Dimolybdenum and Ditungsten Cyclopentadienyl Carbonyls with Electron-Rich Phosphido Bridges. Synthesis of the Hydrido Phosphido Complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ and Unsaturated Bis(phosphido) Complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(CO)_x]$ (x = 1, 2; R, R′, R″ = Et, Cy, ^{t}Bu)

M. Esther García, Víctor Riera, Miguel A. Ruiz,* M. Teresa Rueda, and David Sáez

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain

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New hydrido complexes of the type $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ (M = Mo, W) have been prepared through the thermal reaction of $[Mo_2Cp_2(CO)_6]$ with $HPCy_2$, H_2PCy, or $HPEt_2$ or the thermal reaction of $[W_2Cp_2(CO)_4]$ with HPR_2 (R = Cy, Et, Ph). In contrast, UV irradiation of $[M_2Cp_2(CO)_6]$ and HPRR′ leads with good yield to the bis(phosphido) complexes $[M_2Cp_2(\mu\text{-}PRR')_2(\mu\text{-}CO)]$ (R = R′ = Cy, Et, Ph; R = Cy, R′ = H). Related complexes having different phosphido groups, $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(\mu\text{-}CO)]$ (R = Cy, ^{t}Bu, Ph; R′ = Cy, ^{t}Bu, Et; R″ = Cy, ^{t}Bu, Et, H), can be prepared in high yield through the photochemical reaction of $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}H)(CO)_4]$ and HPR′R″ or $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR'R'')(CO)_4]$ and HPR_2. All triply bonded compounds react easily with carbon monoxide at room temperature or under moderate heating to finally yield the corresponding *trans*-dicarbonyl complexes $[M_2Cp_2(\mu\text{-}PRR')_2(CO)_2]$ or $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(CO)_2]$. Some of the intermediates in these carbonylation reactions have been identified, including the *cis*-dicarbonyl complex $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBu_2)(CO)_2]$ and the tricarbonyl complex $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$. The structures of the new complexes are analyzed on the basis of the corresponding IR and NMR (^{1}H, ^{31}P, ^{13}C) data, and the reaction pathways operative in these highly efficient syntheses of bis(phosphido) complexes is discussed on the basis of the available data and some cross-experiments.

Introduction

Recently we have shown that the diphenylphosphido ligand is an useful bridging group able to stabilize highly reactive dinuclear cyclopentadienyl species such as the paramagnetic[1] $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ or the hydroxycarbyne[2] $[W_2Cp_2(\mu\text{-}COH)(\mu\text{-}PPh_2)_2]BF_4$. To tune the reactivity of the unsaturated dimetal center in the above species, we must be able to modify the steric and electronic properties of the bridging phosphido ligand. This can be done, provided that suitable precursors having different substituents on phosphorus, $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ or $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(\mu\text{-}CO)]$, are available. Surprisingly, since the first report on $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ by Hayter,[3] relatively few related complexes have been described. These include the dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}L)(CO)_4]$ with L = PPh_2,[4] P^tBu_2,[5] PH_2,[6,7] PHMe,[6] PHPh,[8,9] and the ditungsten analogues with L = PHPh,[10] PH_2,[6,7] $PC_4H_2Ph_2$.[11] The triply bonded precursors $[M_2Cp_2(\mu\text{-}PR_2)_2(\mu\text{-}CO)]$ are even more scarce. In fact, before our ditungsten diphenylphosphido complex[2] only two other related complexes had been reported, these being the molybdenum monocarbonyls $[Mo_2Cp_2(\mu\text{-}RPC_6H_4PR)(\mu\text{-}CO)]$ (R = Ph,[12a] ^{t}Bu[12b]) and $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$.[13] Thus, the search for related complexes with either equal or different bridging phosphido groups was itself a synthetic target. Recently, Mays and co-workers have reported the synthesis of the mixed-phosphide com-

* To whom correspondence should be addressed. E-mail: mara@sauron.quimica.uniovi.es.

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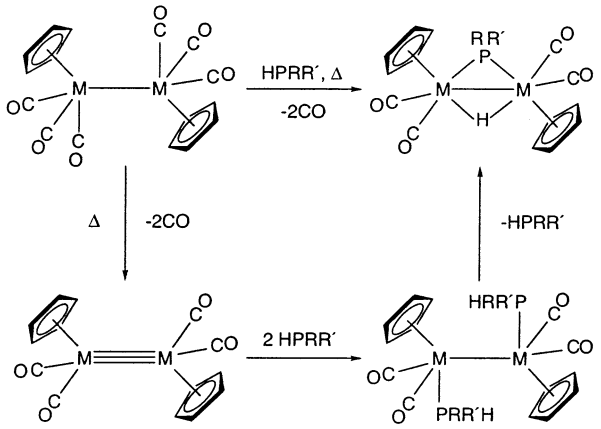
Scheme 1. Synthesis of Hydrido Phosphido Complexes



pound $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PHPh)(CO)_2]$ through the reaction of $Li[Mo_2Cp_2(\mu\text{-}PHPh)(CO)_4]$ with $ClPPh_2$[14a] and that of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PPhEt)(CO)_2]$ from the phosphaalkene complex $[Mo_2Cp_2(\mu\text{-}PPhCHMe)(CO)_4]$ and PPh_2H.[14b]

In this paper we report the synthesis of new bis(phosphido) complexes of the type $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR_2')(CO)_x]$ (M = Mo, W; x = 1−3) having basic and bulky groups such as Et, Cy, and ^{t}Bu. These can be conveniently accessed through the reaction of primary or secondary phosphines with suitable hydrido phosphido precursors of the type $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$.

Results and Discussion

Synthesis of Hydrido Phosphido Complexes. There are two well-established methods to generate dimolybdenum or tungsten phosphido complexes of the type $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ starting from phosphines having P−H bonds (Scheme 1). The first one involves the thermal reaction of $[Mo_2Cp_2(CO)_6]$ and the corresponding phosphine and has been successfully used for HP^tBu_2[5] and $HPPh_2$ or H_2PPh.[8] The second method involves the rapid addition of phosphine to the triply bonded $[M_2Cp_2(CO)_4]$ to yield intermediates of the type $[M_2Cp_2(CO)_4(PRR'H)_2]$. The latter then experience elimination of 1 equiv of HPRR′ (either spontaneously or under moderate heating) to yield the final hydrido phosphido complexes, and this method has been successfully used for PH_3, PH_2Me, and $PHMe_2$ (M = Mo, W)[6] and PH_2Ph (M = Mo).[9] We have found that the first method also works well for $HPCy_2$, $HPEt_2$, and H_2PCy. Thus, refluxing toluene solutions of $[Mo_2Cp_2(CO)_6]$ with the above phosphines (T = 80 °C for $HPEt_2$ due to its low boiling point) gives the corresponding hydridoderivatives **1a**−**c** in good yield. Ditungsten complexes, however, cannot be prepared in this way, due to the low decarbonylation rate of $[W_2Cp_2(CO)_6]$, and the second method must be used instead. Thus, addition of 2 equiv of HPR_2 (R = Cy, Et, Ph) to $[W_2Cp_2(CO)_4]$ (prepared in situ from $[W_2Cp_2(CO)_6]$) followed by further stirring at room temperature (Cy), 40 °C (Et), or 60 °C (Ph) gives the corresponding phosphido complexes $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ (**2a**,**b**,**d**: **a**, R = Cy; **b**, R = Et; **d**, R = Ph) in good overall yields (ca. 60% based on $[W_2Cp_2(CO)_6]$). This second method is also more convenient than the first one when using volatile phosphines, due to the lower operating temperature. Thus, $HPEt_2$ must be reacted with $[Mo_2Cp_2(CO)_6]$ below 80 °C, and even so, important evaporation of phosphine takes place, requiring an excess of reagent to be added. This inconvenience is avoided when reacting $HPEt_2$ with $[Mo_2Cp_2(CO)_4]$, which yields compound **1b** at 60 °C in ca. 1 h.

Structural Characterization of Compounds 1 and 2. Spectroscopic data for the new compounds **1a**−**c** and **2a**,**b**,**d** (Table 1 and Experimental Section) indicate that all these compounds have the same structure (Chart 1), it being the transoid one crystallographically characterized for $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ (R = R′ = Me,[3b] ^{t}Bu;[5] R = Ph, R′ = Et[14b]). This is particularly clear when the corresponding IR or NMR data are compared with those reported for related complexes[3−11] and need not be discussed in detail.

The ^{13}C NMR spectra of compounds **1** and **2** exhibit the expected CO resonances. By recalling that ^2J(PC) couplings in complexes of the type $[MCpX(CO)_2(PR_3)]$ (M = Mo, W; X = halogen, alkyl, hydride, etc) usually follow the order $J_{cis} > J_{trans}$,[15,16] we expect for the carbonyl ligand trans to the phosphido bridge a PC coupling lower than that for the carbonyl trans to the hydrido bridge. Accordingly, compounds **1a**,**b** exhibit only two CO resonances, appearing as a singlet and as a doublet, respectively. In the case of **1c**, the C_2 axis relating both metal centers is no longer an element of symmetry, and this renders both cyclopentadienyls and all four carbonyls inequivalent (two doublets and two singlets as expected).

The above data are in excellent agreement with those reported for $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PRPh)(CO)_4]$ at −40 °C (R = H, Ph).[8,9] The latter complexes were found to experience a fluxional process rendering all carbonyl and both cyclopentadienyl ligands equivalent, so that just very broad ^{13}C carbonyl resonances were observed at room temperature. Obviously, our dimolybdenum complexes **1a**−**c** are more rigid, as they exhibit NMR spectra at room temperature consistent with their static structure. The same can be said of the ditungsten derivatives with diethyl- or dicyclohexylphosphido bridges **2a**,**b**, which also display two carbonyl resonances at room temperature, as expected. The diphenylphosphido derivative **2d**, however, is fluxional and gives a single, very broad ^{13}C carbonyl resonance at 229.0 ppm, which at 233 K transforms into a doublet (232.2 ppm) and a singlet (224.2 ppm), as expected. Thus, it is concluded that, irrespective of the metal, the dynamic behavior of this family of compounds is strongly dependent on the hydrocarbon substituents on phosphorus. From the abundant studies on the steric[17] and electronic[18] influence of substituents on phosphines, we can estimate for

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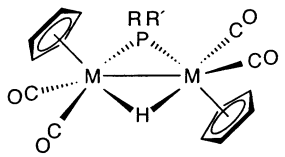
Table 1. Selected IR and NMR Data for New $[M_2Cp_2(\mu\text{-H})(\mu\text{-PRR}')(CO)_4]$ Compounds

M	R	R′	compd	ν(CO)[a]	δ(CO)[b] (J_{PC})	δ(P)[b] (J_{PW})	$\delta(\mu\text{-H})$[b] [J_{PH}] (J_{HW})
Mo	Cy	Cy	**1a**	1945 (w,sh),1928 (vs), 1860 (s)	244.1 (19), 235.9	218.8[c]	−13.2 [34]
Mo	Et	Et	**1b**	1942 (w,sh), 1930 (vs), 1866 (s)	243.5 (24), 235.9	179.8[c]	−12.3 [35][c]
Mo	Cy	H	**1c**	1953 (w, sh), 1935 (vs), 1871 (s)	242.8 (19), 237.1 242.2 (20), 236.7	152.6[c]	−12.4 [35]
W	Cy	Cy	**2a**	1918 (vs), 1841 (s)	232.2 (br), 223.4 (br)	139.6 (182)[c]	−16.4 [24] (40)
W	Et	Et	**2b**	1919 (vs), 1846 (s)	233.8 (20), 225.6	99.6 (197)[c]	−14.9 [25] (39)
W	Ph	Ph	**2d**	1959 (w, sh), 1926 (vs), 1853 (s)[d]	232.2 (17), 224.2[e]	109.2 (209)	−14.8 [27] (39)

[a] Recorded in toluene solution, unless otherwise stated. ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^{1}H), 121.50 (^{31}P), or 75.47 MHz (^{13}C) unless otherwise stated. δ in ppm relative to internal TMS (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4; J in hertz. [c] In toluene-d_8 solution. [d] In dichloromethane solution. [e] At 233 K; when recorded at 290 K, only a broad resonance at 229 ppm is observed.

