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Reactions Leading to Formation and Cleavage of Metal–Metal and Metal–μ-Phosphido Bonds in Binuclear Molybdenum and Tungsten Complexes. Structural Analyses of $W_2(CO)_8(\mu\text{-}PPh_2)_2$ and Its Two-Electron Reduction Product, $[Li(THF)_3]_2[W_2(CO)_8(\mu\text{-}PPh_2)_2]$

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Abstract: Reduction of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (M = Mo (**1**-Mo) or W (**1**-W)) and reactions of various binuclear molybdenum and tungsten anionic products were found generally to proceed with a remarkably facile scission or formation of M–M and M–(μ-PPh_2) bonds. Thus, complexes **1** are converted by $M'BR_3H$ (M' = Li, R = Et; M' = K, R = *sec*-Bu) or $LiAlH_4$ in THF to the M–M bond cleaved $[M_2(CO)_8(\mu\text{-}PPh_2)_2]^{2-}$ (**2**) or to $[(CO)_4\overline{M(\mu\text{-}PPh_2)M}(CO)_4(PPh_2H)]^-$ (**3**) depending on the nature and, usually, the amount of the reductant. Reactions of **1** with LiR (R = Me (**a**), *n*-Bu (**b**), Ph (**c**)) afford the acyl anions $[(CO)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_3(C(O)R)]^-$ (**4a–c**), which yield the carbene complexes $(CO)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_3(C(OMe)R)$ (**5a,c**) when treated with Me_3OBF_4. The M–M bond of **3** is readily broken by CO and *n*-BuLi to give $[(CO)_5M(\mu\text{-}PPh_2)\text{-}M(CO)_4(PPh_2H)]^-$ (**6**) and **2**, respectively. Treatment of **3** with CF_3COOH leads to a fragmentation of the binuclear unit with the formation of *cis*-$M(CO)_4(PPh_2H)_2$ and $M(CO)_5(PPh_2H)$. The dianions **2** are converted to the M–M-bonded **3** and **4a** when reacted with 1 equiv of CF_3COOH and MeI (in THF or DMF), respectively. Possible mechanisms of these reactions are discussed. The structures of **1**-W and its 2-electron reduction product, $[Li(THF)_3{}^+]_2$**2**-W, were determined by single-crystal X-ray diffraction analyses. Both crystals are monoclinic of space group $P2_1/c$, with a = 9.830 (2) Å, b = 19.802 (4) Å, c = 16.889 (5) Å, β = 103.72°, and Z = 4 for **1**-W and a = 11.265 (5) Å, b = 19.546 (3) Å, c = 16.446 (5) Å, β = 122.07 (3)°, and Z = 2 for $[Li(THF)_3{}^+]_2$**2**-W. The structure of **1**-W was solved and refined to R = 0.030 and R_w = 0.033 by using 5206 independent reflections, whereas the structure of $[Li(THF)_3{}^+]_2$**2**-W was solved and refined to R = 0.051 and R_w = 0.062 by using 3987 independent reflections. Both structures possess a planar W_2P_2 core. The W–W distance of 3.0256 (4) Å in **1**-W increases to a nonbonding value of 4.1018 (4) Å in **2**-W, and the W–P–W bond angles of 75.14° (mean) in **1**-W widen to 104.20° in **2**-W. The Li^+ ion in $[Li(THF)_3{}^+]_2$**2**-W possesses an almost regular tetrahedral oxygen environment, being attached to three THF molecules and an equatorial CO of **2**-W.

Binuclear transition-metal complexes represent an important group of compounds,[1] which may be regarded as the simplest chemical models for metal clusters. In this general context, phosphido-bridged complexes have received a good deal of attention,[2] especially with respect to synthesis, structure, and bonding. However, on the whole, their chemistry has not been systematically explored.

In order to fill some of this void, we have been examining, over the past few years, the chemistry of binuclear phosphido-bridged complexes, particularly those of iron, $Fe_2L_x(\mu\text{-}PR_2)_2$ (L = CO, x = 6; L = NO, x = 4).[3-8] These studies have led to the observation of cleavage and formation reactions of each of Fe–Fe and Fe–(μ-PR_2) bonds, sometimes under surprisingly mild conditions. A facile scission of M–(μ-PR_2) bonds, which were at one time regarded as chemically inert,[9] occurs by the coupling of the phosphide with such ligands as hydride and alkyl.[3,5,6,8,10-12] All of the foregoing cleavage reactions may either generate a vacant site at the metal or lead to fragmentation of a binuclear species. Thus, they are of considerable relevance to the chemistry of metal clusters, and especially to their catalytic activity.

This paper is concerned with reduction chemistry of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (M = Mo (**1**-Mo) or W (**1**-W)) and with the behavior of resultant binuclear anions. The two neutral complexes were first prepared by Chatt and Thornton[13] by reaction of $M(CO)_6$ with Ph_2PPPh_2. Although improved syntheses were later developed by Treichel[14] and Keiter,[15] little chemistry of **1**-Mo and **1**-W has been reported. Dessy and co-workers[16,17] studied the electrochemistry of the related methyl derivatives $M_2(CO)_8(\mu\text{-}PMe_2)_2$ and some spectroscopic properties of reduced $[M_2(CO)_8(\mu\text{-}PMe_2)_2]^{2-}$. More recently, Keiter[15] reported several

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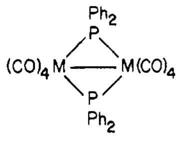
binuclear anions derived from **1**-W.



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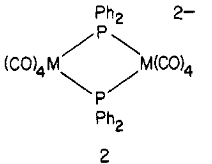

2

M = Mo or W

We now describe various aspects of chemical reduction of **1**-Mo and **1**-W as well as some chemistry of new binuclear molybdenum and tungsten anions. Much of this chemistry concerns reactions at M–M and M–(μ-PPh_2) bonds. Also reported herein is a complete characterization by X-ray diffraction of **1**-W and its 2-electron reduction product, $[Li(THF)_3]_2[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ ($[Li(THF)_3{}^+]_2$**2**-W). This crystallographic study is of particular importance, as it represents, to the best of our knowledge, the first example of structure determination of geometrically similar binuclear doubly bridged species differing in charge by the presence or absence of two valence electrons. Dahl and co-workers[18,19] have determined the structures of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ and $[Na(2,2,2\text{-crypt})]_2[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]$; however, in these two complexes, the geometry of the Fe_2P_2 core is considerably different, being folded in the Fe–Fe-bonded former species and planar in the Fe–Fe-nonbonded latter species. In the present case, the essentially cis-octahedral geometry of four carbonyl groups and two PPh_2 bridges around each tungsten center is maintained in both binuclear complexes, albeit with some important changes in bond distances and angles.

Some of the reaction chemistry (but not the crystallography) reported herein was communicated in a preliminary form.[20]

Experimental Section

General Procedures and Measurements. Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out at ambient temperatures under an atmosphere of purified N_2 with standard procedures.[21] Melting points were measured in vacuo on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 283B spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were obtained on a Varian Associates EM 360L or Bruker AM-500 spectrometer. ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.62 MHz. Both ^1H and ^{13}C chemical shifts are given in ppm downfield from the internal standard Me_4Si. ^{31}P NMR spectra were obtained on the Bruker HX-90 at 36.43 MHz; chemical shifts are reported with reference to 85% H_3PO_4 and are reproducible to ±0.1 ppm. Except as noted, these NMR spectra were collected at room temperature. Ultraviolet (UV)–visible spectra were recorded on a Beckman DU-7 spectrophotometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. THF was distilled from Na and benzophenone under an atmosphere of N_2 immediately before use. Other solvents were purified according to procedures described by Perrin, Armarego, and Perrin[22] and were deaerated by freeze–thaw cycles or purging with N_2.

Trialkylborohydride (and -deuteride) reagents were obtained as 1.0 M solutions in THF from Aldrich. Methyllithium (1.6 M solution in diethyl ether), phenyllithium (1.8 M solution in 70:30 cyclohexane–diethyl ether), and *n*-butyllithium (1.6 M solution in hexanes) were also purchased from Aldrich. PPh_2H, $Mo(CO)_6$, and $W(CO)_6$ were procured from Strem; the hexacarbonyls were purified by sublimation. Other reagents were obtained from various commercial sources and used as received. The complexes $Mo(CO)_5(PPh_2H)$ and $W(CO)_5(PPh_2H)$ were prepared by the general methods of Grim[23] and Strohmeier,[24] respectively, and characterized by comparison of their ν(CO) IR and ^1H and ^{31}P NMR spectra with those reported in the literature.[25-27]

Preparation of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-Mo, 1-W). These two complexes were prepared by a modified procedure of Treichel et al.[14] A solution of $Mo(CO)_5(PPh_2H)$ (47.0 g, 111 mol) in 150 mL of THF was slowly treated with ca. 1 equiv of *n*-BuLi (72.0 mL of 1.6 M solution, 120 mmol), and after the addition was complete the reaction mixture was maintained at reflux for 8 h. The solution was cooled to room temperature, resulting in the formation of a yellow precipitate. The mixture was then stirred in air for ca. 10 h, as the suspended solid changed color to orange-red. The solid was collected by filtration, and the filtrate was evaporated to dryness. The residue was washed first with 50 mL of H_2O and then with 20 mL of acetone, and the second wash was filtered to collect an orange-red powder. The solids collected in the two filtrations were combined and washed consecutively with 20 mL of acetone and 50 mL of pentane. After pumping to dryness, 24.5 g (56% yield) of **1**-Mo was obtained: mp 295 °C (lit.[13] mp 290–305 °C); IR ($CHCl_3$) ν(CO) 2035 (m), 1965 (s, br) cm^{-1}; $^{31}P\{^1H\}$ NMR (THF) δ 232.6; UV-vis (acetone) λ_{max} (ϵ) 355 (18000), 535 (140) nm.

