Oxidative Additions of Coordinated Ligands at Unsaturated Molybdenum and Tungsten Diphosphine-Bridged Carbonyl Dimers. 4. Decarbonylation Reactions of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$ (M = Mo, W)

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The title complexes $[M_2Cp_2(CO)_4(\mu\text{-tedip})]$ (M = Mo, W; Cp = η^5-C_5H_5; tedip = $(EtO)_2POP(OEt)_2$) have been synthesized in high yield from the reaction of tedip and the corresponding species $[M_2Cp_2(CO)_4]$. The structure of the ditungsten compound has been determined through a single-crystal X-ray study. Thermolytic decarbonylation of the dimolybdenum complex gives the phosphido−phosphonate compound $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ which results from a P−O bond oxidative addition of the backbone of the tedip ligand to the dimetal center. The latter compound reacts rapidly with CO at room temperature to give the tetracarbonyl species $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_4]$, a process that can be reversed either thermal or photochemically. Additional experiments show that the above tetracarbonyl complex can be partially converted into $[Mo_2Cp_2(CO)_4(\mu\text{-tedip})]$, which means that the P−O cleavage of the tedip ligand is reversible. The ditungsten title complex behaves in a related way but gives at 140 °C a mixture of di- and tetracarbonyl phosphido−phosphonate products. Photochemical decarbonylation of the title dimolybdenum compound showed low selectivity and under a variety of experimental conditions gave a mixture of the phosphido−phosphonate complexes $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ and $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(\mu\text{-}CO)]$ and the triply-bonded $[Mo_2Cp_2(CO)_2(\mu\text{-tedip})]$, which could not be isolated from the reaction mixtures. By contrast, photolysis of the ditungsten title compound at −15 °C gave as a major product the hydridocyclopentadienylidene complex $[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-tedip})]$ along with some $[W_2Cp_2(CO)_2(\mu\text{-tedip})]$. The cyclopentadienylidene complex decomposes rapidly at room temperature to give a mixture of the starting compound and $[W_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$. The underlying reaction pathways in the decarbonylation of the title compounds are discussed on the basis of the above data and several separate experiments.

Introduction

Our previous studies on the decarbonylation processes of the binuclear species $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$ (Cp = η^5-C_5H_5; dppm = $Ph_2PCH_2PPh_2$; M_2 = W_2,[1] Mo_2,[2] MoW,[3]) have shown that three main types of products can be formed in these reactions (Scheme 1). Thus, in addition to the expected triply-bonded dicarbonyls $[M_2Cp_2(CO)_2(\mu\text{-dppm})]$ (**B**), products derived from either C−H (cyclopentadienyl) bond (**A**) or P−C bond (**B**) cleavage can be obtained, their relative amounts being strongly dependent on the reaction conditions and the nature of the dimetal center. From these studies we have been able to extract several conclusions concerning the relative efficiency of the above bond activation processes: (a) the C−H bond cleavage leading to **A** is a reversible process whereas the P−C bond cleavage leading to **C** is irreversible, (b) the P−C bond cleavage process requires higher thermal activation than the C−H bond cleavage, and (c) the presence of molybdenum atoms in the starting dimer seems to reduce the energy barrier of the P−C bond cleavage pathway, whereas the presence of tungsten atoms increases the thermal stability of the hydridocyclopentadienylidene products **A**.

Because the activation of C−H bonds is a central issue in the chemistry of the organometallic compounds,[4] it was of interest to extend the above studies to complexes having different bridging ligands to evaluate the relative efficiency of the C−H (cyclopentadienyl) bond cleavage

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(3) Part 3: Alvarez, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 1378.

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Scheme 1. Generalized Description of the Decarbonylation Reactions of the dppm-Bridged Dimers [$M_2Cp_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)$] (M = Mo, W)[1−3]

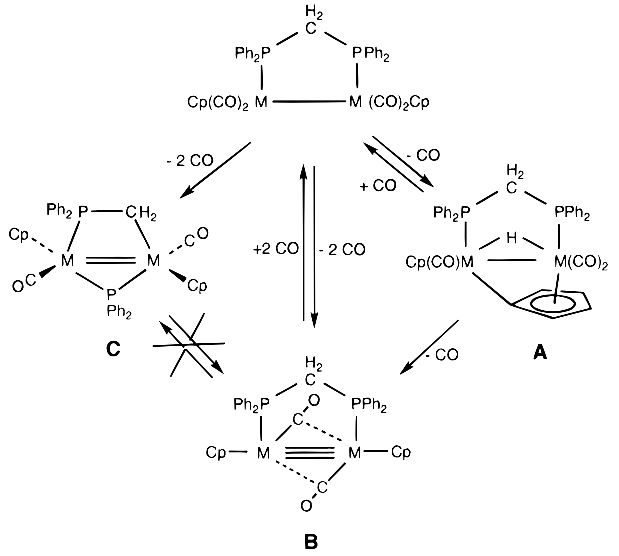
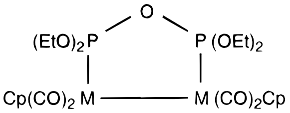


Chart 1



1a (M = Mo)
1b (M = W)

relative to other bond activation processes. We thus decided to study decarbonylation reactions of the tetraethyl pyrophosphite-bridged complexes [$M_2Cp_2(CO)_4(\mu\text{-tedip})$] **1a**, **b** (**a**, M = Mo; **b**, M = W) (Chart 1). The molybdenum complex **1a** had been previously described by us.[5] Interestingly, a minor product was usually obtained during the synthesis of the latter, this being proposed to be [$Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_4$]. Although at that time we could not establish the origin of this side product, the subsequent work carried out on the dppm-bridged complexes[1−3] strongly suggested that P−O cleavage of the backbone of the tedip ligand might well be responsible for the formation of that species. Therefore, we could anticipate the hypothesis that P−O cleavages in the tedip ligand might be competitive processes during decarbonylation of dimers **1a**, **b**.

There is an added interest in the study of P−O bond cleavages at the tedip ligand which arises from two main considerations. In first place, this ligand behaves as a quite robust group when bridging two metal atoms.[6] In fact, there are only a few previous reports of cleavages of this ligand,[7,8] and only one of them has established clearly that the cleavage occurs when the ligand is actually coordinated to a dimetallic center (eq 1).[8] In

$$[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})] \xrightarrow[-H_2]{2Na} Na_2[Mn_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_6] \quad (1)$$

second place, the P−O bond cleavage of tedip generates a diethoxyphosphido bridging group. This therefore constitutes a synthetic route to alkoxyphosphido complexes, a relatively rare type of phosphido species[8−14] of about which little chemical information is only available.

In summary, the present study on the decarbonylations of the tedip-bridged compounds **1a**,**b** was initiated (a) to establish the relative efficiencies of the C−H and P−O bond activation processes likely to occur in the coordinated ligands of these compounds and (b) to learn more about the factors governing the ill-documented P−O cleavage of the backbone of the tedip ligand.