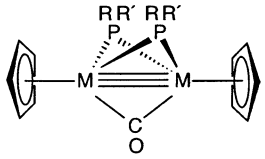
Chart 1



1, 2

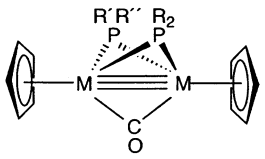
	M	R	R′
1a	Mo	Cy	Cy
1b	Mo	Et	Et
1c	Mo	Cy	H
2a	W	Cy	Cy
2b	W	Et	Et
2d	W	Ph	Ph

Chart 2



3, 4

	M	R	R′
3a	Mo	Cy	Cy
3b	Mo	Et	Et
3c	Mo	Cy	H
4b	W	Et	Et
4d	W	Ph	Ph



5, 6

	M	R	R′	R″
5e	Mo	Cy	Cy	H
5f	Mo	^{t}Bu	Cy	H
5g	Mo	Ph	Cy	Cy
5h	Mo	Ph	Et	Et
5i	Mo	Ph	Cy	H
5j	Mo	Ph	^{t}Bu	^{t}Bu
5k	Mo	Ph	^{t}Bu	H
6e	W	Cy	Cy	H
6h	W	Ph	Et	Et

the groups involved here that the electron-donor influence on the phosphido ligand would follow the sequence Cy > Et > Ph > H, whereas the relative size would decrease in the order Cy > Ph ≈ Et > H. Thus, taking into account that the complexes exhibiting fluxional behavior at room temperature are those with PPh_2 or PHPh bridges, whereas those with similar overall size but more electron-releasing groups PEt_2 (**1b**, **2b**) and PHCy (**1c**) behave as more rigid molecules, we conclude that electronic effects seem to be prevalent in these compounds, with the electron-withdrawing substituents on the phosphido ligand increasing the rate of the fluxional process.

Synthesis of Bis(phosphido) Complexes. As stated above, before our photochemical synthesis of $[W_2Cp_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$ from $[W_2Cp_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4]$ and $HPPh_2$ only two other related monocarbonyls had been reported, these being prepared through prolonged thermal[12] or photochemical[13] treatment of suitable precursors. The interesting point of our method was 2-fold. First, it was fast, with reaction times around 1 h at room temperature. Second, it allowed the synthesis of mixed bis(phosphido) derivatives, by appropriate choice of substrate and phosphine. Indeed, we have found that this synthetic approach is quite general, and a large number of mixed bis(phosphido) derivatives can be synthesized in this rational way. Apparently, this preparative route to mixed phosphido complexes has not been explored in detail previously, although we can quote a precedent in the synthesis of $[Fe_2(\mu\text{-PCy}_2)(\mu\text{-PPh}_2)(CO)_4(\mu\text{-dppm})]$ from $[Fe_2(\mu\text{-PCy}_2)(\mu\text{-H})(\mu\text{-CO})(CO)_4(\mu\text{-dppm})]$ and $HPPh_2$.[19] Moreover, we have found that symmetric bis(phosphido) complexes can be synthesized in a one-pot reaction from $[M_2Cp_2(CO)_6]$ and the corresponding HPR_2 under photochemical conditions, a process expectedly involving the corresponding hydrido compounds **1** and **2** as intermediate species.

Irradiation of toluene solutions of $[Mo_2Cp_2(CO)_6]$ with UV light in the presence of ca. 3 equiv of $HPCy_2$ or $HPEt_2$ gives the corresponding monocarbonyls $[Mo_2Cp_2(\mu\text{-PR}_2)_2(\mu\text{-CO})]$ (**3a**,**b**: **a**, R = Cy; **b**, R = Et) (Chart 2). When the smaller H_2PCy is used, the stoichiometry must be fixed to 2 equiv of phosphine in order to avoid further additions of the ligands. The corresponding monocarbonyl complex $[Mo_2Cp_2(\mu\text{-PHCy})_2(\mu\text{-CO})]$ (**3c**) is obtained as a mixture of two isomers (see later). In a similar way, UV irradiation of $[W_2Cp_2(CO)_6]$ with $HPEt_2$ or $HPPh_2$ gives the related monocarbonyls $[W_2Cp_2(\mu\text{-PR}_2)_2(\mu\text{-CO})]$ (**4b**,**d**) in good yields (**d**, R = Ph).

IR and ^{31}P NMR monitoring of the above reactions indicates that several species are involved as intermediates in the formation of monocarbonyls **3** and **4**. Apart from the corresponding hydrido complexes **1** and **2**, we have also identified the corresponding dicarbonyl compounds $[M_2Cp_2(\mu\text{-PR}_2)_2(CO)_2]$ as intermediates in these reactions, these being observed in larger amounts for the smaller phosphines H_2PCy and $HPEt_2$. As expected, these dicarbonyl complexes can be formed from **3** or **4** and CO, as we will discuss later.

Irradiation of toluene solutions of the hydrido complexes **1** or **2** and the appropriate primary or secondary phosphine proceeds rapidly, presumably with H_2 elimination, to give with good yields the corresponding mixed bis(phosphido) monocarbonyls **5** and **6**, analogous to the "symmetric" compounds **3** and **4** (Scheme 2). The method is quite general, and reaction times are ca. 1 h on a 0.1 g scale. For example, **1a** and PH_2Cy give $[Mo_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-PHCy})(\mu\text{-CO})]$ (**5e**), while **1c** and PH^tBu_2 give $[Mo_2Cp_2(\mu\text{-PHCy})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-CO})]$ (**5f**) and $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_4]$ reacts with $PHCy_2$, $PHEt_2$, or PH_2Cy to yield respectively $[Mo_2Cp_2(\mu\text{-PPh}_2)(\mu\text{-PR′R″})(\mu\text{-CO})]$ (**5g**−**i**: **g**, R′ = R″ = Cy; **h**, R′ = R″ = Et; **i**, R″ = H; R′ = Cy). As for ditungsten species, compound **2a** and PH_2Cy give $[W_2Cp_2(\mu\text{-PCy}_2)(\mu\text{-PHCy})(\mu\text{-CO})]$ (**6e**), while **2b** and $PHPh_2$ lead expectedly to $[W_2Cp_2(\mu\text{-PEt}_2)$-

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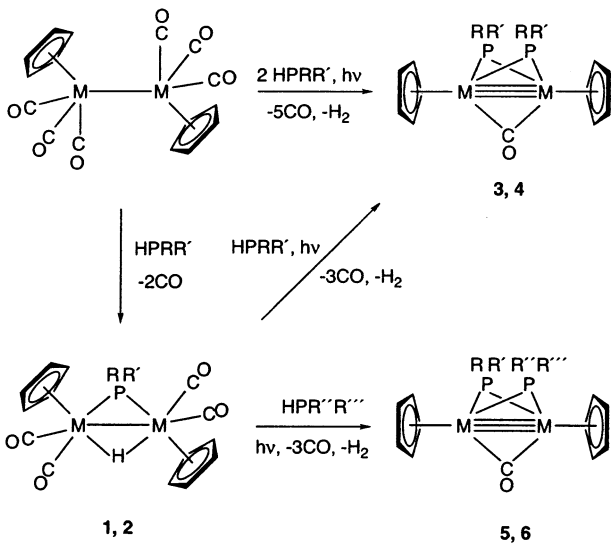
Table 2. Selected IR and NMR Data for New $[M_2Cp_2(\mu\text{-}PRR')_2(\mu\text{-}CO)]$ and $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(\mu\text{-}CO)]$ Compounds

M	R	R′	R″	compd	ν(CO)[a]	δ(CO)[b] [J_{PC}]	δ(P)[b]	J_{PP}	J_{PW}
Mo	Cy	Cy		**3a**	1689	307.0 [7]	263.7[c]		
Mo	Et	Et		**3b**	1693	298.0 [7][c]	212.3[c]		
Mo	Cy	H		**3c**	1703	304.7 [7] (**A**)[d]	167.3		
						303.2 [7] (**B**)	167.8, 165.3	27	
W	Et	Et		**4b**	1654	305.0	147.1[c]		376
W	Ph	Ph		**4d**	1635[e]	303.9	144.7		389
Mo	Cy	Cy	H	**5e**	1694	306.7 (**D**)[f]	240.9 (PCy_2), 166.9	27	
						(**E**)	238.7 (PCy_2), 166.7	22	
Mo	^{t}Bu	Cy	H	**5f**	1695	297.8[g]	280.6 (PBu^t_2), 179.5[c]	27	
Mo	Ph	Cy	Cy	**5g**	1692	306.3 [7]	243.4 (PCy_2), 194.5[c]	23	
Mo	Ph	Et	Et	**5h**	1696	304.9	222.5 (PEt_2), 192.7	26	
Mo	Ph	Cy	H	**5i**	1702	304.4 [7]	193.3 (PPh_2), 168.2[c]	28	
Mo	Ph	^{t}Bu	^{t}Bu	**5j**	1694	306.2 [7]	288.9 (PBu^t_2), 198.6	22	
Mo	Ph	^{t}Bu	H	**5k**	1702	304.1 [7]	201.5 (PH^tBu), 196.9	27	
W	Cy	Cy	H	**6e**	1655	307.5 (**D**)	181.2 (PCy_2), 111.8	<1	358, 368
						306.2 (**E**)[f]	182.1 (PCy_2), 107.4	9	358, 370
W	Ph	Et	Et	**6h**	1657	304.4	152.9 (PEt_2), 136.5	6	374, 392

[a] Recorded in toluene solution, unless otherwise stated. ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^{1}H), 121.50 (^{31}P), or 75.47 MHz (^{13}C) unless otherwise stated. δ in ppm relative to internal TMS (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4; J in hertz. [c] In toluene-d_8 solution. [d] Ratio **A**:**B** = 6:4. [e] In dichloromethane solution. [f] Ratio **D**:**E** = 7:3. [g] In benzene-d_6 solution.

Scheme 2. Synthesis of Bis(phosphido) Complexes



(μ-PPh_2)(μ-CO)] (**6h**). In some cases, intermediate dicarbonyl species can be detected during the formation of these mixed-metal compounds, as we have noted also for the "symmetric" monocarbonyls **3** and **4**.

