure Determination of Compound 4. Data collection for compound **4** was performed on a Nonius Kappa CCD single diffractometer, using graphite-monochromated Mo Kα radiation. Images were collected at a 35 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program Collect.[49] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[50] A semiempirical absorption correction was applied using the program SORTAV.[51] Using the program suite WinGX,[46] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[47] All non-hydrogen atoms were refined anisotropically. During the refinement stages, one cyclohexyl group was found to be disordered. The disorder could be conveniently modeled, but all the involved atoms were refined isotropically, as in most cases their temperature factors become nonpositive definites. All hydrogen atoms were geometrically placed; they were given an overall isotropic thermal parameter and were refined using a riding model. Further details of the data collection and refinements are given in Table 7.

X-ray Structure Determination of Compounds 6a, 6b, and 7a. Data collection was performed on a Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (15−70 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.[52] Data reduction and cell refinement were performed with the program CrysAlis Pro RED.[52] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[52] Using the program suite WinGX,[46] the structure was solved by direct methods using SIR92[53] (**6a** and **7a**) or by Patterson interpretation and phase expansion (**6b**) and refined with full-matrix least-squares on F^2 using SHELXL97.[47] Compound **6a** was found to crystallize as two independent molecules in the asymmetric unit. During the final stages of the refinement, all non-H atoms were refined anisotropically and all hydrogen atoms were geometrically placed and refined

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using a riding model. For compound **6b** all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at calculated geometric positions and were given an overall isotropic thermal parameter, although they were located in the Fourier map. Compound **7a** was found to crystallize with a molecule of toluene; all atoms of this solvent molecule were assigned an occupancy factor of 0.5, this providing a satisfactory refinement. All non-hydrogen atoms were refined anisotropically. Although all hydrogen atoms were located in the Fourier map, they were fixed at calculated geometric positions and were given an overall isotropic thermal parameter. Further details of the data collection and refinements are given in Table 7.

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Supporting Information Available: CIF file giving the crystallographic data for the structural analysis of compounds **3b**, **4**, **6a**, **6b**, **7a**·C_7H_8, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.