1-W was synthesized by a similar procedure starting with 30.0 g (58.8 mmol) of $W(CO)_5(PPh_2H)$ and 1 equiv of *n*-BuLi in 150 mL of THF: yield 14.2 g (50%); IR (THF) ν(CO) 2038 (m), 1960 (s, br) cm^{-1}; $^{31}P\{^1H\}$ NMR (THF) δ 180.9 (J_{PW} = 164.7 Hz); UV-vis (acetone) λ_{max} (ϵ) 340 (9200), 542 (160) nm.

Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-Mo, 1-W) with Complex Hydrides. (i) General Spectroscopic Studies. A red suspension of **1**-Mo or **1**-W (generally ca. 0.1 g) in THF (generally 2–5 mL) was treated with 1 or 2 equiv of the desired complex hydride (or deuteride) ($LiBEt_3H$, $LiBEt_3D$, $KB(\textit{sec}\text{-}Bu)_3H$, $LiAlH_4$), usually at room temperature. (The reaction of **1**-W with 1 equiv of $LiBEt_3$ was conducted at ca. −30 °C for 20 min followed by slow warming to 25 °C.) The resulting mixture was usually stirred until no further change was apparent in its $^{31}P\{^1H\}$ NMR spectrum (generally up to 2 h).

(ii) Preparation of $[(Ph_3P)_2N][(CO)_4\overline{Mo(\mu\text{-}PPh_2)Mo}(CO)_4(PPh_2H)]$ ($(Ph_3P)_2N^+$3-Mo). **1**-Mo (0.30 g, 0.38 mmol) in 6 mL of THF was treated with ca. 1 equiv of $LiBEt_3H$ (0.4 mL of 1.0 M solution, 0.4 mmol), and the resulting mixture was stirred for about 5 min. The solvent was removed, and the residue was treated with 1 equiv (0.22 g, 0.38 mmol) of $(Ph_3P)_2NCl$ in ca. 7 mL of CH_2Cl_2. The resulting solution was concentrated to an oil. Ethanol was added to induce precipitation of an orange solid, which was collected by filtration and dried, yield 0.20 g (40%). Anal. Calcd for $C_{68}H_{51}Mo_2NO_8P_4$: C, 61.60; H, 3.88. Found: C, 61.00; H, 3.64. Spectroscopic data for this and other new complexes prepared herein are provided in Table I.

(iii) Preparation of $K_2[M_2(CO)_8(\mu\text{-}PPh_2)_2]\cdot 2THF$ ($(K^+)_2$2-Mo·2THF, $(K^+)_2$2-W·2THF). To a suspension of **1**-Mo (2.00 g, 2.54 mmol) in 15 mL of THF was added 2 equiv of $KB(\textit{sec}\text{-}Bu)_3H$ (2.60 mL of 1.0 M solution, 2.60 mmol). The mixture was stirred for ca. 2 h, and a yellow solid was filtered off and dried, yield 2.10 g (82%). Anal. Calcd for $C_{36}H_{28}K_2Mo_2O_9P_2$ (including 1THF): C, 46.14; H, 3.01. Calcd for $C_{40}H_{36}K_2Mo_2O_{10}P_2$ (including 2THF): C, 47.63; H, 3.60. Found: C, 46.05; H, 3.20. ^1H NMR supports the presence of 2 molecules of THF.

The corresponding tungsten complex[15] was prepared similarly by treatment of 0.50 g (0.52 mmol) of **1**-W in 6 mL of THF with 2 equiv of $KB(\textit{sec}\text{-}Bu)_3H$. The yield of a yellow solid was 0.52 g (85%).

Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-Mo, 1-W) with RLi (R = Me, Ph, *n*-Bu). A suspension of 0.30 g (0.38 mmol) of **1**-Mo in 10 mL of THF was treated with 1 equiv of MeLi (0.24 mL of 1.6 M solution, 0.39 mmol). The mixture was stirred for 5 min and then filtered. Solvent was removed from the filtrate to yield 0.36 g (92%) of $Li[(CO)_4\overline{Mo(\mu\text{-}PPh_2)_2Mo}(CO)_3(C(O)Me)]\cdot 3THF$ (Li^+**4a**-Mo·3THF) as a red solid. Anal. Calcd for $C_{45}H_{47}LiMo_2O_{11}P_2$: C, 52.75; H, 4.62. Found: C, 52.39; H, 4.92.

A similar reaction between **1**-W and MeLi afforded $Li[(CO)_4W(\mu\text{-}$

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Table I. Spectroscopic Data for **2–6**[a]

complex[b]	NMR,[c] δ		IR, ν(CO),[f] cm^{-1}
	^{31}P{^{1}H}[d]	^{1}H[e]	
(Li$^+$)$_2$**2**-Mo	–48.1		
(K$^+$)$_2$**2**-Mo[g]	–47.9		1951 (s), 1875 (s), 1825 (s), 1775 (s)[m]
(Li$^+$)$_2$**2**-W	–98.0 (J_{PW} = 154.7)		
(K$^+$)$_2$**2**-W[h]	–97.6[i]		1965 (w), 1875 (m), 1825 (s), 1765 (m)[m]
Li$^+$**3**-Mo	106.9, 21.2 ($^1J_{PH}$ = 327.2,[j] J_{PP} = 19.5)		2015 (w), 1980 (w), 1920 (s), 1900 (sh), 1880 (m), 1835 (w)
K$^+$**3**-Mo	105.5, 20.9 (J_{PP} = 19.5)		
(Ph$_3$P)$_2$N$^+$**3**-Mo	108.4, 23.2 (J_{PP} = 17.2), 20.8		
Li$^+$**3**-W	87.1 (J_{PW} = 137.6, 244.1), –4.3 (J_{PW} = 228.7, $^1J_{PH}$ = 357.6,[j] J_{PP} = 17.2)		2007 (w), 1975 (m), 1915 (s), 1900 (sh), 1880 (m), 1843 (sh)
K$^+$**3**-W	84.1,[i] –7.4 (J_{PW} = 228.7, J_{PP} = 18.9)		
Li$^+$**4a**-Mo	219.9, 174.5 (J_{PP} = 10.3)	2.69 (d, $^4J_{PH}$ = 1.2)[l]	2030 (m), 1985 (m), 1920 (vs), 1875 (m), 1530 (w)
Li$^+$**4b**-Mo	219.0, 173.7 (J_{PP} = 10.3)		
Li$^+$**4c**-Mo	220.5, 177.0 (J_{PP} = 10.3)		2035 (m), 1995 (m), 1930 (vs), 1880 (m), 1505 (w)
Li$^+$**4a**-W	167.4 (J_{PW} = 161.8, 175.2), 136.8 (J_{PW} = 123.9, 242.3, J_{PP} = 17.2)	2.73 (d, $^4J_{PH}$ = 1.2)[l]	2025 (m), 1985 (m), 1920 (vs), 1860 (m), 1525 (w)
Li$^+$**4b**-W	166.7 (J_{PW} = 161.6, 177.1), 137.1 (J_{PW} = 123.8, 244.1, J_{PP} = 17.2)		
Li$^+$**4c**-W	167.2 (J_{PW} = 170.2, 163.3), 138.4 (J_{PW} = 122.1, 242.4, J_{PP} = 17.2)		2020 (m), 1980 (m), 1910 (vs), 1860 (m)
5a-Mo	227.2, 187.1 (J_{PP} = 9.5)	4.40 (s), 3.14 (d, $^4J_{PH}$ = 1.3)	2040 (w), 2005 (m), 1955 (s, br)
5c-Mo	223.8, 192.2 (J_{PP} = 8.6)	3.88 (s)	2030 (w), 2000 (m), 1930 (vs)
5a-W	173.5 (J_{PW} = 128.9, 173.6), 140.8 (J_{PW} = 230.4, 123.8, J_{PP} = 13.8)	4.22 (s), 3.13 (d, $^4J_{PH}$ = 1.1)	2045 (w), 2005 (m), 1945 (s)
5c-W	172.5,[i] 147.2[i] (J_{PP} = 12.0)	3.76 (s)	2035 (m), 2003 (m), 1945 (vs)
Li$^+$**6**-Mo	24.7 ($^1J_{PH}$ = 322.3[j]), –22.1 (J_{PP} = 20.6)		2048 (m), 2005 (m), 1950 (sh), 1930 (vs), 1880 (vs), 1845 (s)
(Ph$_3$P)$_2$N$^+$**6**-Mo	25.3, –21.3 (J_{PP} = 20.6), 20.1		
Li$^+$**6**-W	8.2 (J_{PW} = 226.9), –61.1 (J_{PW} = 164.8, 159.3, J_{PP} = 19.5)[k]		2025 (w), 2000 (m), 1920 (vs), 1870 (s), 1830 (m)[k]

[a] At room temperature. [b] Solvent molecules not included in the formula. [c] J values in Hz. [d] In THF solution unless otherwise indicated. [e] In CDCl$_3$ solution unless otherwise indicated. Me group signals only. Abbreviations: s, singlet; d, doublet. [f] In THF solution unless otherwise indicated. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. [g] ^{13}C{^{1}H} NMR (MeCN-d_3) δ 226.5 (J_{PC} = 4.6 Hz), 220.4 (J_{PC} = 6.5 Hz). UV–vis (acetone) λ_{max} (ϵ) 320 (14 000), ~400 (sh) nm. [h] Reported in ref 15. UV–vis (acetone) λ_{max} (ϵ) 322 (12 000), ~400 (sh) nm. [i] J_{PW} not observed because of low solubility. [j] ^{31}P NMR. [k] In MeCN solution. [l] In acetone-d_6 solution. [m] In Nujol mull.