From the above reactions it can be concluded that, to combine two different phosphido ligands, it is not important which ligand is first incorporated into the substrate (i.e., the one present in the phosphido hydrido complex). However, this cannot be assumed in all cases. For example, when the relatively bulky PPh_2 and P^tBu_2 groups are combined, the order of incorporation of ligands becomes critical. Thus, the photochemical reaction of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(CO)_4]$ with $HPPh_2$ leads expectedly to $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)]$ (**5j**), but the reaction between $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ and HP^tBu_2 leads instead to a ca. 1:1:1 mixture of **5j**, $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$,[13] and $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PH^tBu)(\mu\text{-}CO)]$ (**5k**). While the formation of the bis(diphenylphosphido) complex is due to slow photochemical decomposition of the starting substrate (we note that the reaction time in this case is substantially longer, ca. 3 h), the formation of **5k** requires the transformation of a P−^{t}Bu moiety into a P−H one. This must occur at the intermediate steps leading to **5k**, as the μ-P^tBu_2 ligand, once formed, is stable under these reaction conditions (i.e., **5j** does not transform into **5k**). Although we have not been able to find any precedent for this degradation of a HP^tBu_2 molecule upon coordination to a metal complex, several reasonable proposals can be envisaged, as we will discuss later on.

Structural Characterization of Compounds 3−6. Spectroscopic data for compounds **3**−**6** are all similar (Table 2) and indicative of the presence of two bridging phosphido groups and a bridging carbonyl. The structure is therefore the same as that crystallographically determined for $[Mo_2Cp_2(\mu\text{-}PhPC_6H_4PPh)(\mu\text{-}CO)]$[12a] and $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$,[13] for which the short intermetallic distances (ca. 2.5 Å) are consistent with the formulation of a triple metal−metal bond.

The bridging carbonyl in complexes **3**−**6** gives rise to a C−O stretching band at ca. 1700 cm^{-1} (M = Mo) or 1655 cm^{-1} (M = W) and to characteristic ^{13}C resonances at ca. 305 ppm. Assignment of ^{31}P NMR resonances in the mixed-phosphido complexes **5** and **6** can be unambiguously done by comparison with the chemical shifts of the "symmetric" compounds **3** and **4** and analysis of the one-bond P−H couplings when necessary. For compound **6h**, as chemical shifts for PEt_2 or PPh_2 groups are quite similar, assignment of the ^{31}P resonances is based on the measured P−W couplings, expected to be higher for P atoms bearing better electron acceptor groups.

Chemical shifts for the phosphorus atoms in compounds **3**−**6** follow the same general trend observed for the tetracarbonylic complexes **1** and **2**, i.e., P^tBu_2 > PCy_2 > PEt_2 ≅ PPh_2 > PHCy. Thus, they rather seem to be following the steric demands of the hydrocarbon groups attached to the phosphorus bridge. We note, however, that chemical shifts of phosphido bridges are quite sensitive to many structural features (C−P−C and M−P−M angles, M−M, M−P lengths, etc.);[20,21] therefore, we will not attempt to correlate these shifts with

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

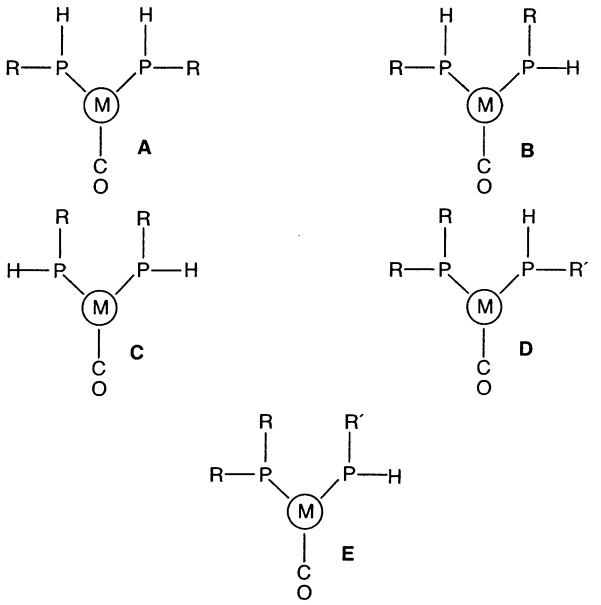


Figure 1. Possible structures of monocarbonyl complexes having P−H bonds, viewed along the M−M bond (Cp groups omitted).

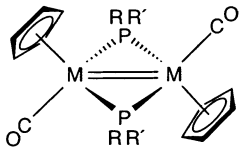
any single geometric or electronic property of the phosphido bridge.

Complexes with bridging PHCy or PH^{t}Bu groups can exist as several isomers depending on the orientation of the H atom (Figure 1). This is the case for the molybdenum complexes **3c** and **5e**,**f**,**i**,**k** and the ditungsten compound **6e**. Complex **3c** displays two isomers in solution, one having equivalent P atoms (δ_P 167.3 ppm) and one having non equivalent P atoms (δ_P 167.8, 165.3 ppm). The latter must be therefore the unique asymmetric conformer **B**, while the former is presumably conformer **A** and not **C**, on the basis of steric grounds.

Species with a single PHR bridge can exist as isomers of types **D** and **E**, but complexes **5f**,**i**,**k** display single isomers in solution. Presumably, these compounds adopt the less sterically demanding structure **D**. However, compounds **5e** and **6e** display two isomers in solution with similar ratios (ca. 70:30). On steric grounds, we would expect for the major isomer a structure of type **D**, while the minor isomer would adopt structure **E**. This is in agreement with ^3J(P−H) values measured for the P−H hydrogens in compounds **5e** and **6e**. These three-bond couplings are strongly dependent on the dihedral angle (ϕ) defined by the bonds involved.[22] On this basis, we expect for structure **D** (ϕ(H−P−M−P) close to 90°) a ^3J(P−H) value smaller than that for structure **E** (ϕ(H−P−M−P) close to 180°). Indeed, the major isomer in these compounds displays a ^3J(P−H) value of 2−3 Hz for the P-bonded hydrogen, to be compared to ^3J(P−H) = 7 Hz for the corresponding hydrogen in the minor isomer.

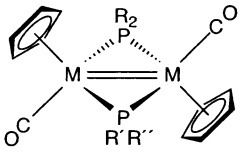
Carbonylation Reactions of Triply Bonded Complexes 3−6. As noted above, during the synthesis of the monocarbonylic complexes **3**−**6** we were able to detect in some cases intermediate species likely to be the dicarbonyl compounds, analogous to the well-characterized doubly bonded complex [$Mo_2Cp_2(\mu$-$PPh_2)_2$-$(CO)_2$].[13] We then decided to study the reactions of CO with the triply bonded complexes **3**−**6** as a synthetic route to the mentioned dicarbonyl compounds. There were two further points of interest in these reactions. First, they would provide us some insight on the reaction pathways operative in the photochemical synthesis of monocarbonyl compounds **3**−**6**. Second, they would represent a first check on the ligand-acceptor ability of these highly unsaturated molecules having double or triple intermetallic bonds.

Chart 3



7, 8

	M	R	R′
7a	Mo	Cy	Cy
7b	Mo	Et	Et
7c	Mo	Cy	H
8b	W	Et	Et
8d	W	Ph	Ph



9, 10

	M	R	R′	R″
9e	Mo	Cy	Cy	H
9f	Mo	^{t}Bu	Cy	H
9g	Mo	Ph	Cy	Cy
9h	Mo	Ph	Et	Et
9i	Mo	Ph	Cy	H
9j	Mo	Ph	^{t}Bu	^{t}Bu
9k	Mo	Ph	^{t}Bu	H
10e	W	Cy	Cy	H
10h	W	Ph	Et	Et

All compounds **3**−**6** react with CO at atmospheric pressure to yield the corresponding dicarbonyl derivatives **7**−**10**, which are selectively obtained as trans isomers (Chart 3). The rate of carbonylation appears to be dominated by the steric (rather than electronic) properties of the bridging groups. Thus, all complexes combining PEt_2, PPh_2, or PHCy bridges are rapidly carbonylated at room temperature within a few minutes, while those incorporating PCy_2 or P^tBu_2 groups require several hours and/or higher temperatures for complete carbonylation (for example, 3 h at 80 °C for **3a**).

We have been able to detect and characterize two intermediate species in some of these carbonylation reactions. In the first place, IR and ^{31}P NMR monitoring of the slow carbonylation of **5j** at 80 °C reveals that a cis isomer of the final product, *cis*-[$Mo_2Cp_2(\mu$-$PPh_2)(\mu$-$P^tBu_2)(CO)_2$] (**11**), is first formed, which then slowly transforms into **9j**. It is important to note that in the absence of CO compound **11** does not transform into its trans isomer **9j** at either room temperature or 80 °C and that it gives back the monocarbonyl **5j** under UV irradiation within a few minutes. Incidentally, compound **11** appears to be the first example of a bis(phosphido) species of the type [$M_2Cp_2(\mu$-X)(μ-Y)$(CO)_2$] (X, Y = 3e donor groups) exhibiting a *cis*-dicarbonyl geometry. We note, however, that both cis and trans geometries are well-known for the related bis(thiolate) complexes [$Mo_2Cp_2(\mu$-$SR)_2(CO)_2$].[23] More importantly, we trust that compound **11** represents the first stage in the carbonylation reactions of triply bonded complexes **3**−**6**, as we will discuss later on.

(21) (a) Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. *Inorg. Chem.* **1989**, *28*, 4120. (b) Eichele, K.; Wasylishen, R. E.; Corrigan, J. F.; Taylor, N. J.; Carty, A. J.; Feindel, K. W.; Bernard, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1541.

(22) Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 11.

(23) Pètillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178*−*180*, 203.

Table 3. Selected IR and NMR Data for New $[M_2Cp_2(\mu\text{-}PRR')_2(CO)_2]$ and $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'R'')(CO)_2]$ Compounds

M	R	R′	R″	compd	ν(CO)[a]	δ(CO)[b] [J_{PC}]	δ(P)[b]	J_{PP}	J_{PW}
Mo	Cy	Cy		**7a**	1851 (d, sh), 1833 (s)		95.4		
Mo	Et	Et		**7b**	1860 (d, sh), 1840 (s)	237.3 [13]	78.7		
Mo	Et	Et		**12**	1930 (vs), 1863 (s), 1817 (s)	241 [4], 237.9[c]	194.7[c]		
Mo	Cy	H		**7c**[d]	1872 (d, sh), 1849 (s)	236.4	45.4		
W	Et	Et		**8b**	1863 (d, sh), 1838 (s)	228.2 [4]	16.7		291
W	Ph	Ph		**8d**	1882 (d, sh), 1852 (s)[e]		34.7		301
Mo	Cy	Cy	H	**9e**	1865 (d, sh), 1839 (s)	238.0 [12], 237.4 [15]	109.9 (PCy_2), 41.7[f]	9	
Mo	^{t}Bu	Cy	H	**9f**	1867 (d, sh), 1837 (s)		170.6 (P^tBu_2), 52.7[f]	<1	
Mo	Ph	Cy	Cy	**9g**	1874 (d, sh), 1848 (s)[g]		107.4 (PCy_2), 83.3	7	
Mo	Ph	Et	Et	**9h**	1880 (d, sh), 1851 (s)		85.6, 85.2	9	
Mo	Ph	Cy	H	**9i**	1878 (d, sh), 1857 (s)		96.4 (PPh_2), 48.1[f]	8	
Mo	Ph	^{t}Bu	^{t}Bu	**9j**	1865 (d, sh), 1853 (s)		174.1 (P^tBu_2), 94.7[f]	4	
Mo	Ph	^{t}Bu	^{t}Bu	**11**	1926 (s), 1871 (m)	248.7[7]	213.0 (P^tBu_2), 148.0[f]	14	
Mo	Ph	^{t}Bu	H	**9k**	1882 (d, sh), 1856 (s)		91.6 (PPh_2), 83.5	8	
W	Cy	Cy	H	**10e**	1860 (d, sh), 1837 (s)	225.3 [5], 224.6	44.7 (PCy_2), −20.1	6	284, 276
W	Ph	Et	Et	**10h**	1873 (d, sh), 1849 (s)	225.3 [4]	32.7 (PPh_2), 20.0	6	305, 287

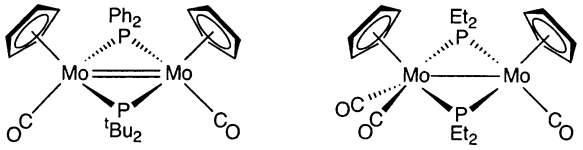
[a] Recorded in toluene solution, unless otherwise stated. ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 300.13 (^{1}H), 121.50 (^{31}P), or 75.47 MHz (^{13}C) unless otherwise stated. δ in ppm relative to internal TMS (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4; J in hertz. [c] Recorded at 193 K. [d] Data for the anti isomer; δ_P 46.2 for the syn isomer. [e] In dichloromethane solution. [f] In toluene-d_8. [g] In tetrahydrofuran solution.