Results and Discussion

Synthesis and Structure of Compounds 1. The preparation and structure of the dimolybdenum compound **1a** was described previously.[5] Here we include an improved preparation based on the reduction of the reaction time between [$Mo_2Cp_2(CO)_4$] and tedip and the absence of any heating during the workup of the reaction mixture (See Experimental Section). Under these conditions, no other phosphorus-containing products are obtained. The ditungsten complex **1b** is analogously prepared by addition of tedip to the triply-bonded dimer [$W_2Cp_2(CO)_4$]. Spectroscopic data for **1b** (Table 1 and Experimental Section)[15] are related to those of **1a** and indicate that the complex also exists as a mixture of two isomers in solution (labeled *A* and *B*). The ratio *A*:*B* is higher for the ditungsten complex (~5 for **1b** and ~2.5 for **1a**, both in $CDCl_3$ at 291 K), a situation analogous to that found for the dppm-bridged complexes.[1,2] It is then likely that, contrary to our earlier proposal for **1a**,[5] the structure of the isomers present in the tedip-bridged complexes **1a**,**b** could be adequately represented by those determined crystallo-

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[15] In a tedip-bridged ditungsten complex having chemically equivalent phosphorus atoms, the ^{31}P NMR subspectrum corresponding to the isotopomer having a single ^{183}W nucleus (~24% natural abundance) can be described as derived from an AA′X spin system (A = P; X = W). Analysis of this subspectrum by the method of the effective Larmor frequencies allows the calculation of J_{AX} and $J_{A'X}$ (and their relative sign), while $|J_{AA'}|$ is measured directly in the subspectrum. See, for example: Günther, H. *NMR Spectroscopy*; Wiley: Chichester, U.K., 1980; p 160.

Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Compounds

compound	$\nu_{st}(CO)^a$/cm^{-1}	δ P (J_{PW})^b	J_{PP}
$[W_2Cp_2(CO)_4(\mu\text{-tedip})]$ (**1b**)	1929 (m), 1892 (vs)	134.7 (512, −16) (isomer *A*)	100[c]
	1853 (m), 1835 (m)	124.8 (isomer *B*)	
$[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (**2a**)	1882 (m), 1839 (vs)	347.0, 139.9	9
$[W_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (**2b**)	1875 (m), 1836 (vs)	303.1 (340, 333), 105.6 (394)	3[d]
$[Mo_2Cp_2(O)\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)]$ (**3a**)	1830 (vs)	360.4, 144.4	14
$[W_2Cp_2(O)\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)]$ (**3b**)	1820 (vs)[e]	338.9 (457, 301), 101.7 (441, 11)	1
$[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_4]$ (**4a**)	1959 (ms), 1942 (vs), 1882 (m)	317.2, 198.0 (isomer *A*)	68
	1862 (m), 1850 (m, sh)	312.8, 191.7 (isomer *B*)	74[f]
$[W_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_4]$ (**4b**)	1949 (s), 1930 (vs), 1866 (s)	253.7 (275, 196), 185.3 (287) (isomer *A*)	43
	1842 (m)[g]	253.7 (275, 196), 166.0 (395) (isomer *B*)	43[h]
$[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(\mu\text{-}CO)]$ (**5**)	1690 (vs)	347.0, 125.6	40
$[Mo_2Cp_2(CO)_2(\mu\text{-tedip})]$ (**6a**)	1778 (vs)	179.0	
$[W_2Cp_2(CO)_2(\mu\text{-tedip})]$ (**6b**)	1767 (vs)	136.4[i]	
$[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-tedip})]$ (**7**)	1948 (vs), 1871 (vs)[j]	147.7 (414), 133.1 (482)	64[i]

[a] Recorded in toluene solution, unless otherwise stated. [b] Recorded at 121.50 MHz and 291 K in C_6D_6 solution, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; *J* in hertz. When two nonequivalent atoms are present, the most deshielded resonance is assigned to the bridging phosphido group, except for **7**. [c] In $CDCl_3$, PP and PW coupling constants in the major isomer obtained from the corresponding ^{183}W "satellite" lines (see note in ref 15); ratio $A/B \sim 5$. [d] Toluene-d_8 solution. [e] $\nu_{st}(W-O) = 934$ cm^{-1} in Nujol mull. [f] In $CDCl_3$ solution at 223 K, ratio $A/B \sim 0.5$; $\delta = 318.7$ (d, $J_{PP} = 65$) and 190.6 (br) ppm in $CDCl_3$ at 291 K. [g] CH_2Cl_2 solution. [h] Recorded at 81.02 MHz and 195 K in CD_2Cl_2 solution, ratio $A/B \sim 1.3$; $\delta = 253.7$ (d, $J_{PP} = 42$, $J_{PW} = 269$, 191) and 175.0 (br) ppm in CD_2Cl_2 at 291 K. [i] Recorded at 161.98 MHz and 243 K in toluene-d_8 solution. [j] A third band is expected, but could not be identified (see text).

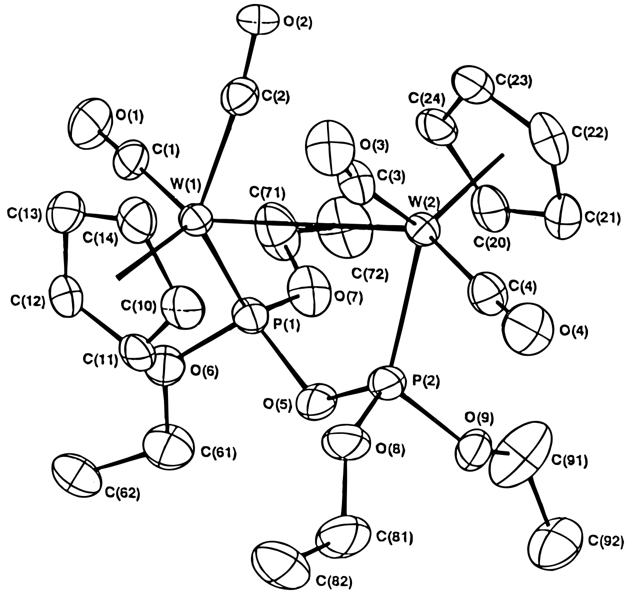


Figure 1. CAMERON diagram of the molecular structure of $[W_2Cp_2(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$ (**1b**). Ellipsoids represent 30% probability.

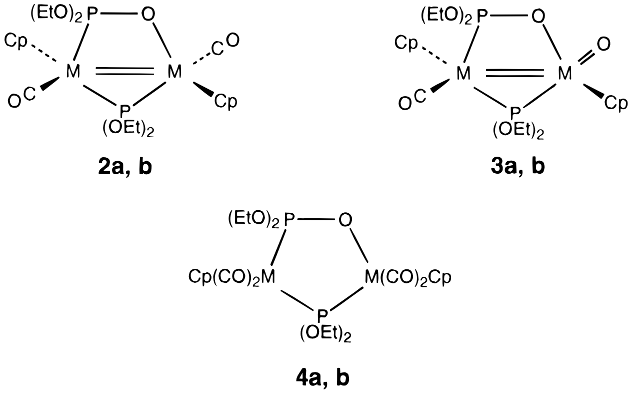
graphically for $[Mo_2Cp_2(CO)_4\{\mu\text{-}H^tBuPCH_2P^tBuH\}]$[16] (isomer *A*) and $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$[17] (isomer *B*). In order to further confirm the above hypothesis, we carried out an X-ray diffraction study on the ditungsten complex **1b**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1b