PPh$_2$)$_2$W(CO)$_3$(C(O)Me)]·3THF (Li$^+$**4a**-W·3THF), also as a red solid, in 95% yield. Anal. Calcd for C$_{45}$H$_{47}$LiO$_{11}$P$_2$W$_2$ (including 3THF): C, 45.02; H, 3.95. Calcd for C$_{41}$H$_{39}$LiO$_{10}$P$_2$W$_2$ (including 2THF): C, 43.64; H, 3.48. Found: C, 43.36; H, 3.33. ^{1}H NMR agrees better with the presence of 3 molecules of THF.

Reactions of **1**-Mo and **1**-W with PhLi were conducted similarly, except that the crude solid products were extracted with ca. 5 mL of MeCN and the extracts were evaporated to yield (≥90%) red Li[(CO)$_4$M(μ-PPh$_2$)$_2$M(CO)$_3$(C(O)Ph)] (Li$^+$**4c**-Mo, Li$^+$**4c**-W). The products were characterized spectroscopically (Table I).

The corresponding alkylation reactions with *n*-BuLi were studied spectroscopically (^{31}P{^{1}H} NMR). The products were not isolated.

Reactions of [(CO)$_4$M(μ-PPh$_2$)$_2$M(CO)$_3$(C(O)R)]$^-$ (4-Mo, 4-W) with Me$_3$OBF$_4$. In a typical preparation, 0.050 g (0.34 mmol) of Me$_3$OBF$_4$ was added to Li$^+$**4a**-W·3THF, prepared from 0.30 g (0.31 mmol) of **1**-W and 1 equiv of MeLi (0.19 mL of 1.6 M solution, 0.31 mmol) in THF and freed of the solvent. Nitromethane (5 mL) was then introduced into this mixture, resulting in the formation of a red solution. The solution was stirred for a few minutes, and the solvent was removed. The solid residue was extracted with 30 mL of THF, and the extract was filtered through activated alumina. Evaporation of the solvent afforded 0.28 g (90% yield based on **1**-W) of red (CO)$_4$W(μ-PPh$_2$)$_2$W(CO)$_3$(C(OMe)-Me)·0.5THF (**5a**-W·0.5THF). Anal. Calcd for C$_{36}$H$_{30}$O$_{8.5}$P$_2$W$_2$: C, 42.05; H, 2.94. Found: C, 42.21; H, 2.94. The presence of 0.5 molecule of THF is supported by the ^{1}H NMR spectrum.

The carbene complexes (CO)$_4$Mo(μ-PPh$_2$)$_2$Mo(CO)$_3$(C(OMe)Me) (**5a**-Mo), (CO)$_4$Mo(μ-PPh$_2$)$_2$Mo(CO)$_3$(C(OMe)Ph) (**5c**-Mo), and (CO)$_4$W(μ-PPh$_2$)$_2$W(CO)$_3$(C(OMe)Ph) (**5c**-W) were prepared as red or red-brown solids in 70, 65, and 30% yields (based on **1**-Mo or **1**-W), respectively, by analogous procedures. However, there was no observed (^{31}P{^{1}H} NMR) reaction when Li$^+$**4a**-Mo·3THF and 1.5 equiv of MeI were stirred in THF for 1 week.

Reactions of [(CO)$_4$M(μ-PPh$_2$)M(CO)$_4$(PPh$_2$H)]$^-$ (3-Mo, 3-W). (i) With CO. Carbon monoxide was slowly passed into a solution of **3**-Mo, prepared by reaction of **1**-Mo (0.30 g, 0.38 mmol) with LiBEt$_3$H (0.46 mL of 1.0 M solution, 0.46 mmol) in 5 mL of THF. After 30 min solvent was removed, and the residue was extracted with 5 mL of MeCN. The extract was filtered, evaporated to dryness, and treated with 0.22 g (0.38 mmol) of (Ph$_3$P)$_2$NCl in 5 mL of CH$_2$Cl$_2$. The resulting solution was stirred for 15 min and concentrated to ca. 1 mL. Addition of 10 mL of ethanol afforded a pale yellow precipitate that was collected by filtration. The yield of [(Ph$_3$P)$_2$N][(CO)$_5$Mo(μ-PPh$_2$)Mo(CO)$_4$(PPh$_2$H)] ((Ph$_3$P)$_2$N$^+$**6**-Mo) was 0.29 g (56% based on **1**-Mo). Anal. Calcd for C$_{69}$H$_{51}$Mo$_2$NO$_9$P$_4$: C, 61.21; H, 3.80. Found: C, 60.64; H, 3.88.

The previously reported[15] [(CO)$_5$W(μ-PPh$_2$)W(CO)$_4$(PPh$_2$H)]$^-$ (**6**-W) was prepared by a strictly parallel procedure, except that the passage of CO continued for 4 h. The anion was isolated as Li$^+$**6**-W and characterized spectroscopically.

(ii) With O$_2$. Dry oxygen was passed into a solution of **3**-Mo or **3**-W, prepared from ca. 0.1 g of **1**-Mo or **1**-W and 1 equiv of LiBEt$_3$H in THF, for 10–15 min. The resulting solution was examined by ^{31}P NMR spectroscopy.

(iii) With *n*-BuLi. A solution of **3**-W, prepared from 0.1 g (0.1 mmol) of **1**-W and 1 equiv of LiBEt$_3$H (0.1 mL of 1.0 M solution, 0.1 mmol) in 2 mL of THF, was cooled to –78 °C. Addition of *n*-BuLi (0.07 mL of 1.6 M solution, 0.1 mmol) immediately afforded a yellow precipitate of [Li(THF)$_3$$^+$]$_2$**2**-W essentially quantitatively.

The corresponding reaction of **3**-Mo produced similar results.

(iv) With CF$_3$COOH. A solution of **3**-Mo, prepared from 0.10 g (0.13 mmol) of **1**-Mo and 1 equiv of LiBEt$_3$H (0.13 mL of 1.0 M solution, 0.13 mmol) in 2 mL of THF, was treated with 10 μL (0.13 mmol) of CF$_3$COOH. During the addition, the solution changed color from red to yellow-brown. A ^{31}P NMR spectrum showed the presence of *cis*-Mo(CO)$_4$(PPh$_2$H)$_2$ (δ 15.1, $^1J_{PH}$ = 332 Hz) and Mo(CO)$_5$(PPh$_2$H) (δ 4.0, $^1J_{PH}$ = 335 Hz), characterized by a comparison of their spectroscopic data with those reported in the literature.[25,26]

A similar reaction between **3**-W and 1 equiv of CF$_3$COOH was shown by ^{31}P NMR to yield *cis*-W(CO)$_4$(PPh$_2$H)$_2$ (δ –3.8, $^1J_{PH}$ = 351 Hz) and W(CO)$_5$(PPh$_2$H) (δ –16.2, $^1J_{PH}$ = 366 Hz), identified on the basis of ^{31}P NMR data from the literature.[27]

The reactions of **3**-Mo and **3**-W with 1 equiv of CF$_3$COOH were also examined by variable-temperature ^{31}P{^{1}H} NMR spectroscopy. Solutions of the binuclear anions were cooled to –78 °C and treated with CF$_3$COOH. ^{31}P{^{1}H} NMR spectra of the reaction mixtures were periodically recorded as the temperature gradually increased to ca. 25 °C.

Reactions of $[M_2(CO)_8(\mu\text{-}PPh_2)_2]^{2-}$ (2-Mo, 2-W). (i) With O_2. A suspension of $[Li(THF)_3{}^+]_2$**2**-W, prepared by reaction between 0.1 g (0.1 mmol) of **1**-W and 2 equiv of $LiBEt_3H$ (0.2 mL of 1.0 M solution, 0.2 mmol) in 2 mL of THF, was stirred in air for 2 days. The mixture was filtered to collect red crystals and a white powder. Washing with water (1 mL) and then with acetone (1 mL) left the red crystals of **1**-W, yield 0.08 g.

Similar results were obtained when $(K^+)_2$**2**-Mo·2THF in THF was stirred in air for 3 days.

(ii) With CF_3COOH. A yellow suspension of $(K^+)_2$**2**-Mo·2THF (0.1 g, 0.1 mmol) in THF (2 mL) was treated with 1 equiv of CF_3COOH (8 μL, 0.1 mmol), immediately resulting in the formation of a red solution. Examination of this solution revealed the presence of **3**-Mo: δ 105.5 (d), 20.9 (d, J_{PP} = 19.5 Hz).

The foregoing reaction was also conducted by using $(K^+)_2$**2**-Mo·2THF (0.5 g, 0.5 mmol) and 2 equiv of CF_3COOH (80 μL, 1.0 mmol) in THF (6 mL). The yellow-brown solution was stirred for a few minutes, the solvent was removed, and the residue was extracted with pentane (50 mL). The extract was filtered, and the pentane was removed to afford approximately 0.2 g of a ca. 3:2 (based on observed intensities of the PH signals in the ^1H NMR spectrum) mixture of *cis*-$Mo(CO)_4(PPh_2H)_2$ and $Mo(CO)_5(PPh_2H)$.[25] ^1H NMR (acetone-d_6) δ 6.68 (d, $^1J_{PH}$ = 343 Hz, rel int 1), 6.23 (d, $^1J_{PH}$ = 336 Hz, rel int ~3). The $^{31}P\{^1H\}$ NMR spectrum was the same as that for the products of reaction of **3**-Mo with CF_3COOH (vide supra).