Carbonylation of the bis(diethylphosphido) derivative **3b** is fast at room temperature. When this reaction is carried out at −50 °C, it can be shown that the tricarbonyl intermediate $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$ (**12**) is first formed. Compound **12** can be spectroscopically characterized but was not isolated, as it transforms progressively at room temperature into the corresponding *trans*-dicarbonyl complex **7b**. Tricarbonyl complexes such as **12** are rare species, placed midway between the usually more stable tetracarbonylic or dicarbonylic structures ($[M_2Cp_2(\mu\text{-}X)(\mu\text{-}Y)(CO)_n]$, n = 4, 2). In fact, previous examples of stable group 6 complexes related to **12** are limited to cases where a restricted cis-type conformation is imposed by the bridging ligands, as it is in the case of $[Mo_2Cp_2(\mu\text{-}PhPC_6H_4PPh)(CO)_3]$[12a] or $[M_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4SiMe_2C_5H_4)(\mu\text{-}PMe_2)_2(CO)_3]$ (M = Mo, W).[24] The relevance of complex **12** in the present context is derived from its spontaneous thermal decay to the corresponding *trans*-dicarbonyl derivative **7b**, as this allows us to propose it as a general intermediate in the carbonylation pathway of the triply bonded complexes **3**−**6**, as we will discuss later on.

The above results indicate that, despite the formal unsaturation of all complexes **7**−**10**, these doubly bonded species are stable toward carbonylation. To this we must add the knowledge that Hayter's compound $[Mo_2Cp_2(\mu\text{-}PMe_2)_2(CO)_4]$ does not decarbonylate in refluxing toluene,[3a] whereas $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PPhH)(CO)_4]$ does it slowly to give the corresponding dicarbonyl $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PPhH)(CO)_2]$,[14a] a close analogue of complexes **9**. All this seems to clearly indicate that the stability of the unsaturated dicarbonyls **7**−**10** and related bis(phosphido) complexes toward CO addition is mainly steric in origin.

Structural Characterization of Compounds 7−12. Spectroscopic data for dicarbonylic complexes **7**−**10** are all similar and indicative of the presence of two bridging phosphido groups and two terminal carbonyl ligands (Table 3). The relative trans geometry of the latter is derived from the relative intensities of the C−O stretching bands (weak and strong, in order of decreasing frequency).[25] This arrangement implies the presence of a C_2 axis passing through the phosphorus atoms, which makes equivalent both hydrocarbon groups R on the PR_2 bridges, easily denoted by the appearance of single resonances for P−C atoms in the ^{13}C NMR spectra (see Experimental Section). This symmetry element is absent in those complexes with PRR′ bridges, which then exhibit separated resonances for the carbonyl or cyclopentadienyl ligands (Table 3 and Experimental Section). The structure of compounds **7**−**10** is therefore the same as that crystallographically determined for $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$,[13] for which the short intermetallic distance of ca. 2.71 Å justifies the formulation of a double intermetallic bond.

Chart 4



11 **12**

The ^{31}P spectra of *trans*-dicarbonyl complexes **7**−**10** reveal two characteristic features: first, a strong shielding of the P nucleus (100−160 ppm) relative to the corresponding triply bonded monocarbonyls and, second, a low J(PP) coupling (when observed, 4−9 Hz). These spectroscopic features have been also recognized for the related complexes $[Mo_2L_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ (L = C_5H_5, C_5H_4Me)[26] and $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PPhH)(CO)_2]$,[14a] and they seem to be characteristic of these *trans*-dicarbonylic structures with an essentially planar M_2P_2 core. In this context, it is interesting to note that the *cis*-dicarbonyl **11**, which possibly has a somewhat puckered Mo_2P_2 core (Chart 4), exhibits ^{31}P shifts 40−50 ppm higher than those corresponding to the trans isomer **9j**. Thus, a simple conformational change, rather than a modification of the intermetallic bond order (and the M−M length), accounts for about half the shielding observed between triply and doubly bonded complexes.

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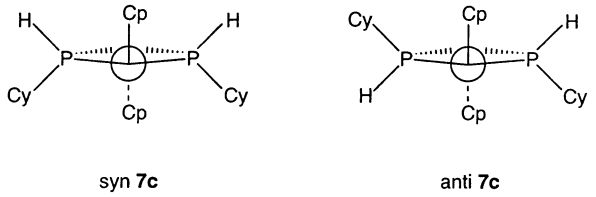


Figure 2. Schematic view of the isomers observed for compound **7c** along the Mo−Mo bond (CO groups omitted).

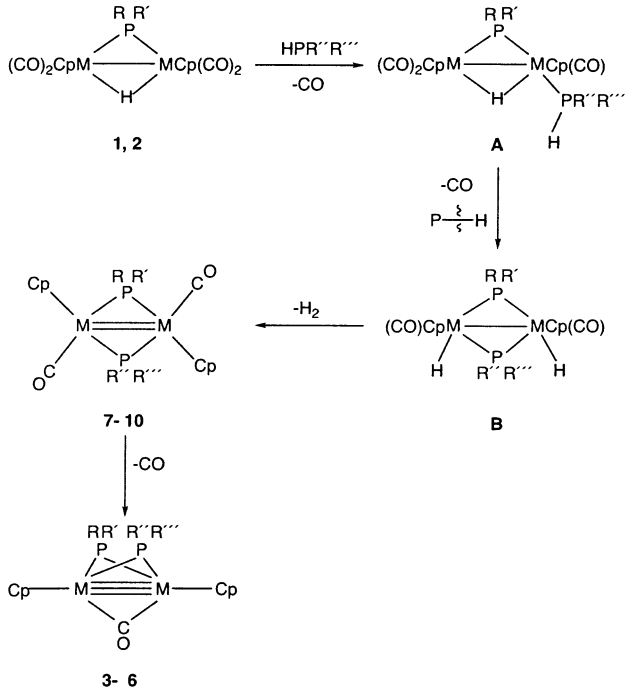
The structure of compound **11** is firmly supported on spectroscopic data. The cis arrangement of the carbonyl ligands is clearly denoted by the relative intensities of the C−O stretching bands (strong and medium, in order of decreasing frequencies).[25] The phosphido bridges are now placed on a symmetry plane rather than along the C_2 axis present in the trans isomers. This implies that both R groups attached to the phosphorus bridges are not equivalent, in agreement with the observation of two P−C(Ph) or P−C(^{t}Bu) ^{13}C resonances.

Compound **7c** is obtained as a mixture of two isomers, presumably differing in the relative orientation of both PHCy groups (syn and anti isomers; see Figure 2). Crystallization of the mixture allows the isolation of the minor isomer as a pure solid, which can be unambiguously identified as the anti isomer. This is derived from the observation of single ^{13}C or ^{1}H resonances for both carbonyl and cyclopentadienyl ligands of the molecule. In contrast, the major isomer exhibits separated ^{1}H resonances for both Cp ligands, and it is thus identified as the syn isomer. These assignments also lead to the reasonable suggestion that the relative conformation of the phosphido bridges is preserved during the carbonylation/decarbonylation processes connecting compounds **3** and **7**, so that monocarbonyl isomers **A** would lead to dicarbonyl syn isomers while isomers **B** would lead to anti isomers and vice versa.

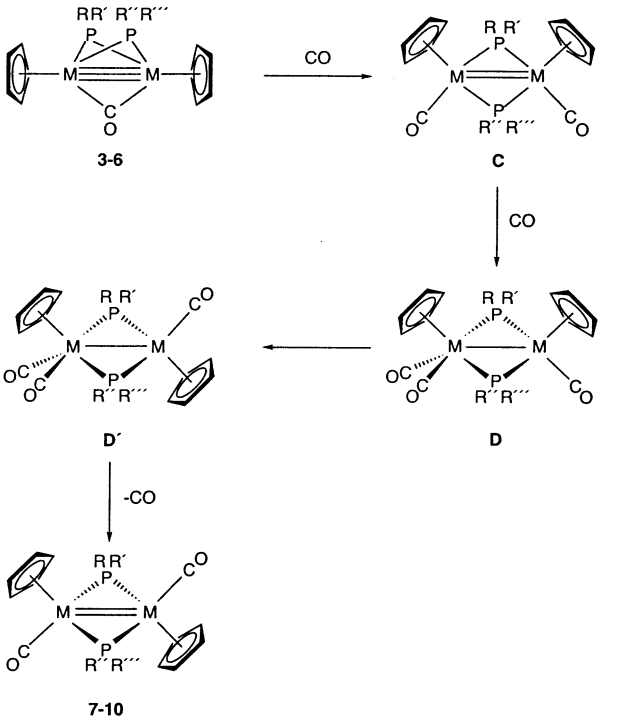
The tricarbonylic nature of compound **12** is clearly denoted by the presence of three strong C−O stretching bands in its IR spectrum. The frequencies and intensities are very similar to those found for [$Mo_2(\mu$-η^5:η^5-$C_5H_4SiMe_2C_5H_4)(\mu$-$PMe_2)_2(CO)_3$], for which an X-ray study revealed the presence of a plane of symmetry containing the metal atoms and relating the phosphido bridges and the carbonyl ligands of the dicarbonylic moiety.[24] We then conclude that compound **12** adopts a similar structure (Chart 4). In agreement with this, the CO ligands give rise to two ^{13}C resonances in the terminal region, with relative intensities 1:2, and the Cp or Et groups exhibit two chemical environments in each case. The ^{31}P chemical shift of the phosphido bridges in **12** (194.7 ppm) is similar to that of the monocarbonyl complex **3b** (212.3 ppm), and both values are much higher than that of the *trans*-dicarbonyl **7b** (81.3 ppm). This again illustrates the very anomalous low shift of the doubly bonded dicarbonyls, so that the observed values can be hardly correlated in a simple way with the intermetallic bond order or other geometric parameter related to it as, for example, M−M lengths or M−P−M angles.