W(1)−W(2)	3.2731(6)		
W(1)−P(1)	2.352(3)	W(2)−P(2)	2.351(3)
W(1)−C(1)	1.95(1)	W(2)−C(3)	1.96(1)
W(1)−C(2)	1.93(1)	W(2)−C(4)	1.95(1)
P(1)−O(5)	1.623(8)	P(2)−O(5)	1.639(8)
P(1)−O(6)	1.587(8)	P(2)−O(8)	1.597(8)
P(1)−W(1)−W(2)	75.65(7)	P(2)−W(2)−W(1)	77.17(7)
P(1)−W(1)−C(1)	81.2(3)	P(2)−W(2)−C(3)	111.7(3)
P(1)−W(1)−C(2)	116.8(3)	P(2)−W(2)−C(4)	78.3(3)
C(1)−W(1)−C(2)	77.5(5)	C(3)−W(2)−C(4)	76.5(5)
P(1)−O(5)−P(2)	115.3(4)		

The molecular structure of **1b** (Figure 1 and Table 2) has been found to be entirely analogous to that of $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$.[17] The higher acceptor character of the tedip ligand (compared to that of dppm) is surely responsible for a significant reduction in the intermetallic bond distance (3.2731(6) Å for **1b** vs 3.327(1) Å for the Mo_2 complex), while the W−P distances are also shorter as expected. Apart from this, both structures are virtually identical, and the strong twisting of the tedip bridge allows the molecule to adopt a totally *anti* disposition of the cyclopentadienyl ligands. Overall, there is an approximate C_2 axis passing through the bridgehead O(5) atom and the midpoint of the intermetallic vector which relates the carbonyls, phosphorus atoms, and cyclopentadienyl ligands in the molecule.

Chart 2



2a, b **3a, b** **4a, b**

Thermal Decarbonylation of Compounds 1. The dimolybdenum complex **1a** is easily decarbonylated in refluxing toluene to give in high yield the unsaturated dicarbonyl $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (**2a**) (Chart 2), a product resulting from the oxidative addition of a P−O bond in the tedip ligand to the dimetal center. Separate experiments indicated that this reaction can be carried out at somewhat lower temperature, the minimum value being ∼95 °C. Under the latter conditions, the reaction proceeds analogously, but at a lower rate as expected.

Complex **2a** is quite oxygen-sensitive. Upon brief exposure to air, it rapidly decomposes giving in low yield

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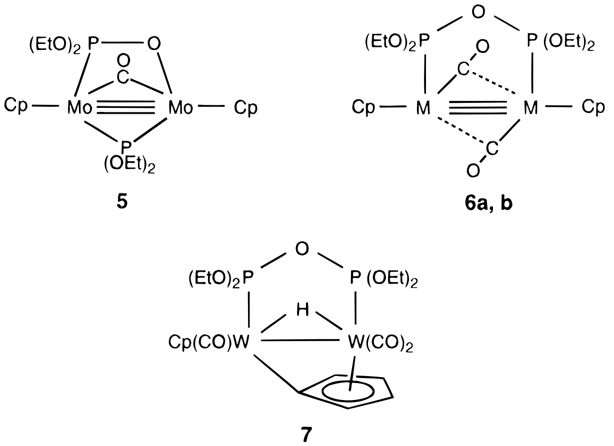
the oxo derivative $[Mo_2Cp_2(O)\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)]$ (**3a**) as the only carbonyl-containing product.

As expected from its electronic and coordinative unsaturation, complex **2a** reacts almost instantaneously with CO (1 atm) at room temperature. However, two rather than one carbonyl ligands are incorporated to the dimetal center, thus destroying completely the intermetallic bond to give quantitatively the tetracarbonyl complex $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_4]$ (**4a**), a process that can be reversed thermal or photochemically. Interestingly, complex **4a** is detected as an intermediate species in the formation of **2a** from **1a**, an observation that will be addressed later on. On the other hand, complex **4a** turned out to be the side product previously described by us in our earlier preparation of **1a**.[5] From the above data, it seems that formation of **4a** in our earlier synthesis of **1a** must have been due to unadvertized overheating of the reaction mixture during the vacuum distillation of the solvent. Finally, further spectroscopic analysis of **4a** (to be discussed separately) has allowed us to correct our earlier ^{31}P NMR data and to establish that this complex exists in solution as an equilibrium mixture of two isomers.

The ditungsten compound **1b** behaves somewhat differently from its molybdenum analogue. In first place, higher temperatures have to be used (refluxing xylenes, ~140 °C) in order to induce any transformation of **1b** at a reasonable rate. Moreover, the major species obtained under these conditions is the tetracarbonyl **4b**, in fact an isomer of the starting complex, along with small amounts of the expected dicarbonyl **2b**. A separate experiment showed that **4b** does not transform into **2b** at a significant rate under the above experimental conditions. Surprisingly, carbonylation of **2b** (to give **4b**) does not occur at room temperature, but needs to be carried out at least at ~60 °C. The above behavior is substantially different from that shown by the dimolybdenum compounds **2a** and **4a** and is also quite unexpected. While the reluctance of **4a** to experience decarbonylation is not surprising for a ditungsten complex (relative to its molybdenum analogue), there is no simple explanation for the considerable kinetic barrier toward addition of CO in the case of the unsaturated tungsten dicarbonyl **2b**. The transformation **2**/**4** involves several processes: (a) formation of two new M−CO bonds, (b) full cleavage of the M−M bonds, and (c) geometrical rearrangement of the bridging groups, from a *trans* to *cis* relative disposition (see later). By assuming that M−CO and M−M bonds are stronger for tungsten, then factors a and b have an opposite influence at facilitating the conversion of **2** into **4**. Finally, the necessary geometrical rearrangement of the bridging groups should be easier for the species having the less strongly bound ligands, possibly the molybdenum complex.

The Reversibility of the P−O Bond Oxidative Addition of the tedip Ligand. As we have noted above, the tetracarbonyl **4a** is detected as an intermediate species during the thermolytic formation of **2a** from **1a**. This is more clearly detected when this reaction is carried out at 95 °C. In order to better understand the transformation **4a**/**2a**, we carried out separate decarbonylation experiments on pure samples of **4a**. When heated in toluene at 95 °C, **4a** slowly transforms into **2a** as expected. Surprisingly, however, considerable amounts of complex **1a** are formed during the course of this reaction. This implies that reductive elimination between the phosphonate and phosphido bridges (to regenerate the tedip ligand) takes place under the above reaction conditions. In other words, the oxidative addition of the P−O (backbone) bond of the tedip ligand to the dimolybdenum center is a reversible process. To our knowledge, reversibility for this type of P−O bond cleavage has been never observed previously.

Chart 3



Having established that the transformation **1a**/**4a** and its reverse are both possible at 95 °C or above, we wanted to know which species would be the most stable in a thermodynamic sense. For this we carried out two parallel thermolytic experiments (on **1a** and **4a**, respectively) under a CO atmosphere (in order to suppress as much as possible the formation of **2a**) in toluene at 110 °C. Under these conditions, almost the same mixture of **1a** and **4a** (ratio **4a**/**1a** ~3) is obtained after 1 h independent of whether we start from **1a** or **4a**. Some dicarbonyl **2a** was still detected in the above experiments, which means that the true ratio at 110 °C is surely somewhat lower. In any case, the measured ratios did not change upon increase of reaction time. Thus, we conclude that around 110 °C **1a** and **4a** are effectively in equilibrium, if we suppress their decarbonylation (to give **2a**), and have therefore similar thermodynamic stability, with **4a** being possibly somewhat more stable.

Photochemical Decarbonylation of Compounds 1. In contrast to the thermolytic decarbonylation of the title compounds, which are highly selective, their photochemical reactions lead generally to mixtures of products. Moreover, the composition of these mixtures is strongly dependent on experimental conditions, as well as on the nature of the metal (Mo or W).