Similar results were obtained when $[Li(THF)_3{}^+]_2$**2**-W reacted with 1 and 2 equiv of CF_3COOH in THF. The products *cis*-$W(CO)_4(PPh_2H)_2$ and $W(CO)_5(PPh_2H)$ were characterized by ^{31}P NMR spectroscopy (vide supra).

(iii) With MeI and EtI. A suspension of $[Li(THF)_3{}^+]_2$**2**-W, prepared by reaction of 0.50 g (0.52 mmol) of **1**-W and 2 equiv of $LiBEt_3H$ (1.1 mL of 1.0 M solution, 1.1 mmol) in 10 mL of THF, was treated with MeI (0.32 mL, 5.2 mmol), and the resulting mixture was stirred for 48 h. Solvent was then removed, and the residue was extracted with 10 mL of MeCN. Filtration afforded 0.18 g of red **1**-W. The filtrate was evaporated to dryness, and the remaining red solid was washed with 4 mL of hexane and dried. The yield of Li^+**4a**-W, identified by $^{31}P\{^1H\}$ NMR spectroscopy, was 0.33 g (64%).

A solution of 0.20 g (0.20 mmol) of $(K^+)_2$**2**-Mo·2THF in 2 mL of DMF was treated with 13 μL (0.21 mmol) of MeI and the reaction contents were stirred for 5 h. A $^{31}P\{^1H\}$ NMR spectrum of the solution showed the presence of unreacted **2**-Mo (δ −46.1 (s)) and **4a**-Mo (δ 217.4 (d), 172.7 (d, J_{PP} = 12.0 Hz)), in addition to uncharacterized species (δ 207.7 (s), 171.9 (s); 200.7 (d), 164.1 (d, J_{PP} = 5.1 Hz)).

When a suspension of 0.1 g of $(K^+)_2$**2**-Mo·2THF in 2 mL of MeI (or EtI) was stirred for 3 (or 12) days, the reaction mixture changed color from yellow to orange. Solvent was removed to afford **1**-Mo, characterized by $^{31}P\{^1H\}$ NMR spectroscopy.

(iv) With Me_3OBF_4. To a mixture of $(K^+)_2$**2**-Mo·2THF (0.2 g, 0.2 mmol) and Me_3OBF_4 (0.06 g, 0.4 mmol) was added with stirring 6 mL of $MeNO_2$ to produce a red solution within 1 min. Solvent was then removed, and the solid residue was extracted with 40 mL of THF. The extract was filtered and concentrated, and a $^{31}P\{^1H\}$ NMR spectrum was recorded (δ 232.6 (s); 227.1 (d), 187.1 (d, J_{PP} = 9.5 Hz) which indicated the presence of **1**-Mo and **5a**-Mo.

The corresponding reaction of $(K^+)_2$**2**-W·2THF proceeded similarly.

Crystallographic Analyses of $W_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-W) and $[Li(THF)_3]_2[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ ($[Li(THF)_3{}^+]_2$2-W). Suitable crystals of **1**-W were obtained from a THF solution by slow evaporation at room temperature. Crystals of $[Li(THF)_3{}^+]_2$**2**-W formed upon storage of a THF solution for 24 h, also at ca. 25 °C. The crystal used for X-ray diffraction was sealed in a 0.3 mm Lindemann glass capillary filled with N_2.

Diffraction measurements were carried out on an Enraf-Nonius CAD-4 fully automated diffractometer. Cell parameters were refined from 25 randomly selected reflections obtained by using the CAD-4 automatic routines. Crystal data and data collection parameters are listed in Table II. All data processing was performed on a PDP 11/44 computer with use of the Enraf-Nonius SDP program library. Intensity data of $[Li(THF)_3{}^+]_2$**2**-W were corrected for decay, shown by the loss of intensity of the standard reflections (total loss in intensity during the total exposure time, 25.3%). An empirical absorption correction was applied to the data by using the ψ-scan data from close to axial (i.e., χ > 80°) reflections. Neutral atom scattering factors were taken from the literature.[28a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[28b]

Table II. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for **1**-W and $[Li(THF)_3{}^+]_2$**2**-W

	1-W	$[Li(THF)_3{}^+]_2$**2**-W
mol formula	$C_{32}H_{20}O_8P_2W_2$	$C_{56}H_{68}Li_2O_{14}P_2W_2$
fw	962.1	1408.7
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	9.830 (2)	11.265 (5)
b, Å	19.802 (4)	19.546 (3)
c, Å	16.889 (3)	16.446 (5)
β, deg	103.72 (2)	122.07 (3)[a]
V, Å^3	3193.7	3068.6
Z	4	2
D(calcd), g cm^{-3}	2.00	1.52
μ(Mo Kα), cm^{-1}	75.0	80
cryst size, mm	0.30 × 0.35 × 0.42	0.20 × 0.25 × 0.30
transmission factors	0.735–0.999	0.654–0.999
radiation	graphite-monochromated Mo Kα (λ = 0.7107 Å)	
scan type	$\omega/2\theta$	$\omega/2\theta$
θ range, deg	2.5–28	3–27
scan speed, deg min^{-1}	0.6–6.7	0.6–6.7
scan range, deg in ω[b]	1.2 + 0.35 tan θ	1.4 + 0.35 tan θ
aperture width, mm	1.3 + tan θ	1.3 + tan θ
aperture height, mm	4	4
intensity monitors[c]	3	4
orientation monitors[d]	4	3
no. of collected data ($\pm h,k,l$)	8134	7099
unique data with $I > 3\sigma(I)$	5206	3987
final no. of variables	397	215
R[e]	0.030	0.051
R_w[f]	0.033	0.062
w	1	1
error in observn of unit weight	3.42	3.96
largest parameter shift	0.28	0.31

[a] This value may be reduced to 100.07 (3)° by using space group $P2_1/n$, for which a = 11.265 (5) Å, b = 19.546 (3) Å, and c = 14.165 (5) Å. The transformation matrix is /1,0,0/0,−1,0/−1,0,−1/. [b] Extended by 25% on both sides for background measurements. [c] Measured after each hour. [d] New orientation matrix, if angular change >0.1, measured after each 800 reflections. [e] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [f] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Both structures were solved by the heavy-atom method. The electron density maps of $[Li(THF)_3{}^+]_2$**2**-W revealed that the THF molecules were poorly defined. After some unsuccessful attempts at refinement by placing the THF molecules in different close positions, they were placed in an average orientation with a high B factor (15 Å^2) and held fixed during final refinement. It is important to note that the positional parameters of all the other atoms were not modified by the different models used for the THF molecules. Owing to this disordered structure, hydrogen atoms were not included in the structure factor calculations.

Hydrogen atoms of **1**-W were located at calculated positions and held fixed (B = 5 Å^2) during refinement. Full-matrix least-squares refinement with anisotropic thermal parameters for all the refined atoms converged to the final R factors shown in Table II. Atomic parameters of **1**-W are listed in Table III, whereas atomic parameters of $[Li(THF)_3{}^+]_2$**2**-W are given in Table IV. Listings of anisotropic temperature factors for both compounds, fractional coordinates of hydrogen atoms for **1**-W, and structure factor amplitudes for both compounds are available as supplementary material.[29]

Results and Discussion

Preparation of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-Mo, 1-W). The title complexes were prepared by a modified literature procedure[14] in which the appropriate $M(CO)_5(PPh_2H)$ in THF was deprotonated with *n*-BuLi, and the resulting mixture was first refluxed (rather than photolyzed) and then treated with O_2. This modification can be conveniently applied to large scale (tens of grams) syntheses with yields essentially comparable to those reported by Treichel.[14] The reactions were shown by ^{31}P NMR spectroscopy to proceed

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(28) (a) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974, Vol. IV, Table 2.2.B. (b) Reference 28a, Table 2.1.B.

(29) See paragraph at end of paper regarding supplementary material.