Reaction Pathways in the Formation of Bis(phosphido) Complexes. Although the present work is mainly synthetic in nature and no mechanistic studies have been attempted, we have recognized some trends and have identified intermediates in some cases; therefore, we can give a general picture of the main reaction pathways operating in this highly efficient photochemical preparation of bis(phosphido) complexes (Scheme 3). The photochemical route from [$M_2Cp_2(CO)_6$] to the phosphido hydrido complexes **1** and **2** is possibly not very different from the thermal route (Scheme 1) and will not be discussed. The photochemical reaction of the latter with a second molecule of phosphine having a P−H bond is a critical step toward the bis(phosphido) derivatives and would be surely initiated by simple carbonyl substitution to yield the tricarbonyl intermediate **A**. It has been shown previously that the photochemical reaction of [$Mo_2Cp_2(\mu$-H)(μ-$PPh_2)(CO)_4$] with tertiary phosphines or phosphites affords slowly (ca. 24 h) the tricarbonyl derivatives [$Mo_2Cp_2(\mu$-H)(μ-$PPh_2)$-$(CO)_3(PR_3)$] (as a mixture of two isomers).[8] This is in contrast with the short reaction times required in our reactions (ca. 1 h). This difference can be explained by considering the coupling to the substitution step of an irreversible process such as hydrogen elimination. Indeed, a further decarbonylation on intermediate **A** could promote the oxidative addition of the P−H bond in the incoming phosphine to give dihydride **B**, which, upon H_2 elimination, would yield the *trans*-dicarbonyl complexes **7**−**10** (experimentally observed as intermediate species in some cases). The latter in turn would rapidly decarbonylate under the UV light to finally yield the triply bonded monocarbonyls **3**−**6**. In the case of the reaction of [$Mo_2Cp_2(\mu$-H)(μ-$PPh_2)(CO)_4$] with HP^{t}Bu$_2$, the elimination of one of the ^{t}Bu groups leading to compound **5k** must occur at the intermediate **A** (i.e., before a bridging P^{t}Bu$_2$ is formed). This can occur in several reasonable ways. For example, a β-elimination of the ^{t}Bu group on P would liberate 2-methylpropene to generate a bonded PH$_2$^{t}Bu ligand, which then would transform (via the corresponding intermediate **B**) into a bridging PH^{t}Bu group. Alternatively, the bonded PH^{t}Bu$_2$ ligand can eliminate ^{t}BuH to generate a phos-

Scheme 3. Photochemical Synthesis of the Triply Bonded Complexes 3−6



Scheme 4. Carbonylation Reactions of the Triply Bonded Complexes 3−6



phinidene (P^{t}Bu) intermediate which, upon insertion into the hydrido bridge, would also lead to a bridging PH^{t}Bu group. Although we have not found any precedent for this degradation of a bonded PH^{t}Bu$_2$ ligand, there are precedents of related (P−C into P−H) transformations for phosphorus ligands having very sterically demanding groups.[27]

The fast photochemical transformation of the dicarbonyls **7**−**10** into the triply bonded complexes **3**−**6** cannot be reproduced thermally even under severe heating. In contrast, the latter are rapidly carbonylated at room temperature, except for those complexes incorporating the bulky PCy$_2$ or P^{t}Bu$_2$ groups, which require a moderate heating of the solution (up to 80 °C) if carbonylation is to be completed in a reasonable time. Actually, the transformation of monocarbonyls **3**−**6** into the *trans*-dicarbonyls **7**−**10** does not seem to be a simple process. The reactions of carbon monoxide with the di-*tert*-butylphosphido complex **5j** and the diethylphosphido complex **3b** are especially revealing in this respect and allow us to draw a general reaction pathway for all these reactions (Scheme 4). As we have shown above, complex **5j** reacts with CO at 80 °C to yield first the *cis*-dicarbonyl complex **11**. We assume that similar cis complexes (**C** in Scheme 4) are formed in all cases but are not detected. Separate experiments have shown that complex **11** does not transform into its trans isomer **9j** unless CO is present (and even so, it does it slowly at 80 °C). We trust this is because the cis−trans isomerization requires the formation of the tricarbonylic intermediate **D**, which we assume to be the next general intermediate in these reactions. Complex **12** is, of course, the representative example of such an intermediate and decays specifically to the corresponding *trans*-dicarbonyl complex **7b**, as we have shown above. However, spectroscopic data for **12** suggest that the Cp ligands are in a relative cis geometry (Chart 4). Therefore, we must assume that these tricarbonyl intermediates can experience some cis−trans rearrangement (to give **D′**) before CO is lost and the final *trans*-dicarbonyls **7**−**10** are formed. In this context, it is interesting to note that similar proposals have been made in order to account for the CO-catalyzed cis−trans isomerization of the related thiolate complexes [Mo$_2$Cp$_2$(μ-SMe)$_2$(CO)$_2$] and the reduction products of the cations [Mo$_2$Cp$_2$(μ-SR)$_2$(CO)$_3$(MeCN)]$^{2+}$ (R = Me, Ph).[23]

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Experimental Section

General Comments. All manipulations and reactions were carried out under a nitrogen (99.9995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures[28] and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 65−70 °C. Compounds [W$_2$Cp$_2$(CO)$_x$] (x = 6,[29] 4[30]) and [Mo$_2$Cp$_2$(μ-H)(μ-PR$_2$)(CO)$_4$] (R = ^{t}Bu,[5] Ph[8]) were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz Schlenk tubes, refrigerated by tap water (ca. 15 °C). 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 refrigerated by tap water. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired. Carbonylation experiments were carried out using Schlenk tubes equipped with Young valves. Filtrations were performed using diatomaceous earth. NMR spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}) or 75.47 MHz (^{13}C{^{1}H}) at 290 K on CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

Preparation of [Mo$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_4$] (1a). A toluene solution (35 mL) of [Mo$_2$Cp$_2$(CO)$_6$] (0.625 g, 1.28 mmol) and HPCy$_2$ (260 μL, 1.28 mmol) was refluxed for 1 h 15 min to yield a dark orange solution, which was filtered. Petroleum ether was then added, and the mixture was allowed to crystallize at −20 °C to give compound **1a** 0.532 g, 84%) as a dark orange microcrystalline solid. Anal. Calcd for C$_{26}$H$_{33}$O$_4$PMo$_2$ (**1a**): C, 49.38; H, 5.22. Found: C, 49.57; H, 5.15. ^{1}H NMR: δ 5.32 (s, 10H, Cp), 2.81−0.79 (m, 22H, Cy), −13.2 (d, J_{HP} = 34, 1H, μ-H). ^{13}C{^{1}H} NMR: δ 244.1 (d, J_{CP} = 19, 2 × CO), 235.9 (s, 2 × CO), 90.4 (s, Cp), 41.1 (d, J_{PC} = 15, C^1(Cy)), 32.2, 30.2 (2 × s, C^2 and C^6(Cy)), 28.2, 27.6 (2 × s, C^3 and C^5(Cy)), 27.15 (s, C^4(Cy)).

Preparation of [Mo$_2$Cp$_2$(μ-H)(μ-PEt$_2$)(CO)$_4$] (1b). A toluene solution (25 mL) of [Mo$_2$Cp$_2$(CO)$_6$] (0.300 g, 0.61 mmol) and HPEt$_2$ (83 μL, 0.71 mmol) was heated at 80 °C for 1 h 20 min. Then, a further 50 μL (0.43 mmol) of HPEt$_2$ was added, and heating was continued for 20 min. Solvent was then removed under vacuum, the residue was dissolved in a minimum amount of toluene, and this solution was chromatographed on alumina (activity IV). Elution with dichloromethane/petroleum ether (1:3) gave an orange band. Removal of solvents from the latter yielded compound **1b** as an orange microcrystalline solid (0.192 g, 61%). Anal. Calcd for C$_{18}$H$_{21}$O$_4$PMo$_2$ (**1b**): C, 41.23; H, 4.00. Found: C, 41.35; H, 3.95. ^{1}H NMR

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(toluene-d_8): δ 4.73 (s, 10H, Cp), 2.82 (m, 2H, CH_2), 1.05 (dt, $J_{HP} = 16$, $J_{HH} = 7$, 6H, CH_3), 0.78 (m, 2H, CH_2), −12.3 (d, $J_{HP} = 35$, 1H, μ-H). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 243.5 (d, $J_{CP} = 19$, 2 × CO), 235.9 (s, 2 × CO), 90.3 (s, Cp), 28.8 (d, $J_{CP} = 19$, CH_2), 11.4 (d, $J_{CP} = 5$, CH_3).

Preparation of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCyH)(CO)_4]$ (1c). The procedure is completely analogous to that described for **1a**. By using $[Mo_2Cp_2(CO)_6]$ (0.35 g, 0.71 mmol) and H_2PCy (96 μL, 0.71 mmol) (reaction time 1 h) compound **1c** is obtained as a yellow microcrystalline solid (0.325 g, 85%). Anal. Calcd for $C_{20}H_{23}O_4PMo_2$ (**1c**): C, 43.65; H, 4.18. Found: C, 43.50; H, 4.25. ^1H NMR: δ 5.35 (dd, $J_{PH} = 325$, $J_{HH} = 4$, 1H, PH), 5.20 (s, 5H, Cp), 5.12 (s, 5H, Cp), 2.11−1.08 (m, 11H, Cy), −12.4 (d, $J_{HP} = 35$, 1H, μ-H). $^{13}C\{^1H\}$ NMR: δ 242.8 (d, $J_{PC} = 19$, CO), 242.2 (d, $J_{PC} = 20$, CO), 237.1 (s, CO), 236.7 (s, CO), 90.6, 90.1 (2 × s, 2 × Cp), 42.8 (d, $J_{PC} = 22$, C^1(Cy)), 36.3, 35.9 (2 × s, C^2 and C^6(Cy)), 27.9, 27.8 (2 × d, $J_{PC} = 12.5$, C^3 and C^5(Cy)), 26.5 (s, C^4(Cy)).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4]$ (2a). A diglyme solution (30 mL) of $[W_2Cp_2(CO)_4]$ (ca. 0.75 mmol, prepared in situ) and $HPCy_2$ (155 μL, 0.766 mmol) was stirred at room temperature for 16 h under a N_2 purge to give a dark orange mixture. Solvent was then removed under vacuum, the residue was dissolved in a minimum amount of toluene, and this solution was chromatographed on silica gel (Aldrich, 70−230 mesh). Elution with dichloromethane/petroleum ether (2:5) gave an orange band. Removal of solvents from the latter yielded compound **2a** as an orange microcrystalline solid (0.355 g, 58%). Anal. Calcd for $C_{26}H_{33}O_4PW_2$ (**2a**): C, 38.63; H, 4.08. Found: C, 38.93; H, 4.12. ^1H NMR: δ 5.44 (s, 10H, Cp), 2.70−0.89 (m, 22H, Cy), −16.40 (d, $J_{HP} = 24$, $J_{HW} = 40$, 1H, μ-H). $^{13}C\{^1H\}$ NMR: δ 232.2 (br, 2 × CO), 224.4 (br, 2 × CO), 88.0 (s, Cp), 39.2 (d, $J_{PC} = 23$, C^1(Cy)), 30.8, 30.1 (2 × s, br, C^2 and C^6(Cy)), 27.1, 26.5 (2 × s, br, C^3 and C^5(Cy)), 26.2 (s, C^4(Cy)).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PEt_2)(CO)_4]$ (2b). The procedure is analogous to that described for **2a**, but with $HPEt_2$ (90 μL, 0.785 mmol) instead and a reaction time of 5 h at 50 °C. After chromatography on silica, compound **2b** was obtained along with a small amount of $[W_2Cp_2(CO)_6]$. Filtration of the mixture through alumina (activity IV) and removal of solvents under vacuum yielded compound **2b** as a pure orange microcrystalline solid (0.320 g, 61%). Anal. Calcd for $C_{18}H_{21}O_4PW_2$ (**2b**): C, 30.87; H, 3.00. Found: C, 30.81; H, 3.01. ^1H NMR: δ 5.30 (s, 10H, Cp), 3.07 (br, 2H, CH_2), 1.04 (br, 2H, CH_2), 1.32 (dt, $J_{PH} = 17$, $J_{HH} = 7$, 6H, CH_3), −14.93 (d, $J_{HP} = 25$, $J_{HW} = 39$, 1H, μ-H). $^{13}C\{^1H\}$ NMR: δ 233.8 (d, $J_{PC} = 20$, 2 × CO), 225.6 (s, 2 × CO), 89.6 (s, Cp), 28.1 (d, $J_{PC} = 26$, CH_2), 12.2 (d, $J_{PC} = 4$, CH_3).