Visible−UV light irradiation of toluene solutions of the dimolybdenum complex **1a** at 15 °C led to a mixture of the dicarbonyl **2a**, the monocarbonyl $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(\mu\text{-}CO)]$ (**5**), and the triply-bonded dicarbonyl $[Mo_2Cp_2(CO)_2(\mu\text{-tedip})]$ (**6a**) (Chart 3). A separate experiment showed that **5a** is cleanly formed upon photolysis of **2a** under the same conditions. Unfortunately, we could not find conditions for the selective formation of **6a**. Modification of reaction time, temperature, or solvent did not significantly change the ratio **6a**/(**2a** + **5**) in the product mixture, which was found to be ~0.2. Besides, attempts to isolate **6a** through chromatography of the corresponding reaction mixtures led only to its decomposition. In spite of all the above problems, spectroscopic information on **6a** obtained from the crude reaction mixtures is informative enough to identify this species as the tedip analogue of the triply-bonded, dppm-bridged complexes $[M_2Cp_2(CO)_2(\mu\text{-dppm})]$.[1,2]

The photolytic reactions of the ditungsten complex **1b** were found to be more strongly dependent on experimental conditions. When carried out at −15 °C, the P−O bond cleavage of the tedip ligand is fully suppressed, and a mixture of the triply-bonded **6b** and the hydridocyclopentadienylidene complex $[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-tedip})]$ (**7**) is obtained (ratio **7**/**6b** ∼4). However, when the photolysis is carried out at 15 °C, the P−O cleavage product **2b** is the major species formed, along with a small amount of **6b**. The relative ratio **2b**/**6b** did not change significantly with the reaction time, which indicates that these species do not interconvert under the experimental conditions. Finally, the use of a N_2 purge through the solution during the photolysis at 15 °C notably accelerates the reaction, but the oxoderivative **3b** is the only carbonyl-containing product obtained instead. Separate experiments showed that **3b** is formed by the action of oxygen on **2b** but not on **6b**.

Attempts to isolate **6b** from the above reaction mixtures were unsuccessful, although spectroscopic analysis of the cleanest crude reaction mixtures provides enough information for structural purposes. Fortunately, complex **2b** can be isolated as an essentially pure solid because it is selectively formed upon photolysis of the tetracarbonyl **4b**, thus avoiding the need for chromatographic purification. Interestingly, an intermediate species can be detected during the course of this reaction, a matter that will be addressed later on. Finally, the cyclopentadienylidene complex **7** could not be isolated as a pure solid either, but its spectroscopic data could be easily obtained from crude reaction mixtures, as this species is the major product of the photolytic experiment at −15 °C.

Complex **7** was found to be thermally unstable, its solutions yielding rapidly at room temperature a mixture of **1b** and **2b**, with the latter being present in higher amounts (eq 2). This implies that (a) the C−H bond oxidative addition leading to **7** is a reversible process, as found in the dppm-bridged analogous systems,[1,2] and (b) the P−O bond cleavage in the tedip ligand must be a very fast process at room temperature, otherwise the triply-bonded **6b** should have been formed instead (i.e., **7** to give **1b** + **6b**). Finally, this explains why the photochemical decarbonylation of **1b** at 15 °C gives just **2b** and also means that the presence of a bridging tedip ligand destabilizes (relative to the dppm-bridged analogues) the hydridocyclopentadienylidene complex. This effect can be attributed to the higher acceptor properties of the tedip ligand (compared to dppm), which makes the dimetal center less electron-rich, and this is usually a factor disfavoring oxidative addition reactions.

$$[W_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(\mu\text{-}H)(CO)_3(\mu\text{-tedip})] \xrightarrow{rt} [W_2Cp_2(CO)_4(\mu\text{-tedip})] + [W_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2] + CO \quad (2)$$

Structural Characterization of Complexes 2−7. With the exception of the tetracarbonyls **4**, all complexes **2**−**7** are structurally related to the products obtained upon decarbonylation of the dppm-bridged species $[MM'Cp_2(CO)_4(\mu\text{-dppm})]$ (M = Mo or W).[1−3] This is particularly evident from the IR and ^{31}P NMR data, so that a detailed analysis of each compound is not needed.

Compounds **2**−**7** exhibit $\nu_{st}(CO)$ bands with the same pattern as their dppm-derived analogues but shifted toward higher frequencies (some 20−50 cm^{-1}), as expected. The ^{31}P NMR data deserve some comments. In first place, the diethyl phosphonate and diethoxyphosphido ligands in **2**−**5** span binuclear centers having intermetallic bond orders from 0 to 3. In spite of this, the P atom at phosphido ligand experiences only a relatively modest deshielding (a maximum ∼30 ppm for Mo and ∼50 ppm for the W complexes) upon increase of bond order, and the effect is not linear at all. At the same time, the P atom at the phosphonate ligand experiences an almost equivalent shielding effect. This behavior is very similar to that observed for the same bridging ligands in dimanganese compounds[9] and differs from the general tendencies in the ^{31}P chemical shifts of PPh_2 bridges, where the presence or absence of metal−metal interactions usually implies much higher changes in the phosphorus shielding.[18] We further note two other significant spectroscopic differences between our diethoxyphosphido compounds and their diphenylphosphido analogues: (a) the presence of a terminal oxo ligand induces only a modest deshielding on the diethoxyphosphido resonances (i.e., δ (μ-P) for **3** are only ∼15−35 ppm higher than those for **2**) while changes in the related complexes $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)L]$ (L = CO, O) are ∼100 ppm[2] and (b) the increase in the metal−metal bond order when going from **2a** to **5** has no effect on the diethoxyphosphido chemical shift whereas the related complexes $[Mo_2Cp_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_x]$ (x = 2, 1) exhibit ^{31}P (phosphido) shifts differing by ∼110 ppm. Establishing a clear relationship between ^{31}P shifts and molecular structure is a difficult matter in the above systems.

The tetracarbonyl compounds **4** have no dppm-derived counterparts. Although we had previously identified the dimolybdenum compound **4a** as a side product in the synthesis of **1a**, two relevant spectroscopic characteristics passed unadvertized at the time. In first place, our earlier 36.43 MHz ^{31}P data were erroneous in that the phosphido resonance at 43 ppm (in $CDCl_3$ at 291 K, $J_{PP} = 68$) was in fact a folded signal which happened to appear with the same phase as the phosphonate resonance at 189.9 ppm. Calculation of the right resonance frequency, after taking into account the spectral width used at the time, is in good agreement with the correct value now determined (Table 1). In second place, the ^{31}P NMR spectrum of **4a** has now been found to be temperature dependent. Taking into account these new data for **4a** and those for **4b** we then conclude that both compounds are isostructural and both display two interconvertible isomers in solution (labeled *A* and *B* in Table 1).

At room temperature, isomers *A* and *B* coexist in about the same relative amount and they interconvert

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[18] Carty, A. J.; MacLaughin, 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.