Table III. Positional Parameters of Non-Hydrogen Atoms of **1**-W

atom	*x*	*y*	*z*	*B* (Å^2)^a
W(1)	0.35224 (3)	0.32810 (1)	0.19319 (2)	2.323 (5)
W(2)	0.20904 (3)	0.27530 (1)	0.32075 (2)	2.406 (5)
P(1)	0.1823 (2)	0.38855 (9)	0.2557 (1)	2.50 (3)
P(2)	0.3744 (2)	0.21426 (9)	0.2563 (1)	2.51 (3)
O(1)	0.3953 (8)	0.4677 (4)	0.1126 (5)	6.9 (2)
O(2)	0.6340 (6)	0.3583 (3)	0.3256 (4)	4.6 (1)
O(3)	0.0833 (7)	0.2963 (4)	0.0515 (4)	5.4 (2)
O(4)	0.5370 (7)	0.2633 (4)	0.0845 (4)	6.3 (2)
O(5)	−0.0206 (7)	0.3266 (4)	0.4085 (4)	6.2 (2)
O(6)	−0.0298 (7)	0.2068 (4)	0.1844 (4)	5.8 (2)
O(7)	0.2454 (9)	0.1442 (4)	0.4301 (4)	6.8 (2)
O(8)	0.4374 (7)	0.3475 (3)	0.4597 (3)	4.5 (1)
C(1)	0.3764 (9)	0.4182 (4)	0.1415 (5)	4.0 (2)
C(2)	0.5306 (8)	0.3481 (4)	0.2803 (4)	3.0 (1)
C(3)	0.1795 (8)	0.3072 (4)	0.1039 (4)	3.5 (2)
C(4)	0.4698 (9)	0.2867 (4)	0.1236 (5)	3.9 (2)
C(5)	0.0601 (8)	0.3077 (4)	0.3765 (5)	3.7 (2)
C(6)	0.0556 (8)	0.2316 (4)	0.2321 (5)	3.8 (2)
C(7)	0.2288 (9)	0.1915 (4)	0.3896 (5)	3.9 (2)
C(8)	0.3576 (8)	0.3208 (4)	0.4089 (4)	2.9 (1)
C(9)	0.2271 (7)	0.4627 (3)	0.3209 (4)	2.5 (1)
C(10)	0.1195 (8)	0.4980 (4)	0.3443 (5)	3.2 (2)
C(11)	0.1492 (9)	0.5523 (4)	0.3964 (5)	4.0 (2)
C(12)	0.2868 (9)	0.5735 (4)	0.4258 (5)	3.8 (2)
C(13)	0.3918 (9)	0.5389 (4)	0.4022 (5)	3.9 (2)
C(14)	0.3624 (8)	0.4847 (4)	0.3503 (5)	3.3 (2)
C(15)	0.0174 (8)	0.4141 (4)	0.1871 (4)	2.8 (1)
C(16)	0.0203 (9)	0.4684 (5)	0.1341 (5)	4.1 (2)
C(17)	−0.103 (1)	0.4905 (5)	0.0816 (6)	5.1 (2)
C(18)	−0.227 (1)	0.4587 (6)	0.0803 (6)	5.2 (2)
C(19)	−0.2307 (9)	0.4052 (5)	0.1314 (6)	4.7 (2)
C(20)	−0.1088 (8)	0.3825 (5)	0.1849 (5)	3.8 (2)
C(21)	0.5479 (8)	0.1883 (4)	0.3114 (4)	2.9 (1)
C(22)	0.6355 (9)	0.1562 (5)	0.2699 (5)	3.9 (2)
C(23)	0.7706 (9)	0.1388 (5)	0.3081 (6)	4.7 (2)
C(24)	0.822 (1)	0.1513 (5)	0.3901 (6)	4.9 (2)
C(25)	0.738 (1)	0.1831 (6)	0.4236 (5)	5.1 (2)
C(26)	0.6011 (9)	0.2007 (5)	0.3949 (5)	3.9 (2)
C(27)	0.3115 (7)	0.1384 (4)	0.1980 (4)	2.8 (1)
C(28)	0.2631 (9)	0.1376 (4)	0.1128 (5)	3.5 (2)
C(29)	0.2203 (9)	0.0779 (4)	0.0724 (5)	4.0 (2)
C(30)	0.2245 (9)	0.0184 (4)	0.1142 (5)	4.1 (2)
C(31)	0.2709 (9)	0.0179 (4)	0.1973 (5)	4.3 (2)
C(32)	0.3174 (9)	0.0774 (4)	0.2391 (5)	3.7 (2)

^{a}Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

by the intermediacy of $M(CO)_5(PPh_2Li)$ (δ −49.0, J_{PW} = 91 Hz for M = W; δ −33.2 for M = Mo), which then converted thermally to $[(CO)_5M(\mu\text{-}PPh_2)M(CO)_4(PPh_2H)]^-$ (**6**) and $[M_2(CO)_8(\mu\text{-}PPh_2)_2]^{2-}$ (**2**), before oxidation to **1**.

Reduction of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-Mo, 1-W). Reduction chemistry of **1** and reactions of different binuclear complexes of molybdenum and tungsten are summarized in Scheme I. Spectroscopic data for new complexes are listed in Table I.

Treatment of **1**-Mo with 2 equiv of KB(*sec*-Bu)$_3$H in THF affords $(K^+)_2$**2**-Mo·2THF, which was isolated and characterized by spectroscopy and elemental analysis. The corresponding reaction of **1**-W furnishes the analogous dianionic tungsten complex.[15] These binuclear anions **2** are also readily accessible by reduction of **1** with $LiAlH_4$, deprotonation of **3** with *n*-BuLi (vide infra), or, for tungsten, reaction of **1**-W with 2 equiv of $LiBEt_3H$.

In the UV-visible spectra, the absorption bands with λ_{max} 535 (**1**-Mo) and 542 nm (**1**-W), which account for the red color of **1**, disappear upon reduction of these complexes to **2**. The yellow reduced species $(K^+)_2$**2**·2THF exhibit only high energy, more intense, bands with λ_{max} 320 (**2**-Mo) and 322 nm (**2**-W) each with a shoulder at ca. 400 nm. The $^{31}P\{^1H\}$ NMR spectra of **2**-Mo and **2**-W show a signal at δ ca. −48 and ca. −98, respectively, the position of which varies slightly with the counterion (Table I). These high-field chemical shifts point to the absence of M–M bonding in **2**.[30] The X-ray diffraction analysis (vide infra) of $[Li(THF)_3{}^+]_2$**2**-W confirms this inference.

Table IV. Positional Parameters of Non-Hydrogen Atoms of $[Li(THF)_3{}^+]_2$**2**-W

atom	*x*	*y*	*z*	*B* (Å^2)^a
W	0.19074 (4)	0.01679 (3)	0.12318 (3)	4.172 (9)
P	−0.0665 (3)	0.0619 (2)	0.0260 (2)	3.90 (6)
O(1)	0.306 (1)	0.1154 (7)	0.0306 (9)	12.8 (4)
O(2)	0.4726 (8)	−0.0631 (5)	0.2147 (6)	7.0 (3)
O(3)	0.323 (1)	0.1126 (7)	0.3018 (9)	12.3 (5)
O(4)	0.097 (1)	−0.0781 (6)	0.2343 (6)	8.7 (3)
O(5)	0.520 (1)	−0.1809 (7)	0.3520 (8)	9.7 (3)*
O(6)	0.733 (1)	−0.1577 (6)	0.2863 (7)	8.3 (3)*
O(7)	0.704 (1)	−0.0533 (7)	0.4244 (8)	10.1 (3)*
C(1)	0.262 (1)	0.0790 (8)	0.062 (1)	7.1 (4)
C(2)	0.367 (1)	−0.0331 (7)	0.1799 (8)	5.2 (3)
C(3)	0.270 (1)	0.0783 (8)	0.234 (1)	7.1 (4)
C(4)	0.133 (1)	−0.0454 (7)	0.1930 (7)	5.5 (3)
C(5)	−0.148 (1)	0.0618 (6)	0.0978 (7)	4.5 (3)
C(6)	−0.070 (1)	0.0817 (8)	0.1937 (8)	6.6 (4)
C(7)	−0.137 (1)	0.0827 (9)	0.2481 (9)	8.1 (4)
C(8)	−0.276 (1)	0.0650 (9)	0.2066 (9)	8.1 (4)
C(9)	−0.351 (1)	0.046 (1)	0.114 (1)	9.0 (5)
C(10)	−0.286 (1)	0.0454 (9)	0.0577 (9)	7.7 (4)
C(11)	−0.092 (1)	0.1519 (6)	−0.0105 (7)	4.5 (3)
C(12)	−0.019 (1)	0.1811 (7)	−0.0477 (8)	5.8 (4)
C(13)	−0.041 (2)	0.2495 (8)	−0.081 (1)	7.5 (5)
C(14)	−0.139 (2)	0.2877 (8)	−0.079 (1)	9.7 (5)
C(15)	−0.218 (2)	0.2604 (9)	−0.047 (1)	11.5 (5)
C(16)	−0.198 (1)	0.1915 (8)	−0.014 (1)	9.0 (4)
C(17)	0.3824	−0.2010	0.2976	15
C(18)	0.3353	−0.2309	0.3564	15
C(19)	0.4643	−0.2464	0.4467	15
C(20)	0.5829	−0.2120	0.4477	15
C(21)	0.7500	−0.1340	0.2070	15
C(22)	0.8200	−0.1920	0.1950	15
C(23)	0.9150	−0.2150	0.2900	15
C(24)	0.8740	−0.1840	0.3500	15
C(25)	0.8450	−0.0390	0.4950	15
C(26)	0.8350	0.0150	0.5500	15
C(27)	0.7150	0.0570	0.4930	15
C(28)	0.6200	0.0100	0.4200	15
Li	0.613 (2)	−0.116 (1)	0.319 (2)	6.6 (5)*

^{a}Atoms with asterisks were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Atoms without esd were included in structure factor calculations but not refined.

When 1 equiv of $LiBEt_3H$ reacted with **1**-Mo at room temperature, and with **1**-W at −30 °C followed by warming to 25 °C, red monoanions **3** were generated in THF solution. The anion **3**-Mo was isolated as $(Ph_3P)_2N^+$**3**-Mo and characterized by elemental analysis. Use of 2 equiv of $LiBEt_3H$ in conjunction with **1**-Mo at room temperature afforded a mixture of **2**-Mo and **3**-Mo.