Preparation of $[W_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (2d). The procedure is completely analogous to that described for **2a**. $[W_2Cp_2(CO)_4]$ (ca. 2 mmol) in diglyme (40 mL) and $HPPh_2$ (350 μL, 2.01 mmol), were reacted for 2 h at 60 °C under a N_2 purge. After workup, compound **2d** was obtained as an orange microcrystalline solid (0.996 g, 63%). Anal. Calcd for $C_{26}H_{21}O_4PW_2$ (**2d**): C, 39.21; H, 2.64. Found: C, 39.30; H, 2.71. ^1H NMR: δ 7.90−7.10 (m, 10H, Ph), 5.00 (s, 10H, Cp), −14.83 (d, $J_{HP} = 27$, $J_{HW} = 39$, 1H, μ-H). $^{13}C\{^1H\}$ NMR (233 K): δ 232.3 (d, $J_{PC} = 17$, 2 × CO), 224.2 (s, 2 × CO), 140.7 (d, $J_{PC} = 44$, C^1(Ph)), 133.0−126.0 (m, Ph), 90.1 (s, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(\mu\text{-}CO)]$ (3a). A toluene solution (30 mL) of $[Mo_2Cp_2(CO)_6]$ (0.200 g, 0.41 mmol) and $HPCy_2$ (260 μL, 1.28 mmol) was irradiated with UV−visible light at 15 °C for 2 h 30 min while nitrogen was gently bubbled through the solution, to give a black-green mixture. Solvent was then removed under vacuum, the residue was dissolved in a minimum amount of toluene, and this solution was chromatographed on alumina (activity IV). Elution with petroleum ether gave a yellow-green fraction containing unidentified phosphorus side products, which were discarded. Elution with dichloromethane/petroleum ether (2:1) gave a purple band. Removal of solvents from the latter yielded compound **3a** as a purple microcrystalline solid (0.177 g, 60%). Anal. Calcd for $C_{35}H_{54}OP_2Mo_2$ (**3a**): C, 56.46; H, 7.26. Found: C, 56.39; H, 7.21. ^1H NMR: δ 5.57 (s, 10H, Cp), 1.90−1.10 (m, 44H, Cy). $^{13}C\{^1H\}$ NMR: δ 307.0 (t, $J_{PC} = 7$, μ-CO), 90.5 (s, Cp), 44.4 (AA′X multiplet, $J_{CP} + J_{CP'} = 15$, C^1(Cy)), 34.5, 30.8 (2 × s, 2 × C^2(Cy)), 28.2(AA′X multiplet, $J_{CP} + J_{CP'} = 10$, C^3(Cy)), 27.8 (AA′X multiplet, $J_{CP} + J_{CP'} = 11$, C^3(Cy)), 26.52, 26.46 (2 × s, 2 × C^4(Cy)). The second resonance of the C^1(Cy) carbon atoms was obscured by that from the solvent.

Preparation of $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(\mu\text{-}CO)]$ (3b). $[Mo_2Cp_2(CO)_6]$ (0.300 g, 0.61 mmol) and $HPEt_2$ (230 μL, 2.00 mmol) were reacted for 3 h as described for **3a**. After workup, compound **3b** was obtained as a purple microcrystalline solid (0.275 g, 87%). Anal. Calcd for $C_{19}H_{30}OP_2Mo_2$ (**3b**): C, 43.19; H, 5.68. Found: C, 42.95; H, 5.70. ^1H NMR: δ 5.48 (s, 10H, Cp), 1.82 (dq, $J_{HP} = 16$, $J_{HH} = 8$, 4H, CH_2), 1.70 (m, 4H, CH_2), 0.97 (dt, $J_{HP} = 16$, $J_{HH} = 8$, 6H, CH_3), 0.46 (dt, $J_{HP} = 19$, $J_{HH} = 8$, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 298.0 (t, $J_{PC} = 7$, μ-CO), 90.0 (s, Cp), 36.8, 31.8 (2 × m, 2 × CH_2), 13.3, 11.1 (2 × s, 2 × CH_3).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCyH)_2(\mu\text{-}CO)]$ (3c). $[Mo_2Cp_2(CO)_6]$ (0.150 g, 0.31 mmol) and H_2PCy (100 μL, 0.75 mmol) were reacted for 7.5 h as described for **3a**. After workup (elution with dichloromethane/petroleum ether (1:1)), compound **3c** was obtained as a blue greenish microcrystalline solid (0.123 g, 69%). This material was shown by NMR to be a mixture of two isomers (**A** and **B**, see text; ratio **A**:**B** = 6:4). Anal. Calcd for $C_{23}H_{34}OP_2Mo_2$ (**3c**): C, 47.60; H, 5.86. Found: C, 47.45; H, 5.83. Isomer **A**: ^1H NMR δ 7.33 (dd, $J_{HP} = 334$, $J_{HH} = 2$, 2H, PH), 5.51 (s, 10H, Cp), 1.80−0.70 (m, 22H, Cy); $^{13}C\{^1H\}$ NMR δ 304.7 (t, $J_{PC} = 7$, μ-CO), 90.3 (s, Cp), 43.5 (AA′X multiplet, $J_{CP}+J_{CP'} = 27$, C^1(Cy)), 32.8−25.2 (Cy). Isomer **B**: ^1H NMR δ 7.42 (dd, $J_{HP} = 336$, 2, 1H, PH), 7.22 (dd, $J_{HP} = 326$, 4, 1H, PH), 5.51 (s, 10H, Cp); $^{13}C\{^1H\}$ NMR δ 303.2 (t, $J_{PC} = 7$, μ-CO), 90.0 (s, Cp), 45.9 (d, $J_{CP} = 28$, C^1(Cy)), 44.0 (d, $J_{CP} = 26$, C^1(Cy)), 32.8−25.2 (Cy).