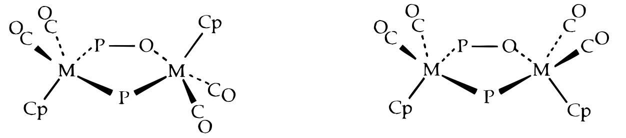


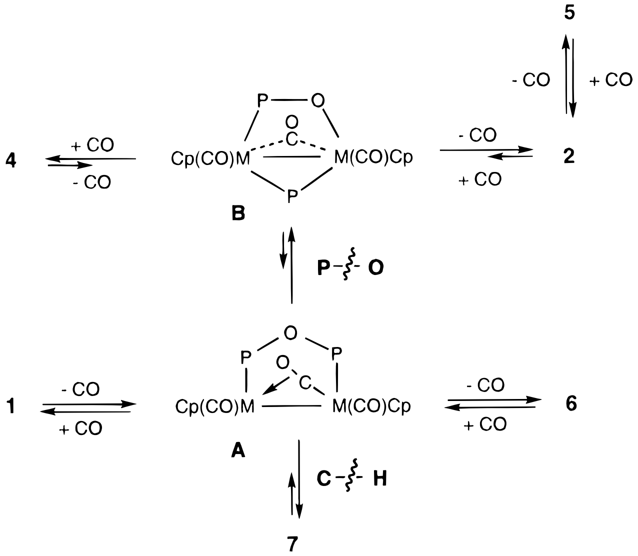
Figure 2. Proposed structures for the isomers detected for compounds **4** in solution [P = P(OEt)$_2$].

rapidly on the NMR time scale, so that averaged NMR spectra (^{1}H, ^{31}P, ^{13}C) are obtained. On lowering the temperature, the spectra broaden and eventually split to display two complete sets of resonances, each corresponding to one of the isomers. The relative amount of isomers is temperature and metal dependent so that, for example, the *A*:*B* ratio reaches values of ~0.5 for **4a** at 223 K but of ~1.3 for **4b** at 195 K (as determined by ^{31}P spectroscopy). The ^{13}C NMR spectrum of **4a** (at 223 K) shows four distinct CO and ethoxy resonances for the major isomer *B*, and the same can be guessed for the minor isomer *A*, although partial overlap of signals occurs. This situation is retained in the averaged (room temperature) spectra of both **4a** and **4b**. Thus, a one-to-one relationship between all NMR-active nuclei (in turn chemically nonequivalent) can be established between isomers *A* and *B*. In other words, each isomer behaves as a nonfluxional molecule, and the temperature dependence of the spectra are due to the changes in the rate at which isomers *A* and *B* interconvert. We then propose for these isomers the structures shown in Figure 2. They all show local *cis*-MCp(CO)$_2$LL′ "piano-stool" environments, in agreement with the ^{13}C NMR data and the similarity of the ν_{st}(CO) pattern in the IR spectra of compounds **4** with that of compounds **1**. Incidentally, the IR spectra of compounds **4** in petroleum ether shows seven ν_{st}(CO) bands, in agreement with the presence in solution of two low-symmetry tetracarbonyl species. The proposed difference between the structures of these isomers lies in the relative orientation of the Cp rings (and CO groups) bonded at different metal atoms, which can be arranged *cis* or *trans* with reference to the pseudoplane defined by the metal atoms and bridging ligands.

As noted above, we have not been able to isolate the triply-bonded complexes **6**. In spite of this, there are data enough to identify them as the tedip-bridged analogues of the compounds [M$_2$Cp$_2$(CO)$_2$(μ-dppm)]. The X-ray structure of the tungsten complex[1a] has shown the presence of the two linear semibridging carbonyls in the molecule. This is also likely the case for complexes **6**, which show a single ν_{st}(CO) band at ~1770 cm^{-1}, some 35 cm^{-1} higher than the corresponding dppm-bridged species, as expected. Finally, the intact tedip ligand in complexes **6** gives rise expectedly to a single ^{31}P NMR resonance close to those of the starting materials **1**.

The spectroscopic data for the hydridocyclopentadienylidene species **7** closely resemble those for [W$_2$(μ-η^1,η^5-C$_5$H$_4$)Cp(μ-H)(CO)$_2$L(μ-dppm)] (L = CO, CN^{t}Bu), the structure of the CN^{t}Bu having been confirmed by an X-ray study.[1] This is particularly evident in the ^{1}H NMR spectrum, due to the presence of four different multiplets corresponding to the C$_5$H$_4$ group and a relatively highly shielded hydrido resonance (−13.45 ppm) similarly coupled to each of the phosphorus (J_{HP} = 36, 35) and tungsten atoms (J_{HW} = 55, 40) of the molecule. According to the proposed structure, three strong to medium ν_{st}(CO) bands are expected to be present in the IR spectra of **7**. Of these, we have been only able to unambiguously assign two, the third band being obscured by either those of **6b** (present in the reaction mixture) or **2b** (rapidly formed from **7** at room temperature).

Scheme 2. Proposed Reaction Pathways in the Decarbonylation Reactions of Compounds 1 [P = P(OEt)$_2$]



Reaction Pathways in the Decarbonylations of Compounds 1. The results discussed above indicate that, depending on the metal and reaction conditions, decarbonylation of the tedip-bridged complexes **1** can lead, in addition to the triply-bonded compounds **6**, to either C−H cleavage (complex **7**) or P−O bond cleavage products (complexes **2**, **4**, and **5**). In a broad sense, this behavior is similar to that exhibited by the dppm-bridged compounds [MM′Cp$_2$(CO)$_4$(μ-dppm)][1−3] (Scheme 1) and can be understood considering similar reaction pathways by taking into account that the P−O cleavage of the backbone of the tedip ligand plays a role analogous to the P−C(sp^3) cleavage of dppm (Scheme 2).

Initial decarbonylation of the tetracarbonyls **1** should yield the tricarbonyls **A**. The proposed structure for these intermediates as having a μ-η^1,η^2-CO ligand is based on the structural data available on related species, but a structure having a μ-η^1-CO ligand is also possible (see refs 1a and 3 and literature cited therein), although this is not critical for the present discussion. Intermediate **A** could afterward experience three different and reversible processes: (a) further decarbonylation, to give the triply-bonded complexes **6**, (b) a C−H bond oxidative addition of a Cp ligand, to give the hydridocyclopentadienylidene complex **7**, or (c) a P−O bond cleavage of the backbone of the tedip ligand to give a second intermediate **B**. Our data indicate that the latter process is fully dominant at high temperatures (thermal decarbonylations) and in any case is faster for the molybdenum complex, so that it cannot be completely suppressed even in the low-temperature photochemical decarbonylations of **1a**. On the other hand, the C−H cleavage pathway appears to be only effective for the ditungsten complex and at the lowest temperatures. These observations are similar to those previously found for the dppm-bridged analogues of complex **1**, which we mentioned in the Introduction section.

There are, however, two significant differences: (a) the P−O bond oxidative addition of the tedip ligand (i.e., the **A**/**B** transformation) is a reversible process, and (b) the tricarbonyl intermediate **B** can be either decarbonylated (to give dicarbonyl **2** or, in the molybdenum case, even the monocarbonyl **5**) or carbonylated (to give tetracarbonyls **4**). This allows for the interconversion between the isomeric species **1** and **4**, as clearly proved for the dimolybdenum complexes.