The proposed structures of **3**-Mo and **3**-W have been deduced from spectroscopic data. Unlike the corresponding reduction products of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (R = Me, Ph), $[(CO)_3Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe(CO)_2(PR_2H)]^-$,[3] these complexes contain only terminal CO groups, as revealed by their IR spectra. The $^{31}P\{^1H\}$ NMR spectra show two doublets in the range δ 109–105 (**3**-Mo) and 88–84 (**3**-W) and δ 24–20 (**3**-Mo) and −4 to −8 (**3**-W), with J_{PP} = 17–21 Hz, which are assigned to a bridging PPh_2 ligand supported by an M–M bond[30] and to a terminal PPh_2H ligand, respectively. The spectra are essentially invariant with temperature in the range −70 to 25 °C. The appearance of ^{183}W satellites[31] in the spectrum of Li^+**3**-W further supports the $M(\mu\text{-}PPh_2)M(PPh_2H)$ structural feature of **3**. These satellites are observed as a doublet on each side of the resonance of PPh_2H at δ −4.3 (approximate relative intensities 1:11:1) and as two doublets on each side of the resonance of μ-PPh_2 at δ 87.1 (approximate relative intensities 1:1:11:1:1). Consistent with the presence of

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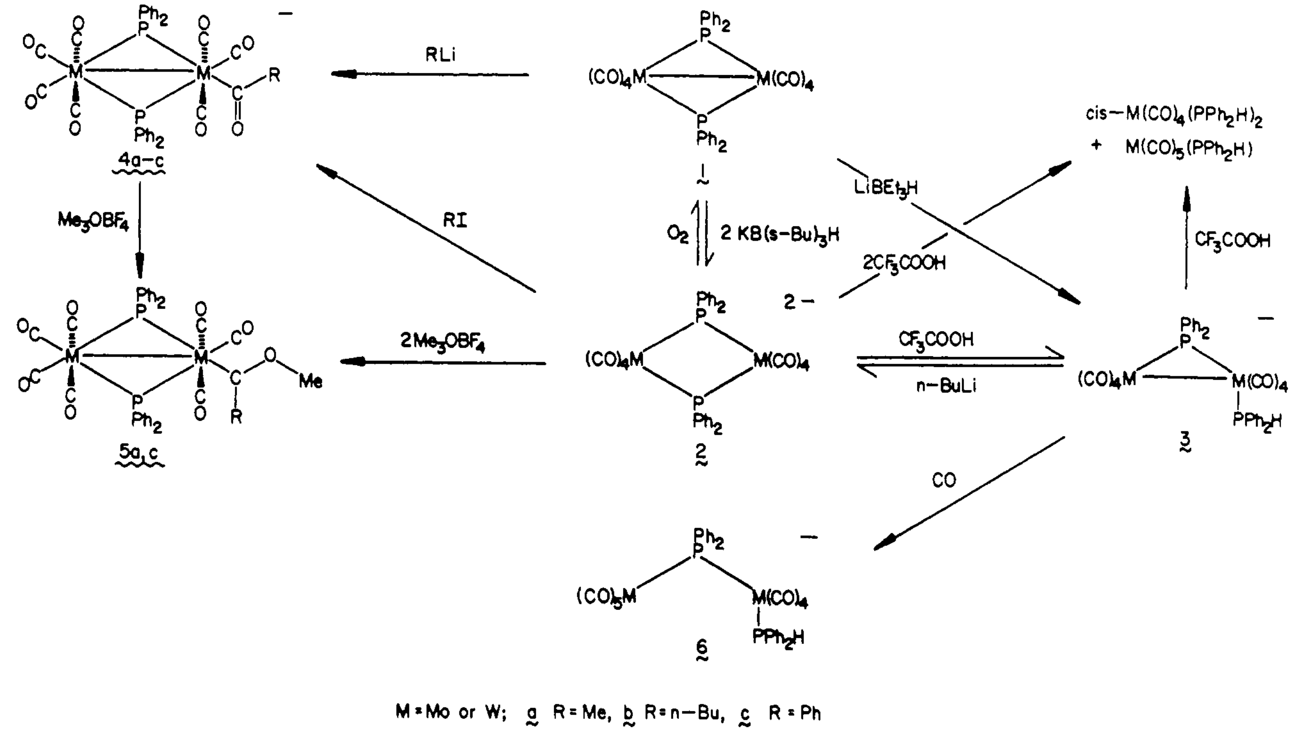
(30) (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163.

(31) Natural abundance of ^{183}W is 14.28%.

Scheme I



a P–H bond, the signal at δ −4.3 is further split into a doublet ($^1J_{PH}$ = 357.6 Hz) when the proton decoupling is not applied. Furthermore, the reaction of **1**-Mo with LiBEt$_3$D affords a solution which shows the δ 21.2 ^{31}P{^{1}H} NMR signal as a 1:1:1 triplet of doublets ($^1J_{PD}$ = 51.3 Hz) to reveal the presence of PPh$_2$D and demonstrate that the PH hydrogen comes from the reducing agent.

Progress of the reduction of **1** by 1 equiv of LiBEt$_3$H was monitored by ^{31}P{^{1}H} NMR spectroscopy with increasing temperature in an attempt to observe reaction intermediates. However, low solubility of **1** in THF precluded the detection of any species other than **1** and **3**. For **1**-Mo, product **3**-Mo was first observed at ca. −53 °C, as the reaction mixture was gradually warmed from −78 °C to room temperature. Comparative data could not be obtained for **1**-W.

Although it was not possible to detect any intermediates in the conversion of **1** to **3**, intermediates in the reduction of Fe$_2$(CO)$_6$(μ-PR$_2$)$_2$ (R = Me, Ph) by LiBEt$_3$H to [(CO)$_3$Fe(μ-PR$_2$)(μ-CO)Fe(CO)$_2$(PR$_2$H)]$^-$ have been recently observed.[6] It may well be that the formation of **3** proceeds by a similar pathway, i.e., (i) addition of H$^-$ to ligated CO of **1** to yield a formyl complex, (ii) migration of H from the formyl to M with cleavage of the M–M bond, and (iii) reductive coupling of M(μ-PPh$_2$) and H to give M(PPh$_2$H). This pathway is supported by the observation that the nucleophiles RLi add to ligated CO in **1** (vide infra). The formation of **2** arises by deprotonation of **3** with additional BR$_3$H$^-$, as was experimentally demonstrated by treating Li$^+$**3**-W with LiBEt$_3$H.

Reactions of M$_2$(CO)$_8$(μ-PPh$_2$)$_2$ (1-Mo, 1-W) with RLi and Preparation of (CO)$_4$M(μ-PPh$_2$)$_2$M(CO)$_3$(C(OMe)R) (5-Mo, 5-W). Reactions of **1** with 1 equiv of RLi in THF afford the binuclear acyl anions **4a** (R = Me) and **4c** (R = Ph) (cf. Scheme I), which were isolated as red, somewhat air-sensitive solvated Li$^+$ salts and characterized by chemical analysis and/or IR and NMR spectroscopy. The corresponding reactions of **1** with *n*-BuLi yield **4b** and **2**, identified by ^{31}P NMR spectroscopy. The pathway leading to the formation of **2** is probably an electron transfer reduction.

Nucleophilic addition of RLi to **1** occurs regiospecifically, and only the equatorial isomer of **4** is observed. This stereochemistry was elucidated from the ^{31}P{^{1}H} NMR spectra which show two doublets in the region characteristic of a PR$_2$ group bridging across an M–M bond.[30] For **4**-W, these doublets are surrounded on each side by two ^{183}W satellite doublets, thus indicating that the two P atoms as well as the two W atoms are inequivalent. The observed stereospecificity is best ascribed to steric factors associated with the presence of bulky μ-PPh$_2$ ligands. From electronic considerations, the less strongly M═CO π-bonded and therefore the more positive carbon atom of an axial CO would be expected to interact with RLi.

Methylation of **4a** and **4c** with Me$_3$OBF$_4$ in MeNO$_2$ affords the binuclear carbene complexes **5a** and **5c**, respectively. However, there is no reaction between **4a**-Mo and MeI in THF. In these sparingly soluble and stable (W) or moderately stable (Mo) to air compounds, the carbene ligand is also present in an equatorial position as evidenced by the ^{31}P{^{1}H} NMR spectra.

Reactions of [(CO)$_4$M(μ-PPh$_2$)M(CO)$_4$(PPh$_2$H)]$^-$ (3-Mo, 3-W). The chemistry of the anions **3** reflects an unusual lability of the M–M bond and the M–P(Ph)$_2$–M bridge system. Accordingly, passage of CO through a solution of Li$^+$**3** in THF results in the formation of the anions **6**, which were isolated as the yellow (Ph$_3$P)$_2$N$^+$ or Li$^+$ salts and characterized by a combination of IR and ^{31}P NMR spectroscopy and elemental analysis. The ^{31}P{^{1}H} NMR spectrum of Li$^+$**6**-W (Table I) is particularly revealing. It exhibits two doublet (J_{PP} = 19.5 Hz) resonances at δ 8.2 (PPh$_2$H) and −61.1 (μ-PPh$_2$), with the ^{183}W satellites showing that the former phosphorus atom is bonded to one tungsten center and the latter one to two.[32] The position of the δ −61.1 signal points to the absence of a W–W bond.[30]

Surprisingly, reactions of Li$^+$**3** with O$_2$ in THF also afford **6**, together with intractable decomposition materials. It is probable that these reactions proceed by the initial oxidation of **3** with release of CO, which then adds to unreacted **3** as in the preceding conversions.