Preparation of $[W_2Cp_2(\mu\text{-}PEt_2)_2(\mu\text{-}CO)]$ (4b). $[W_2Cp_2(CO)_6]$ (0.100 g, 0.150 mmol) and $HPEt_2$ (45 μL, 0.39 mmol) were reacted for 1 h 15 min as described for **3a**. After workup, compound **4b** was isolated as a purple microcrystalline solid (0.086 g, 82%). Anal. Calcd for $C_{19}H_{30}OP_2W_2$ (**4b**): C, 32.40; H, 4.26. Found: C, 32.32; H, 4.19. ^1H NMR: δ 5.31 (s, 10H, Cp), 1.90 (m, 8H, CH_2), 0.89 (dt, $J_{HP} = 17$, $J_{HH} = 7$, 6H, CH_3), 0.41 (dt, $J_{HP} = 18$, $J_{HH} = 8$, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 305.0 (s, μ-CO), 88.8 (s, Cp), 46.2 (AA′X multiplet, $J_{CP} + J_{CP'} = 23$, CH_2), 33.7 (AA′X multiplet, $J_{CP} + J_{CP'} = 25$, CH_2), 13.0, 9.1 (2 × s, 2 × CH_3).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (4d). $[W_2Cp_2(CO)_6]$ (0.150 g, 0.225 mmol) and $HPPh_2$ (78 μL, 0.45 mmol) were reacted in tetrahydrofuran (25 mL) for 1 h 40 min as described for **3a**. After workup, compound **4d** was isolated as a purple microcrystalline solid (0.157 g, 78%). Anal. Calcd for $C_{35}H_{30}OP_2W_2$ (**4b**): C, 46.89; H, 3.35. Found: C, 47.01; H, 3.24. ^1H NMR: δ 7.80−6.55 (m, 20H, Ph), 5.80 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR: δ 303.9 (s, μ-CO), 154.1 (d, $J_{CP} = 42$, C^1(Ph)), 144.0 (d, $J_{CP} = 48$, C^1(Ph)), 131.5−125.0 (m, Ph), 91.0 (s, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PCyH)(\mu\text{-}CO)]$ (5e). Compound **1a** (0.090 g, 0.14 mmol) and H_2PCy (20 μL, 0.15 mmol) were reacted for 40 min as described for **3a**. After workup, compound **5e** was isolated as a purple microcrystalline solid (0.078 g, 84%). Anal. Calcd for $C_{29}H_{44}OP_2Mo_2$ (**5e**): C, 52.58; H, 6.65. Found: C, 52.25; H, 6.53. This material was shown by NMR to be a mixture of two isomers (**D** and **E**, see text; ratio **D**:**E** = 7:3). Pure isomer **D** could be isolated by fractional crystallization of the mixture, thus allowing the unequivocal assignment of NMR resonances. Isomer **D**: ^1H NMR δ 7.40 (ddd, $J_{HP} = 333$, 2, $J_{HH} = 2$, 1H, PH), 5.54 (s, 10H, Cp), 1.90−0.41 (m, 33H, Cy); $^{13}C\{^1H\}$ NMR δ 306.7 (s, br, μ-CO), 91.0 (s, Cp), 46.0−26.5 (Cy). Isomer **E**: ^1H NMR δ 6.88 (dd, $J_{HP} = 322$, 7, 1H, PH), 5.61 (s, 10H, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}PCyH)(\mu\text{-}CO)]$ (5f). Compound **1c** (0.035 g, 0.06 mmol) and HP^tBu_2 (15 μL, 0.08 mmol) were reacted for 1 h as described for **3a**. After workup, compound **5f** was obtained as a purple solid (0.031 g, 81%). Anal. Calcd for $C_{25}H_{40}OP_2Mo_2$ (**5f**): C, 49.19; H, 6.56. Found: C, 48.98; H, 6.51. ^{1}H NMR (toluene-d_8): δ 7.15 (ddd, J_{HP} = 337, 4, J_{HH} = 1, 1H, PH), 5.53 (s, 10H, Cp), 1.74−0.55 (m, 11H, Cy), 0.93 (d, J_{HP} = 14, 9H, ^{t}Bu), 0.77 (d, J_{HP} = 13, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (benzene-d_6): δ 297.8 (s, μ-CO), 90.1 (s, Cp), 44.2 (d, J_{CP} = 28, C^1(Cy)), 43.6 (d, J_{CP} = 8, C^1(^{t}Bu)), 43.0 (d, J_{CP} = 10, C^1(^{t}Bu)), 33.4 (d, J_{CP} = 4, C^2(^{t}Bu)), 32.7 (s, C^2(Cy)), 32.1 (d, J_{CP} = 2, C^2(^{t}Bu), 26.2 (d, J_{CP} = 13, C^3(Cy)), 25.1 (s, C^4(Cy)).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (5g). $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (0.100 g, 0.16 mmol) and $HPCy_2$ (35 μL, 0.17 mmol) were reacted for 1 h as described for **3a**. After workup, compound **5g** was obtained as a black microcrystalline powder (0.093 g, 79%). Anal. Calcd for $C_{35}H_{42}OP_2Mo_2$ (**5g**): C, 57.39; H, 5.74. Found: C, 57.23; H, 5.69. ^{1}H NMR: δ 7.31−6.62 (m, 10H, Ph), 5.58 (s, 10H, Cp), 2.00−0.40 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 306.3 (t, J_{CP} = 7, μ-CO), 153.9 (d, J_{CP} = 31, C^1(Ph)), 145.2 (d, J_{CP} = 40, C^1(Ph)), 133.1−126.6 (Ph), 91.6 (s, Cp), 52.9 (d, J_{CP} = 17, C^1(Cy)), 44.0 (d, J_{CP} = 13, C^1(Cy)), 34.3−26.0 (Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PEt_2)(\mu\text{-}CO)]$ (5h). Complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (0.150 g, 0.242 mmol) and $HPEt_2$ (56 μL, 0.49 mmol) were reacted for 45 min as described for **3a**. After workup, compound **5h** was obtained as a purple microcrystalline solid (0.125 g, 83%). Anal. Calcd for $C_{27}H_{30}OP_2Mo_2$ (**5h**): C, 51.93; H, 4.81. Found: C, 51.65; H, 4.90. ^{1}H NMR: δ 7.27−6.68 (m, 10H, Ph), 5.53 (s, 10H, Cp), 1.70 (dq, J_{HP} = 11, J_{HH} = 8, 2H, CH$_2$), 1.23 (dq, J_{HP} = J_{HH} = 8, 2H, CH$_2$), 0.66 (dt, J_{HP} = 17, J_{HH} = 8, 3H, CH$_3$), 0.47 (dt, J_{HP} = 19, J_{HH} = 8, 3H, CH$_3$). ^{13}C{^{1}H} NMR: δ 304.9 (s, μ-CO), 153.0 (d, J_{CP} = 31, C^1(Ph)), 145.8 (d, J_{CP} = 40, C^1(Ph)), 132.3−126.9 (Ph), 91.5 (s, Cp), 34.6 (d, J_{CP} = 21, CH$_2$), 31.6 (d, J_{CP} = 17, CH$_2$), 13.2 (s, CH$_3$), 10.0 (d, J_{CP} = 6, CH$_3$).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PCyH)(\mu\text{-}CO)]$ (5i). $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (0.125 g, 0.200 mmol) and H_2PCy (35 μL, 0.26 mmol) were reacted for 2 h 15 min as described for **3a**. After workup, compound **5i** was obtained as a purple solid (0.085 g, 65%). A small amount of $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ can be also separated in the chromatography. Anal. Calcd for $C_{29}H_{32}OP_2Mo_2$ (**5h**): C, 53.55; H, 4.92. Found: C, 53.33; H, 5.01. ^{1}H NMR: δ 7.51−6.59 (m, 10H, Ph), 7.01 (d, br, J_{HP} = 339, 1H, PH), 5.51 (s, 10H, Cp), 2.05−0.59 (m, 11H, Cy). ^{13}C{^{1}H} NMR: δ 304.4 (t, J_{CP} = 7, μ-CO), 151.1 (d, J_{CP} = 33, C^1(Ph)), 144.4 (d, J_{CP} = 40, C^1(Ph)), 138.4−127.7 (Ph), 91.9 (s, Cp), 44.6 (d, J_{CP} = 26, C^1(Cy)), 34.1 (s, C^2(Cy)), 27.6 (d, J_{CP} = 13, C^3(Cy)), 26.5 (s, C^4(Cy)).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBu_2)(\mu\text{-}CO)]$ (5j). $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(CO)_4]$ (0.070 g, 0.120 mmol) and $HPPh_2$ (21 μL, 0.12 mmol) were reacted for 45 min as described for **3a**. After workup, compound **5j** was obtained as a red solid (0.085 g, 65%). A small amount of $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ can be also separated in the chromatography. Anal. Calcd for $C_{31}H_{38}OP_2Mo_2$ (**5j**): C, 55.69; H, 5.59. Found: C, 55.39; H, 5.55. ^{1}H NMR: δ 7.35−6.45 (m, 10H, Ph), 5.69 (s, 10H, Cp), 0.82 (d, J_{HP} = 14, 9H, ^{t}Bu), 0.66 (d, J_{HP} = 14, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 306.2 (t, J_{CP} = 7, μ-CO), 155.3 (d, J_{CP} = 33, C^1(Ph)), 143.7 (d, J_{CP} = 37, C^1(Ph)), 133.4−126.4 (Ph), 92.8 (s, Cp), 45.4 (d, J_{CP} = 10, C^1(^{t}Bu)), 41.9 (d, J_{CP} = 8, C^1(^{t}Bu)), 34.7 (d, J_{CP} = 3, CH$_3$)), 33.4 (d, J_{CP} = 5, CH$_3$).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBuH)(\mu\text{-}CO)]$ (5k). $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ (0.200 g, 0.320 mmol) and HP^tBu_2 (90 μL, 0.49 mmol) were reacted for 3 h as described for **3a**. Column chromatography of the reaction mixture with 1:1, 2:1, and 3:1 dichloromethane/petroleum ether mixtures gave fractions containing $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$, compound **5k**, and compound **5j**, respectively. Removal of solvents from the second band yielded complex **5k** as a black solid (0.055 g, 28%). Anal. Calcd for $C_{27}H_{30}OP_2Mo_2$ (**5k**): C, 51.93; H, 4.81. Found: C, 52.15; H, 4.93. ^{1}H NMR: δ 7.11 (d, J_{HP} = 333, 1H, PH), 7.37−6.86 (m, 10H, Ph), 5.52 (s, 10H, Cp), 0.91 (d, J_{HP} = 16, 9H, CH$_3$). ^{13}C{^{1}H} NMR: δ 304.1 (t, J_{CP} = 7, μ-CO), 151.2 (d, J_{CP} = 33, C^1(Ph)), 144.2 (d, J_{CP} = 40, C^1(Ph)), 138.4−127.3 (Ph), 91.9 (s, Cp), 37.0 (d, J_{CP} = 26, C^1(^{t}Bu)), 31.3 (d, J_{CP} = 5, CH$_3$).

Preparation of $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PCyH)(\mu\text{-}CO)]$ (6e). Compound **2a** (0.075 g, 0.093 mmol) and H_2PCy (14 μL, 0.105 mmol) were reacted for 45 min as described for **3a**. After workup, compound **6e** was obtained as a black-blue microcrystalline solid (0.060 g, 75%). Anal. Calcd for $C_{29}H_{44}OP_2W_2$ (**6e**): C, 41.54; H, 5.25. Found: C, 41.32; H, 5.21. This material was shown by NMR to be a 7:3 mixture of two isomers (**D** and **E**, respectively; see text). Isomer **D**: ^{1}H NMR δ 9.14 (ddd, J_{HP} = 348, 3, J_{HH} = 1.6, 1H, PH), 5.77 (s, 10H, Cp), 1.80−0.31 (m, 33H, Cy); ^{13}C{^{1}H} NMR δ 307.5 (s, μ-CO), 90.7 (s, Cp), 49.2−26.4 (Cy). Isomer **E**: ^{1}H NMR δ 8.61 (dd, J_{HP} = 341, 7, J_{HW} = 6, 1H, PH), 5.83 (s, 10H, Cp); ^{13}C{^{1}H} NMR δ 306.2 (s, μ-CO), 91.0 (s, Cp).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PEt_2)(\mu\text{-}CO)]$ (6h). Compound **1b** (0.150 g, 0.242 mmol) and $HPPh_2$ (112 μL, 0.644 mmol) were reacted for 1 h as described for **3a**. After workup (elution with dichloromethane), compound **6h** was obtained as a dark purple microcrystalline solid (0.225 g, 79%). Anal. Calcd for $C_{27}H_{30}OP_2W_2$ (**6h**): C, 40.52; H, 3.75. Found: C, 40.74; H, 3.74. ^{1}H NMR: δ 7.35−7.06 (m, 10H, Ph), 5.76 (s, 10H, Cp), 1.98 (dq, J_{HP} = 11, J_{HH} = 8, 2H, CH$_2$), 1.36 (dq, J_{HP} = 9, J_{HH} = 8, 2H, CH$_2$), 0.59 (dt, J_{HP} = 17, J_{HH} = 8, 3H, CH$_3$), 0.43 (dt, J_{HP} = 19, J_{HH} = 8, 3H, CH$_3$). ^{13}C{^{1}H} NMR: δ 304.4 (s, J_{CW} = 133, μ-CO), 154.8 (d, J_{CP} = 40, C^1(Ph)), 147.4 (d, J_{CP} = 46, C^1(Ph)), 131.5−125.8 (Ph), 89.9 (s, Cp), 37.2 (d, J_{CP} = 26, CH$_2$), 33.0 (d, J_{CP} = 24, CH$_2$), 13.0 (s, CH$_3$), 8.9 (d, J_{CP} = 5, CH$_3$).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCy_2)_2(CO)_2]$ (7a). A toluene solution (6 mL) of compound **3a** (0.075 g, 0.100 mmol) was placed in a Schlenk tube equipped with a Young valve and was frozen by immersion into liquid N_2. After vacuum evacuation, CO was allowed to fill the tube, the valve was closed, and the tube was allowed to reach room temperature. The solution was then further stirred at 80 °C for 3 h to give a dark green solution. Removal of solvents under vacuum and washing of the residue with petroleum ether yielded compound **7a** as a green powder (0.073 g, 93%). Anal. Calcd for $C_{36}H_{54}O_2P_2Mo_2$ (**7a**): C, 55.97; H, 7.00. Found: C, 55.76; H, 7.13. ^{1}H NMR: δ 5.37 (s, 10H, Cp), 2.01−0.78 (m, 44H, Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_2]$ (7b). Compound **3b** (0.100 g, 0.190 mmol) was reacted with CO for 1 h 10 min at room temperature as described for **7a**. After workup, compound **7b** was obtained as a brown-green solid (0.095 g, 90%). Anal. Calcd for $C_{20}H_{30}O_2P_2Mo_2$ (**7b**): C, 43.17; H, 5.40. Found: C, 43.34; H, 5.49. ^{1}H NMR: δ 5.21 (s, 10H, Cp), 2.66 (m, 4H, CH$_2$), 1.42 (m, 4H, CH$_2$), 1.28 (dt, J_{HP} = 16, J_{HH} = 7, 12H, CH$_3$). ^{13}C{^{1}H} NMR: δ 237.3 (t, J_{CP} = 13, CO), 86.4 (s, Cp), 25.5 (AA′X multiplet, J_{CP} + $J_{CP'}$ = 21, CH$_2$), 12.1 (s, CH$_3$).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCyH)_2(CO)_2]$ (7c). $[Mo_2Cp_2(CO)_6]$ (0.150 g, 0.310 mmol) and H_2PCy (100 μL, 0.75 mmol) were reacted for 1 h 15 min as described for **3a**. After workup (elution with dichloromethane/petroleum ether (1:3)) compound **7c** was obtained as a dark green solid (0.158 g, 84%). This material was shown by NMR to be a 6:4 mixture of two isomers (syn and anti; see text). The anti isomer could be separated by fractional crystallization from toluene/petroleum ether. Anal. Calcd for $C_{24}H_{34}O_2P_2Mo_2$ (**7c**): C, 47.38; H, 5.59. Found: C, 47.35; H, 5.61. Anti isomer: ^{1}H NMR (benzene-d_6) δ 5.55 (dd, J_{HP} = 336, 6, 1H, PH), 5.19 (s, 10H, Cp), 2.45−1.20 (m, 22H, Cy); ^{13}C{^{1}H} NMR δ 236.4 (s, CO), 88.3 (s, Cp), 42.5 (d, J_{CP} = 29, C^1(Cy)), 36.0, 35.3 (2 × s, C^2(Cy) and C^6(Cy)), 28.0, 27.9 (2 × d, J_{CP} = 10, C^3(Cy) and C^5(Cy)), 26.6 (s, C^4(Cy)).