Direct evidence for the presence of intermediate **B** in the above reactions could not be obtained in the dimolybdenum system. However, when carrying out the photochemical decarbonylation of **4b** (to give **2b**) was carried out at −40 °C (instead of the temperature used for synthetic purposes, which is ∼−20 °C in order to minimize the reaction time), an intermediate species could be detected through IR and ^{31}P NMR monitoring of the reaction mixture. This new species has ^{31}P resonances not very different from those of the final product [δ 310.5 (d, $J_{PP} = 11$, $J_{PW} = 485, 475$, μ-P) and 84.7 (d, $J_{PP} = 11$, $J_{PW} = 619$, μ-OP)]. We can also tentatively assign to this species $\nu_{st}(CO)$ bands at 1962 (s) and 1649 (m) cm^{-1}, the latter being indicative of the presence of a bridging CO ligand in the molecule. In solution, this species completely decomposes within a few minutes at room temperature (or in a few seconds under vacuum) to give dicarbonyl **2b** and is also extremely air-sensitive, so we have not been able to isolate it. In spite of this, the above data allow us to identify it as the ditungsten intermediate **B**, having a structure similar to that exhibited by the related heterometallic complex $[MoWCp_2\{\mu\text{-}CH_2PPh_2\}\{\mu\text{-}PPh_2\}(\mu\text{-}CO)(CO)_2]$.[3]

Conclusions

The unsaturated intermediates generated through decarbonylation of the tedip-bridged tetracarbonyls **1a**,**b** are able to induce the intramolecular oxidative addition of either C−H bonds of the cyclopentadienyl ligands or P−O bonds of the backbone of the tedip ligand. The latter process requires a somewhat higher thermal energy than the former and is also more facile in the dimolybdenum system. However, the C−H cleavage process is only observed in the ditungsten system. These conclusions are similar to those extracted from our previous studies on the dppm-bridged complexes $[MM'Cp_2(CO)_4(\mu\text{-dppm})]$[1−3] and indicates that the P−O cleavage of the tedip ligand plays a role analogous to the P−C cleavage of dppm. There are, however, two important differences between these two processes at the dimetallic complexes under study: (a) under comparable circumstances, the P−O cleavage of tedip occurs at lower temperatures than the P−C cleavage of dppm, and (b) the former is a reversible process while the latter is irreversible. The fact that backbone cleavage of tedip requires less thermal activation than that of dppm has been previously encountered by us during our studies on the reduction reactions of the dimanganese hydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (L_2 = tedip,[8] dppm[19]). On the other hand, there seems to be no previous precedents for reversibility in the intramolecular backbone cleavages of tedip or dppm ligands. The present work thus provides the first example in the case of tedip. It is to be seen whether cases of similar behavior for the dppm ligand can be found in the future.

Experimental Section

General Comments. The general experimental techniques and manipulation procedures are described in ref 1a. Compounds $[M_2Cp_2(CO)_4]$ (M = Mo, W) were prepared by literature methods.[20] NMR spectra were recorded at 291 K and 300.13 (^1H), 121.5 ($^{31}P\{^1H\}$) or 75.47 MHz ($^{13}C\{^1H\}$) unless otherwise stated. Chemical shifts are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (J) are given in hertz. **2** and **5** are highly air-sensitive, while **6** and **7** (the latter being unstable at room temperature) could not be separated from the corresponding reaction mixtures, so that satisfactory elemental analysis could not be obtained in these cases.

Preparation of $[Mo_2Cp_2(CO)_4(\mu\text{-tedip})]$ (1a). The procedure is a slight modification of that previously described for this species[5] and gives no detectable amounts of **4a** as a side product. A bis(2-methoxyethyl) ether solution (diglyme, 25 mL) of $[Mo_2Cp_2(CO)_4]$ (0.434 g, 1.0 mmol) was stirred with tedip (0.25 mL, 1.0 mmol) to give a deep red solution. Solvent was then removed under vacuum (10^{-2} mmHg) and chromatographed at 15 °C on an alumina column (activity II, 40 × 3 cm) prepared in petroleum ether. Elution with the same solvent gave a minor pink fraction, containing some $[Mo_2Cp_2(CO)_6]$, followed by a red fraction. Removal of solvents under vacuum from the latter yielded complex **1a** as a red powder (0.588 g, 85%). This species must be stored under nitrogen even in solid state, otherwise some decomposition can be observed after a few days.

Preparation of $[W_2Cp_2(CO)_4(\mu\text{-tedip})]$ (1b). A diglyme solution (25 mL) of $[W_2Cp_2(CO)_4]$ (0.610 g, 1.0 mmol) was stirred at 0 °C with tedip (0.25 mL, 1.0 mmol) for 30 min to give a deep red solution. The latter was then filtered and the filter washed with dichloromethane (3 × 10 mL). The filtrate was then concentrated under vacuum (10^{-2} mmHg) to ∼10 mL and stored at −20 °C overnight to give red crystals of **1b** (0.575 g, 66%). Anal. Calcd for $C_{22}H_{30}O_9P_2W_2$, **1b**: C, 30.44; H, 3.46. Found: C, 30.90; H, 3.51. ^1H NMR ($CDCl_3$): δ 5.20 (s, 10H, Cp, isomer *A*), 3.91 (m, 8H, CH_2, isomer *A*), 1.36, 1.30 (2t, $J_{HH} = 7$, 2 × 6H, CH_3, isomer *A*). Resonances for isomer *B* were obscured from those of the main isomer except for that of the Cp rings [δ = 5.28 (s)]. Ratio *A*/*B* ∼5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, only resonances from isomer *A* given): δ 233.1 (false t, $J_{CP} + J_{CP'} = 14$, CO), 220.5 (false t, $J_{CP} + J_{CP'} = 10$, CO), 89.3 (s, Cp), 62.5 (false t, $J_{CP} + J_{CP'} = 8$, CH_2), 61.7 (s, br, CH_2), 16.4 (false t, $J_{CP} + J_{CP'} = 6$, CH_3), 15.7 (false t, $J_{CP} + J_{CP'} = 7$, CH_3).

Preparation of $[Mo_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (2a). **1a** (0.050 g, 0.07 mmol) was refluxed in toluene (8 mL) for 1 h to give a black solution. The latter was then filtered at 15 °C through alumina (activity IV, 2 cm). Removal of solvent from the filtrate gave **2a** as an air-sensitive black-greenish powder (0.037 g, 80%). ^1H NMR (200.13 MHz, C_6D_6): δ 5.14 (d, $J_{HP} = 1$, 5H, Cp), 5.12 (d, $J_{HP} = 1$, 5H, Cp), 4.50−4.20 (m, 4H, CH_2), 4.15−3.70 (m, 4H, CH_2), 1.37, 1.35, 1.33, 1.26 (4t, $J_{HH} = 7$, 4 × 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6): δ 239.3 (dd, $J_{CP} = 24, 17$, CO), 231.5 (d, $J_{CP} = 22$, CO), 92.8, 89.3 (2s, Cp), 64.8 (d, $J_{CP} = 9$, CH_2), 64.0 (d, $J_{CP} = 10$, CH_2), 59.3 (s, CH_2), 59.2 (d, $J_{CP} = 6$, CH_2), 17.3−17.0 (m, CH_3).

Preparation of $[W_2Cp_2\{\mu\text{-}OP(OEt)_2\}\{\mu\text{-}P(OEt)_2\}(CO)_2]$ (2b). A toluene solution (15 mL) of **4b** (0.050 g, 0.058 mmol) was irradiated with visible−UV light in a quartz Schlenk tube at −20 °C for 45 min to give a red-purple solution. The latter was then filtered, the solvent removed under vacuum, and the resulting residue washed with petroleum ether (2 × 3 mL) to give **2** as an air-sensitive brown-red powder (0.041 g, 87%).

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(20) Curtis, M. D.; Fotinos, M. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, *22*, 1559.