Deprotonation of Li$^+$**3** with *n*-BuLi in THF solution at −78 °C immediately affords the complexes [Li(THF)$_3$$^+$]$_2$**2** as yellow precipitates. No spectroscopic (^{31}P{^{1}H} NMR) evidence for the presence of [(CO)$_4$M(μ-PPh$_2$)M(CO)$_4$(PPh$_2$)]$^{2-}$ could be obtained in these reactions. By contrast, [(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$H)]$^-$ has been deprotonated to [(CO)$_3$Fe(μ-PPh$_2$)(μ-CO)Fe(CO)$_2$(PPh$_2$)]$^{2-}$, which is stable at low tempera-

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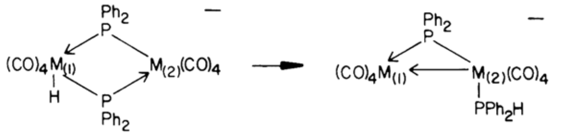
(32) In the reported[15] ^{31}P{^{1}H} NMR spectrum of **6**-W in MeCN-d_3 the two coupling constants J_{PW} for μ-PPh$_2$ could not be resolved.

ture in solution.[4]

The addition of CO to, and a PPh_2 bridge closure following the abstraction of H^+ from, **3** illustrate that the M–M bond in these anions is exceptionally labile. We believe that the lability of this bond arises from its donor–acceptor nature as shown in eq 1. This donor–acceptor bond appears to be a logical consequence of the proposed mechanism of the formation of **3** from **1** and $LiBEt_3H$ based on the observed pathway for the analogous reactions of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (R = Me, Ph) with $LiBEt_3H$[6] (vide supra). The precursor of **3** is thought to be the binuclear hydride species (cf. eq 1) which reacts by reductive coupling of $M(\mu\text{-}PPh_2)$ and H. This would generate coordinative unsaturation (16-electron) at $M_{(1)}$, before donation of 2 electrons from $M_{(2)}$ restores its 18-electron configuration in **3**. Donor–acceptor M–M bonding has been invoked to explain structure and reactivity of some heterobinuclear complexes.[33]



(1)

3

The $M-P(Ph)_2-M$ bridge system of **3** undergoes a remarkably facile collapse leading to the fragmentation of the binuclear unit upon protonation with CF_3COOH. These reactions were monitored by ^{31}P NMR spectroscopy as the temperature gradually increased from −78 to 25 °C. The mononuclear complexes *cis*-$M(CO)_4(PPh_2H)_2$ and $M(CO)_5(PPh_2H)$ were first detected at −8 (M = Mo) and 17 °C (M = W). There was also some decomposition to an insoluble material which was not characterized. No intermediates were observed.

Protonation reactions of some anionic phosphido-bridged binuclear complexes of iron have been shown to proceed by addition of H^+ to one metal center.[6] This may also occur in the present system. Attack of H^+ at the $M(CO)_4$ metal would then be followed by reductive elimination of $M(\mu\text{-}PPh_2)$ and H as $M(PPh_2H)$, to give *cis*-$M(CO)_4(PPh_2H)_2$ and $M(CO)_4$, from which $M(CO)_5(PPh_2H)$ may arise upon ligand scrambling. Although this proposal is attractive, direct protonation at phosphorus following $M-(\mu\text{-}PPh_2)$ bond dissociation cannot be ruled out.

Reactions of $[M_2(CO)_8(\mu\text{-}PPh_2)_2]^{2-}$ (2-Mo, 2-W). Both **2**-Mo and **2**-W undergo oxidation to the corresponding **1** upon contact with air. Oxidation to **1**-Mo has been also observed when $(K^+)_2$**2**-Mo·2THF is stirred in neat MeI or EtI. By contrast, use of the polar solvents in reactions of **2** with MeI leads to the formation of the anionic acetyl complexes **4a**. Accordingly, stirring a mixture of $[Li(THF)_3{}^+]_2$**2**-W and MeI in THF or of $(K^+)_2$**2**-Mo·2THF and MeI in DMF affords the corresponding **4a**. For **2**-Mo, the conversion is not clean, and other, uncharacterized species have been observed by ^{31}P NMR spectroscopy in the reaction mixture.

When **2**-Mo and **2**-W are alkylated with 2 equiv of Me_3OBF_4 in $MeNO_2$, the appropriate carbene complexes **5a** are obtained in addition to **1**. In these reactions, Me_3O^+ alkylates the initially formed acetyl anions **4a**. The formation of **1** probably occurs by solvent oxidation of **2**.

Protonation of **2** by 1 equiv of CF_3COOH cleanly affords the anions **3**. Use of 2 equiv of CF_3COOH leads to the fragmentation of the binuclear structure of **2** with the formation of *cis*-$M(CO)_4(PPh_2H)_2$ and $M(CO)_5(PPh_2H)$, the reaction products being identical with those of the protonation of **3** by 1 equiv of this acid.

Although the foregoing alkylation and protonation reactions of **2** could not be followed spectroscopically owing to low solubilities of various salts of these anions, we consider it likely that they proceed by pathways analogous to those for the corresponding reactions of $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]^{2-}$ (R = Me, Ph). Protonation and alkylation of these iron anions have been shown[6] to be initiated by the addition of H^+ or R^+, respectively, to one metal center. This is then followed by reductive coupling of H and $Fe(\mu\text{-}PR_2)$ or by migration of R onto a ligated CO.

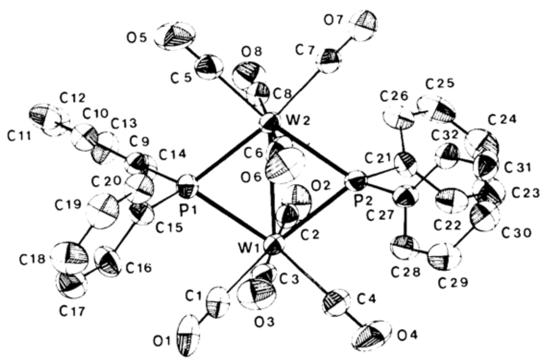


Figure 1. ORTEP plot of **1**-W showing atom numbering scheme. Atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

Table V. Selected Bond Distances (Å) and Angles (deg) for **1**-W

W(1)–W(2)	3.0256 (4)	W(2)–C(7)	2.009 (4)
W(1)–P(1)	2.485 (1)	W(2)–C(8)	2.032 (4)
W(1)–P(2)	2.481 (1)	C(1)–O(1)	1.132 (5)
W(2)–P(1)	2.484 (1)	C(2)–O(2)	1.137 (5)
W(2)–P(2)	2.475 (1)	C(3)–O(3)	1.152 (5)
W(1)–C(1)	2.024 (5)	C(4)–O(4)	1.138 (5)
W(1)–C(2)	2.042 (4)	C(5)–O(5)	1.125 (5)
W(1)–C(3)	2.028 (5)	C(6)–O(6)	1.129 (5)
W(1)–C(4)	2.009 (5)	C(7)–O(7)	1.149 (5)
W(2)–C(5)	2.024 (5)	C(8)–O(8)	1.146 (5)
W(2)–C(6)	2.048 (5)		
W(2)–W(1)–P(1)	52.47 (2)	W(1)–W(2)–P(1)	52.50 (2)
W(2)–W(1)–P(2)	52.29 (2)	W(1)–W(2)–P(2)	52.46 (2)
P(1)–W(1)–C(1)	85.3 (1)	P(1)–W(2)–C(5)	84.7 (1)
P(2)–W(1)–C(4)	82.9 (1)	P(2)–W(2)–C(7)	82.4 (1)
C(1)–W(1)–C(4)	88.0 (2)	C(5)–W(2)–C(7)	88.5 (2)
C(2)–W(1)–C(3)	177.9 (2)	C(6)–W(2)–C(8)	178.4 (2)
C(2)–W(1)–W(2)	91.1 (1)	C(6)–W(2)–W(1)	90.7 (1)
C(2)–W(1)–P(1)	98.6 (1)	C(6)–W(2)–P(1)	94.4 (1)
C(2)–W(1)–P(2)	83.9 (1)	C(6)–W(2)–P(2)	85.3 (1)
C(2)–W(1)–C(1)	88.4 (2)	C(6)–W(2)–C(5)	89.2 (2)
C(2)–W(1)–C(4)	89.2 (2)	C(6)–W(2)–C(7)	91.6 (2)
C(3)–W(1)–W(2)	90.6 (1)	C(8)–W(2)–W(1)	89.6 (1)
C(3)–W(1)–P(1)	83.4 (1)	C(8)–W(2)–P(1)	84.6 (1)
C(3)–W(1)–P(2)	96.1 (1)	C(8)–W(2)–P(2)	96.1 (2)
C(3)–W(1)–C(1)	91.3 (2)	C(8)–W(2)–C(5)	89.6 (2)
C(3)–W(1)–C(4)	88.7 (2)	C(8)–W(2)–C(7)	89.3 (2)
W(1)–P(1)–W(2)	75.03 (3)	W(1)–P(2)–W(2)	75.25 (3)
W(1)–P(1)–C(9)	123.6 (1)	W(1)–P(2)–C(21)	117.0 (1)
W(1)–P(1)–C(15)	116.7 (1)	W(1)–P(2)–C(27)	122.3 (1)
W(2)–P(1)–C(9)	118.3 (1)	W(2)–P(2)–C(21)	123.2 (1)
W(2)–P(1)–C(15)	121.1 (1)	W(2)–P(2)–C(27)	117.8 (1)
C(9)–P(1)–C(15)	102.2 (2)	C(21)–P(2)–C(27)	101.6 (2)
W(1)–C(1)–O(1)	177.2 (5)	W(2)–C(5)–O(5)	178.5 (4)
W(1)–C(2)–O(2)	176.1 (4)	W(2)–C(6)–O(6)	178.7 (4)
W(1)–C(3)–O(3)	177.8 (4)	W(2)–C(7)–O(7)	177.4 (5)
W(1)–C(4)–O(4)	179.6 (4)	W(2)–C(8)–O(8)	177.4 (4)

Molecular Structures of $W_2(CO)_8(\mu\text{-}PPh_2)_2$ (1-W) and $[Li(THF)_3]_2[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ ($[Li(THF)_3{}^+]_2$2-W). Although the structure of the μ-PEt_2 analogue of **1**-W has been determined,[34,35] we undertook a diffraction study of **1**-W to provide the basis for an unambiguous comparison of various structural parameters of $[W_2(CO)_8(\mu\text{-}PR_2)_2]^n$ where n = 0 and 2−.