Preparation of $[W_2Cp_2(\mu\text{-}PEt_2)_2(CO)_2]$ (8b). Complex **4b** (0.086 g, 0.122 mmol) was reacted with CO for 10 min at room temperature as described for **7a**. After workup, compound **8b**

was obtained as a green solid (0.081 g, 90%). Anal. Calcd for $C_{20}H_{30}O_2P_2W_2$ (**8b**): C, 32.80; H, 4.10. Found: C, 32.90; H, 4.15. ^{1}H NMR: δ 5.31 (s, 10H, Cp), 2.80 (m, 4H, CH_2), 1.37 (m, 16H, CH_2 and CH_3). ^{13}C{^{1}H} NMR: δ 228.2 (t, J_{CP} = 4, CO), 85.1 (s, Cp), 29.2 (AA′X multiplet, $J_{CP} + J_{CP'}$ = 30, CH_2), 13.5 (s, CH_3).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (8d). Complex **4d** (0.090 g, 0.100 mmol) was reacted with CO for 10 min at room temperature as described for **7a**. After workup, compound **8d** was obtained as a green solid (0.075 g, 81%). Anal. Calcd for $C_{36}H_{30}O_2P_2W_2$ (**8d**): C, 46.77; H, 3.25. Found: C, 46.66; H, 3.19. ^{1}H NMR: δ 7.80−7.15 (m, 20H, Ph), 5.43 (s, 10H, Cp).

Preparation of $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PCyH)(CO)_2]$ (9e). Complex **5e** (0.080 g, 0.120 mmol) was reacted with CO for 45 min at room temperature as described for **7a**. After workup, compound **9e** was obtained as a microcrystalline green powder (0.065 g, 79%). Anal. Calcd for $C_{30}H_{44}O_2P_2Mo_2$ (**9e**): C, 52.18; H, 6.38. Found: C, 52.25; H, 6.33. ^{1}H NMR: δ 5.40, 5.35 (2 × s, 2 × 5H, 2 × Cp), 5.03 (ddd, J_{HP} = 339, 6, J_{HH} = 2, 1H, PH), 2.51−1.08 (m, 33H, Cy). ^{13}C{^{1}H} NMR: δ 238.0 (t, J_{CP} = 12, CO), 237.4 (t, J_{CP} = 15, CO), 88.2 (s, Cp), 88.0 (s, Cp), 45.7−26.7 (Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}P^tBu_2)(\mu\text{-}PCyH)(CO)_2]$ (9f). Complex **5f** (0.035 g, 0.06 mmol) was reacted with CO for 1.5 h at 60 °C as described for **7a**. After workup, compound **9f** was obtained as a green solid (0.031 g, 86%). Anal. Calcd for $C_{26}H_{40}O_2P_2Mo_2$ (**9f**): C, 48.91; H, 6.27. Found: C, 48.75; H, 6.22. ^{1}H NMR: δ 5.40, 5.32 (2 × s, 2 × 5H, 2 × Cp), 1.30 (d, J_{HP} = 13, 9H, CH_3), 1.27 (d, J_{HP} = 14, 9H, CH_3), 2.30−1.20 (m, 11H, Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PCy_2)(CO)_2]$ (9g). Complex **5g** (0.075 g, 0.102 mmol) was reacted with CO for 45 min at 50 °C as described for **7a**. After workup, compound **9g** was obtained as a green solid (0.072 g, 95%). Anal. Calcd for $C_{36}H_{42}O_2P_2Mo_2$ (**9g**): C, 56.85; H, 5.53. Found: C, 56.64; H, 5.58. ^{1}H NMR: δ 7.65−7.18 (m, 10H, Ph), 5.38 (s, 10H, Cp), 2.00−1.05 (m, 22H, Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PEt_2)(CO)_2]$ (9h). Complex **5h** (0.040 g, 0.064 mmol) was reacted with CO for 30 min at room temperature as described for **7a**. After workup, compound **9h** was isolated as a black-green solid (0.038 g, 90%). Anal. Calcd for $C_{28}H_{30}O_2P_2Mo_2$ (**9h**): C, 51.54; H, 4.60. Found: C, 51.69; H, 4.69. ^{1}H NMR: δ 7.57−7.05 (m, 10H, Ph), 5.25 (s, 10H, Cp), 2.73, 1.57 (2 × m, 2 × 2H, 2 × CH_2), 1.35 (m, 6H, CH_3).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PCyH)(CO)_2]$ (9i). Complex **5i** (0.090 g, 0.138 mmol) was reacted with CO for 5 min at room temperature as described for **7a**. After workup, compound **9i** was obtained as a green solid (0.082 g, 88%). Anal. Calcd for $C_{30}H_{32}O_2P_2Mo_2$ (**9i**): C, 53.11; H, 4.72. Found: C, 52.98; H, 4.63. ^{1}H NMR: δ 7.75−7.10 (m, 10H, Ph), 5.39, 5.31 (2 × s, 2 × 5H, 2 × Cp), 5.36 (d, br, J_{HP} = 339, 1H, PH), 2.01−0.83 (m, 11H, Cy).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBu_2)(CO)_2]$ (9j and 11). Complex **5j** (0.050 g, 0.073 mmol) was reacted with CO for 8 h 30 min at 80 °C as described for **7a**. After workup, compound **9j** was isolated as a gray-green solid (0.038 g, 76%). Anal. Calcd for $C_{32}H_{38}O_2P_2Mo_2$ (**9j**): C, 54.25; H, 5.37. Found: C, 54.39; H, 5.29. If the above carbonylation is carried out for 3 h 30 min, the reaction mixture then contains the cis isomer **11** along with some **9j** and unreacted **5j**. Compound **9j**: ^{1}H NMR δ 7.55−7.15 (m, 10H, Ph), 5.35 (s, 10H, Cp), 1.35 (d, J_{HP} = 13, 18H, CH_3). Compound **11**: ^{1}H NMR δ 7.55−7.05 (m, 10H, Ph), 5.13 (s, 10H, Cp), 1.47 (d, J_{HP} = 14, 9H, CH_3), 1.06 (d, J_{HP} = 13, 9H, CH_3); ^{13}C{^{1}H} NMR δ 248.7 (t, J_{CP} = 7, 2 × CO), 155.2 (d, J_{CP} = 33, C^1(Ph)), 153.6 (d, J_{CP} = 27, C^1(Ph)), 135.1−125.6 (Ph), 86.0 (s, Cp), 42.7 (d, J_{CP} = 17, C^1(^{t}Bu)), 40.9 (d, J_{CP} = 10, C^1(^{t}Bu)), 35.2 (d, J_{CP} = 5, CH_3), 34.0 (d, J_{CP} = 4, CH_3).

Preparation of $[Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}P^tBuH)(CO)_2]$ (9k). Complex **5k** (0.055 g, 0.088 mmol) was reacted with CO for 10 min at room temperature as described for **7a**. After workup, compound **9k** was obtained as a gray-green solid (0.051 g, 89%). Anal. Calcd for $C_{28}H_{30}O_2P_2Mo_2$ (**9k**): C, 51.54; H, 4.60. Found: C, 51.50; H, 4.65. ^{1}H NMR: δ 7.75−7.05 (m, 10H, Ph), 5.73 (br, d, J_{HP} = 336, 1H, PH), 5.45, 5.35 (2 × s, 2 × 5H, 2 × Cp), 1.43 (d, J_{HP} = 16, 9H, CH_3). ^{13}C{^{1}H} NMR: δ 132.8−126.3 (Ph), 87.9, 87.6 (2 × s, 2 × Cp), 33.7 (d, J_{CP} = 36, C^1(^{t}Bu)), 31.1 (d, J_{CP} = 5, CH_3).

Preparation of $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PCyH)(CO)_2]$ (10e). Complex **6e** (0.060 g, 0.072 mmol) was reacted with CO for 18 h at room temperature as described for **7a**. After workup, compound **10e** was obtained as a gray-green solid (0.047 g, 76%). Anal. Calcd for $C_{30}H_{44}O_2P_2W_2$ (**10e**): C, 41.58; H, 5.08. Found: C, 41.65; H, 5.15. ^{1}H NMR: δ 6.33 (d, J_{HP} = 353, 1H, PH), 5.43, 5.39 (2 × s, 2 × 5H, 2 × Cp), 2.41−1.05 (m, 33H, Cy). ^{13}C{^{1}H} NMR: δ 225.3 (t, J_{CP} = 5, CO), 224.6 (s, br, CO), 84.6, 84.4 (2 × s, 2 × Cp), 46.8 (d, J_{CP} = 26, C^1(Cy)), 45.9 (d, J_{CP} = 27, C^1(Cy)), 42.5 (d, J_{CP} = 35, C^1(Cy)), 34.6−25.5 (Cy).

Preparation of $[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PEt_2)(CO)_2]$ (10h). Complex **6h** (0.200 g, 0.250 mmol) was reacted with CO at room temperature for 3 h as described for **7a**. After workup, compound **10h** was isolated as a gray-green solid (0.165 g, 80%). Anal. Calcd for $C_{28}H_{30}O_2P_2W_2$ (**10h**): C, 40.84; H, 3.62. Found: C, 40.62; H, 3.59. ^{1}H NMR: δ 7.58−7.10 (m, 10H, Ph), 5.34 (s, 10H, Cp), 2.85 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.40 (dt, J_{HP} = 14, J_{HH} = 7, 6H, CH_3). ^{13}C{^{1}H} NMR: δ 225.3 (t, J_{CP} = 4, J_{CW} = 196, CO), 148.1 (d, J_{CP} = 46, C^1(Ph)), 133.1 (d, J_{CP} = 10, C^2(Ph)), 126.6 (d, J_{CP} = 10, C^3(Ph)), 126.4 (s, C^4(Ph)), 85.0 (s, Cp), 27.6 (d, J_{CP} = 29, CH_2), 12.1 (d, J_{CP} = 5, CH_3).

Preparation of $[Mo_2Cp_2(\mu\text{-}PEt_2)_2(CO)_3]$ (12). Complex **3b** (0.100 g, 0.190 mmol) was reacted with CO at −50 °C for 15 min as described for **7a**, but using CD_2Cl_2 (1 mL) as solvent. The resulting red solution was shown by NMR to contain compounds **12** and **7b** as major species. Complex **12**, however, transforms readily into the dicarbonyl **7b**, the transformation being complete in ca. 1 h at room temperature. ^{1}H NMR: δ 5.01, 4.96 (2 × s, 2 × 5H, Cp), 2.44, 1.82 (2 × m, 2 × 4H, CH_2), 1.40, 0.98 (2 × m, 2 × 6H, CH_3). ^{13}C{^{1}H} NMR (193 K): δ 241.2 (s, br, CO), 237.9 (s, br, 2 × CO), 88.0, 87.5 (2 × s, 2 × Cp), 29.5 (d, J_{CP} = 9, CH_2), 27.1 (s, CH_2), 12.0 (CH_3).

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