^{1}H NMR (toluene-d_8): δ 5.19 (d, J_{HP} = 1, 5H, Cp), 5.13 (s, 5H, Cp), 4.40−3.70 (m, 8H, CH$_2$), 1.39, 1.36, 1.35, 1.29 (4 × t, J_{HH} = 7, 4 × 3H, CH$_3$). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$, 200 K): δ 228.4 (dd, J_{CP} = 15, 6, CO), 217.8 (d, J_{CP} = 12, CO), 91.5, 87.4 (2s, Cp), 65.1 (d, J_{CP} = 8, CH$_2$), 64.4 (d, J_{CP} = 10, CH$_2$), 60.2 (d, J_{CP} = 6, CH$_2$), 59.6 (s, CH$_2$), 17.3 (d, J_{CP} = 7, CH$_3$), 17.2 (d, J_{CP} = 4, CH$_3$), 17.1 (d, J_{CP} = 8, CH$_3$), 16.7 (d, J_{CP} = 7, CH$_3$).

Isolation of [Mo$_2$Cp$_2$(O){μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)] (3a). **3a** is formed in variable amounts (usually low) as the only carbonyl-containing product after exposure of **2a** to atmospheric oxygen. It can be purified as follows: The crude mixture is dissolved in the minimum amount of toluene and introduced on top of an alumina column (activity II, 10 × 2.5 cm) prepared in petroleum ether at 15 °C. Elution with dichloromethane gives a violet fraction which yields, after removal of solvent under vacuum, pure **3a** as a dark-grey powder. Anal. Calcd for C$_{19}$H$_{30}$O$_7$P$_2$Mo$_2$, **3a**: C, 36.31; H, 4.81. Found: C, 36.05; H, 4.68. ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ 5.87 (s, 5H, Cp), 5.05 (t, J_{HP} = 1, 5H, Cp), 4.4−4.0 (m, 6H, CH$_2$), 3.75 (m, 1H, CH$_2$), 3.45 (m, 1H, CH$_2$), 1.40, 1.29, 1.20, 1.09 (4t, J_{HH} = 7, 4 × 3H, CH$_3$).

Preparation of [W$_2$Cp$_2$(O){μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}-(CO)] (3b). A toluene solution (30 mL) of **1b** (0.100 g, 0.12 mmol) was irradiated with visible−UV light in a quartz Schlenk at 15 °C for 3 h while nitrogen (99.995%) was bubbled through the solution gently. The dark-brown resulting solution was then chromatographed at 15 °C on an alumina column (activity III, 30 × 2.5 cm). Elution with toluene gave a minor fraction containing unreacted **1b**. Elution with dichloromethane/petroleum ether (1 : 1) gave a deep-orange fraction which yielded, after removal of solvents under vacuum, **3b** as a red-orange powder (0.041 g, 50%). Anal. Calcd for C$_{19}$H$_{30}$O$_7$P$_2$W$_2$, **3b**: C, 28.50; H, 3.75. Found: C, 28.91; H, 3.77. ^{1}H NMR (C$_6$D$_6$): δ 5.99 (d, J_{HP} = 1, 5H, Cp), 5.06 (dd, J_{HP} = 2, 1, 5H, Cp), 4.30−3.45 (m, 8H, CH$_2$), 1.39, 1.30, 1.17, 1.15 (4t, J_{HH} = 7, 4 × 3H, CH$_3$). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$): δ 223.1 (dd, J_{CP} = 9, 4, CO), 108.5, 84.2 (2s, Cp), 67.3 (d, J_{CP} = 4, CH$_2$), 64.2 (d, J_{CP} = 4, CH$_2$), 61.3 (d, J_{CP} = 5, CH$_2$), 60.1 (s, CH$_2$), 17.2 (d, J_{CP} = 8, CH$_3$), 16.9 (d, J_{CP} = 6, CH$_3$), 16.8 (d, J_{CP} = 6, CH$_3$), 16.5 (d, J_{CP} = 8, CH$_3$).

Preparation of [Mo$_2$Cp$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_4$] (4a). Carbon monoxide (1 atm) was gently bubbled through a toluene solution (8 mL) of **2a** (0.046 g, 0.07 mmol) for 1 min, and the mixture was further stirred at room temperature for 5 min. Solvent was then removed in vacuum from the resulting red-orange solution, and the residue was dissolved in petroleum ether and chromatographed at 15 °C on an alumina column (activity II, 15 × 2.5 cm) prepared in the same solvent. Elution with toluene gave a red-orange fraction which yielded, after removal of solvent under vacuum, **4a** as a red powder (0.044 g, 87%). Anal. Calcd for C$_{22}$H$_{30}$Mo$_2$O$_9$P$_2$, **4a**: C, 38.17; H, 4.38. Found: C, 38.02; H, 4.25. ^{1}H NMR (CDCl$_3$): δ 5.39 (s, 5H, Cp), 5.30 (s, 5H, Cp), 4.05−3.60 (m, 8H, CH$_2$), 1.33 (t, J_{HH} = 7, 6H, CH$_3$), 1.26, 1.19 (2t, J_{HH} = 7, 2 × 3H, CH$_3$). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$): δ 260.2 (br, CO), 251.9 (s, CO), 243.1 (d, J_{CP} = 24, CO), 241.7 (d, J_{CP} = 37, CO), 95.3, 92.9 (2 × s, Cp), 64.4 (d, J_{CP} = 10, CH$_2$), 63.3 (d, J_{CP} = 12, CH$_2$), 59.5 (d, J_{CP} = 8, CH$_2$), 59.4 (d, J_{CP} = 8, CH$_2$), 16.5 (m, CH$_3$). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$, 223 K): (isomer *B*) δ 262.9 (d, J_{CP} = 30, CO), 252.6 (s, CO), 243.8 (d, J_{CP} = 35, CO), 242.2 (d, J_{CP} = 29, CO), 95.5, 92.8 (2s, Cp), 64.8 (s, br, CH$_2$), 63.5 (d, br, J_{CP} = 9, CH$_2$), 60.4 (s, br, CH$_2$), 58.1 (s, br, CH$_2$), 16.5 (s, br, CH$_3$). (isomer *A*) δ 95.5, 92.9; other resonances for this isomer were too weak and/or obscured by those of the main isomer to be assigned unambiguously.

Preparation of [W$_2$Cp$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(CO)$_4$] (4b). **1b** (0.100 g, 0.12 mmol) was refluxed in xylenes (15 mL) for 1 h to give a dark red solution. The latter was then applied at room temperature on top of a short Florisil column (~4 × 2.5 cm) prepared in petroleum ether. After washing the column with the latter solvent, elution with dichloromethane gave a red fraction which yielded, after removal of solvent under vacuum, **4b** as a red powder (0.066 g, 71%). This yield can be substantially increased (to ~90%) by carrying out the reaction in a closed Young tube under a CO atmosphere, other conditions being the same. Anal. Calcd for C$_{22}$H$_{30}$O$_9$P$_2$W$_2$, **4b**: C, 30.42; H, 3.46. Found: C, 30.30; H, 3.41. FAB-MS, *m/z*: 869 ([M + 1]$^+$), 840 ([M - CO]$^+$), 812 ([M - 2CO]$^+$). ^{1}H NMR (C$_6$D$_6$): δ 5.27 (s, 5H, Cp), 5.07 (s, 5H, Cp), 3.96−3.65 (m, 8H, CH$_2$), 1.26, 1.20, 1.19, 1.06 (4t, J_{HH} = 7, 4 × 3H, CH$_3$). ^{1}H NMR (toluene-d_8, 195 K): δ 5.30 (s, 5H, Cp, isomer *A*), 5.20 (s, 5H, Cp, isomer *B*), 4.97 (s, 5H, Cp, isomer *B*), 4.73 (s, 5H, Cp, isomer *A*), 4.05−3.22 (m, CH$_2$, isomers *A* and *B*), 1.46−0.80 (m, CH$_3$, isomers *A* and *B*). Ratio *A*/*B* ~1.3. ^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$): δ 254.1 (d, J_{CP} = 22, CO), 244.5 (d, J_{CP} = 9, CO), 232.8 (d, J_{CP} = 21, CO), 229.3 (d, J_{CP} = 32, CO), 92.8, 90.6 (2s, Cp), 63.6 (d, J_{CP} = 10, CH$_2$), 62.3 (d, J_{CP} = 12, CH$_2$), 59.2 (d, J_{CP} = 6, CH$_2$), 58.5 (d, J_{CP} = 8, CH$_2$), 15.2 (m, CH$_3$).

Preparation of [Mo$_2$Cp$_2${μ-OP(OEt)$_2$}{μ-P(OEt)$_2$}(μ-CO)] (5). A toluene solution (10 mL) of **2a** (0.040 g, 0.06 mmol) was irradiated in a quartz Schlenk tube with visible−UV light for 45 min at 15 °C to give a black solution. The latter was then filtered, the solvent removed under vacuum, and the residue washed with petroleum ether (4 mL) to leave **5** as an air-sensitive black-brown powder (0.031 g, 73%). ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ 5.52 (d, J_{HP} = 2, 5H, Cp), 5.48 (s, 5H, Cp), 4.11−3.75 (m, 6H, CH$_2$), 3.05 (m, 1H, CH$_2$), 2.70 (m, 1H, CH$_2$), 1.27, 1.13, 0.97, 0.90 (4t, J_{HH} = 7, 4 × 3H, CH$_3$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 296.4 (dd, J_{CP} = 14, 8, μ-CO), 99.0, 92.6 (2s, Cp), 61.8, 61.5, 60.1 (3s, CH$_2$), 59.6 (d, J_{CP} = 10, CH$_2$), 17.2−16.6 (m, CH$_3$).

Photochemical Formation of [Mo$_2$Cp$_2$(CO)$_2$(μ-tedip)] (6a). **6a** is formed, along with **2a** and **5**, upon photolysis of **1a** under a variety of conditions. As separation of this species from the reaction mixtures could not be accomplished, NMR data for **6a** were obtained through analysis of the crude mixture of products. In a representative experiment, a toluene solution (15 mL) of **1a** (0.050 g, 0.07 mmol) was irradiated at 15 °C in a quartz Schlenk tube with visible−UV light for 3 h while bubbling nitrogen through the solution gently. The dark resulting solution was afterward filtered, the solvent removed under vacuum, and the residue dissolved in the appropriate deuterated solvents. Under the above conditions, a mixture of **6a** , **2a**, and **5** in relative amounts (by ^{31}P NMR spectroscopy) of ~1:4:1, respectively, was obtained. ^{1}H NMR (C$_6$D$_6$): (**6a**) δ 5.48 (s, 10H, Cp); other resonances for this species were obscured by those of the other compounds present in the reaction mixture.

Photochemical Formation of [W$_2$Cp$_2$(CO)$_2$(μ-tedip)] (6b) and [W$_2$(μ-η^1,η^5-C$_5$H$_4$)Cp(μ-H)(CO)$_3$(μ-tedip)] (7). A toluene solution (5 mL) of **1b** (0.040 g, 0.048 mmol) was irradiated with visible−UV light in a quartz Schlenk tube for 2 h at −15 °C to give a brown-orange solution. The latter was filtered at the same temperature and the solvent removed under vacuum to give a brown solid shown (by NMR) to contain a mixture of **6b** and **7** in a ~1:4 ratio. Attempts to separate these two compounds were unsuccessful. In addition, **7** was found to be thermally unstable at room temperature. ^{1}H NMR (400.13 MHz, toluene-d_8, 243 K): (**7**) δ 6.15, 5.07, 4.59, 4.47 (4m, 4 × 1H, C$_5$H$_4$), 4.92 (d, J_{HP} = 1, 5H, Cp), 4.15−3.45 (m, 8H, CH$_2$), 1.20, 1.19, 1.11, 0.99 (4 × t, J_{HH} = 7, 4 × 3H, CH$_3$), −13.45 (dd, J_{HP} = 36, 35, J_{HW} = 55, 40, 1H, μ−H). (**6b**) δ 5.08 (s, 10H, Cp), 1.14 (t, J_{HP} = 7, 12H, CH$_3$); the CH$_2$ resonances for this species were obscured by those from the major compound.

X-ray Structure Determination for 1b. A selected crystal was set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other information are summarized

Table 3. Experimental Data for the X-ray Diffraction Study of 1b

mol formula	$C_{22}H_{30}O_9P_2W_2$
mol wt	868.12
crystal shape	parallelepiped
color	dark orange
cryst syst	monoclinic
space group	$P2_1/n$
systematic absences	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$
a, Å	12.672(3)
b, Å	14.017(2)
c, Å	15.305(2)
β, deg	96.89(1)
V, Å^3	2699(1)
Z	4
D_{calcd}, g/cm^{-3}	2.14
μ, cm^{-1}	88.65
temp, K	291
diffractometer	CAD4-Enraf-Nonius
radiation	Mo $K\alpha$ ($\lambda = 0.710\ 69$ Å)
scan type	$\omega - 2\theta$
scan width, deg	$0.8 + 0.345 \tan\theta$
θ range, deg	1−25
octants collected	h, −15, 14; k, 0, 16; l, 0, 18
no. of measd rflns	5148
no. of unique measd rflns	4735
no. of unique rflns used	3268 [with $F_o^2 \geq 3\sigma F_o^2$]
R(int)	0.083
no. of refined parameters	319
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma F_o$	0.031
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$	0.034 ($w = 1$)
absorption correction	DIFABS (min = 0.79, max = 1.16)
largest diff peak, e/Å^3	0.85 (max)/−0.66 (min)

in Table 3. Corrections were made for Lorentz and polarization effects. An empirical absorption correction (DIFABS)[21] was applied. An extinction correction was unnecessary.

Computations were performed by using CRYSTALS.[22] Atomic form factors for neutral W, P, O, C, and H were taken from ref 23. Real and imaginary parts of anomalous dispersion were taken into account. The structure was solved by direct methods and successive Fourier maps. Only some hydrogen atoms could be found on difference maps, so they were all geometrically located and they were given an overall isotropic thermal parameter. Non-hydrogen atoms were anisotropically refined. Refinements were carried out in three blocks by minimizing the function $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma F_o$ and $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$ having values listed in Table 3. In the last stages of refinement, each reflection was assigned a weight unity. A list of selected interatomic bond lengths and angles are given in Table 2, and Figure 1 represents a CAMERON[24] view of the molecule.

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Supporting Information Available: Tables of atomic coordinates for non-hydrogen atoms (S1) and for hydrogen atoms (S2), anisotropic thermal parameters (S3), and bond lengths and angles (S4) for **1b** (4 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors may be also obtained from the authors on request.

OM961036W

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