An ORTEP drawing of the molecular structure of **1**-W is presented in Figure 1. Selected bond lengths and angles are listed in Table V. The structure is characterized by a planar geometry (within ±0.013 Å) of the W_2P_2 core, similar to that found in $M_2(CO)_8(\mu\text{-}PEt_2)_2$ (M = Mo, W).[34,35] The coordination poly-

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[33] See, for example: (a) Jackson, R. A.; Kanluen, R.; Poë, A. *Inorg. Chem.* **1981**, *20*, 1130. (b) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008. (c) Jackson, R. A.; Kanluen, R.; Poë, A. *Inorg. Chem.* **1984**, *23*, 523.

[34] Linck, M. H. *Cryst. Struct. Commun.* **1973**, *3*, 379.

[35] Linck, M. H.; Nassimbeni, L. R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1105.

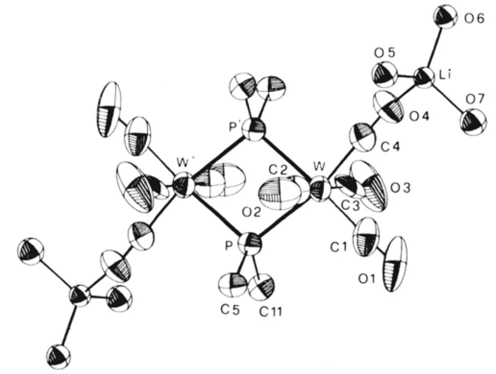

Figure 2. ORTEP plot of $[Li(THF)_3{}^+]_2$**2**-W showing atom numbering scheme. Atoms are drawn at the 50% probability level. Only the oxygen atoms of the THF molecules and the ipso-carbon atoms of the phenyl rings are given. Hydrogen atoms are omitted. Primed atoms refer to their crystallographically equivalent unprimed counterparts.

hedron around each W atom can be described as a distorted pentagonal bipyramid, with C(2), C(3) and C(6), C(8) occupying the axial positions (C(2)–W(1)–C(3) 177.9 (2)°, C(6)–W(2)–C(8) 178.4 (2)°). The equatorial planes, defined by W(2), P(1), P(2), C(1), C(4) (coplanar within ±0.16 Å) and W(1), P(1), P(2), C(5), C(7) (coplanar within ±0.12 Å) are nearly parallel, forming a dihedral angle of 5.9°. The sum of the equatorial bond angles around W(1) and W(2) is 361.0 and 360.6°, respectively. The C(2)···C(3) and C(6)···C(8) interatomic vectors are essentially perpendicular to their equatorial planes, as shown by the C(axial)–W–X(equatorial ligand donor) angles which range from 83.4 (1) to 98.6 (1)°. The atoms C(2), C(8) and C(3), C(6) are slightly staggered as reflected by the torsion angles C(2)–W(1)–W(2)–C(8) and C(3)–W(1)–W(2)–C(6) of 16.5 and 13.7°, respectively.

The W–W bond distance of 3.0256 (4) Å as well as the mean W–P bond length of 2.481 (5) Å are close to the corresponding values of 3.05 (1) and 2.465 (21) Å found in $W_2(CO)_8(\mu\text{-}PEt_2)_2$.[34] The metal–metal bond distance of **1**-W falls in the range reported for some related complexes containing 3-electron bridging thiolato ligands, viz., 3.017 (2) and 3.025 (2) Å in $(CO)_4W(\mu\text{-}SPh)_2W(CO)_2(\mu\text{-}SPh)_2W(CO)_4$,[36] 2.970 (2) Å in $W_2(CO)_8(\mu\text{-}SMe)_2$,[36] and 2.988 (1) Å in $W_2(CO)_8(\mu\text{-}S\text{-}t\text{-}Bu)_2$.[37] However, it is significantly shorter than the W–W distance in a structurally similar binuclear complex containing large bridging iodide, $W_2(CO)_8(\mu\text{-}I)_2$ (3.155 Å).[38] Furthermore, the unsupported W–W single bond in the formally tungsten(I) complex $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ is also substantially longer, 3.222 (1) Å.[39]

The average values of the W–CO (2.027 (14) Å) and C–O (1.139 (10) Å) bond lengths and W–C–O (178 (1)°) bond angles are in the normal ranges.[40]

In the crystal structure of $[Li(THF)_3{}^+]_2$**2**-W, there are strong interactions between the dianion **2**-W and two $Li(THF)_3{}^+$ cations. The lithium ions are coordinated to one equatorial CO oxygen of each W atom, as shown in Figure 2. The "molecules" are then held together by normal van der Waals forces.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Li(THF)_3{}^+]_2$**2**-W

W···W′	4.1018 (4)		
W–P	2.610 (1)	C(2)–O(2)	1.153 (8)
W–P′	2.588 (2)	C(3)–O(3)	1.136 (8)
W–C(1)	1.953 (8)	C(4)–O(4)	1.167 (7)
W–C(2)	2.001 (7)	Li–O(4)	1.90 (1)
W–C(3)	1.999 (8)	Li–O(5)	1.91 (1)
W–C(4)	1.949 (7)	Li–O(6)	1.89 (1)
C(1)–O(1)	1.164 (8)	Li–O(7)	1.91 (2)
P–W–P′	75.80 (5)	W–P–W′	104.20 (5)
P–W–C(1)	100.0 (2)	W–P–C(5)	112.1 (2)
P–W–C(2)	87.9 (2)	W–P–C(11)	117.0 (2)
P–W–C(3)	95.6 (2)	W′–P–C(5)	113.9 (2)
P–W–C(4)	168.6 (2)	W′–P–C(11)	110.4 (2)
P′–W–C(1)	175.6 (2)	C(5)–P–C(11)	99.7 (3)
P′–W–C(2)	90.4 (2)	W–C(1)–O(1)	176.4 (2)
P′–W–C(3)	92.4 (2)	W–C(2)–O(2)	176.2 (2)
P′–W–C(4)	93.3 (2)	W–C(3)–O(3)	177.1 (2)
C(1)–W–C(2)	88.3 (3)	W–C(4)–O(4)	179.3 (2)
C(1)–W–C(3)	89.2 (4)	O(4)–Li–O(5)	107.3 (7)
C(1)–W–C(4)	90.9 (3)	O(4)–Li–O(6)	110.9 (7)
C(2)–W–C(3)	176.0 (3)	O(4)–Li–O(7)	105.3 (7)
C(2)–W–C(4)	88.8 (3)	O(5)–Li–O(6)	112.1 (7)
C(3)–W–C(4)	88.1 (3)	O(5)–Li–O(7)	106.2 (7)
		O(6)–Li–O(7)	114.7 (7)

"Molecule" $[Li(THF)_3{}^+]_2$**2**-W lies at a crystallographic center of inversion, so that the W_2P_2 core is strictly planar. The 2-electron reduction of **1**-W resulted in an increase in the W···W distance to a nonbonding value of 4.1018 (4) Å, with the W atoms being in distorted octahedral environments (cf. Table VI). The dramatic increase of more than 1 Å in the W···W distance upon passing from the neutral parent to its dianion provides experimental evidence of the antibonding dimetal character of the LUMO in neutral $M_2(CO)_8(\mu\text{-}PR_2)_2$ (M = Cr, Mo, W) complexes, as predicted by nonparametrized MO calculations.[41] A similar trend has been observed for the Fe···Fe distances in $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^n$ as *n* goes from 0 (Fe–Fe = 2.623 (2) Å) to 2– (Fe···Fe = 3.630 (3) Å).[18,19] However, that increase is accompanied by a change in geometry of the Fe_2P_2 core from folded to planar.

On passing from **1**-W to **2**-W, the W–CO(equatorial) distances decrease by ca. 0.066 Å, while the W–CO(axial) distances decrease by ca. 0.038 Å. Concomitantly, the equatorial C–O distances increase by ca. 0.030 Å and the axial ones by 0.004 Å. These changes are consistent with the prediction of Teo et al.[41] that the increased electron density in the anions $[M_2(CO)_8(\mu\text{-}PR_2)_2]^{2-}$ is mainly dissipated over the equatorial CO groups, through enhanced M=CO π back-donation. The observed changes also accord with the IR ν(CO) data on $[W_2(CO)_8(\mu\text{-}PMe_2)_2]^n$ (*n* = 0, 2–) of Dessy and Wieczorek.[16] From all of these considerations, it is not surprising that the $Li(THF)_3{}^+$ ions interact with an equatorial rather than an axial CO of **2**-W. Interestingly, however, no real difference in bond length exists between W–C(1) and W–C(4) and between C(1)–O(1) and C(4)–O(4)Li.

As a consequence of the increase in the W···W distance, there is a widening of the W–P–W bond angles from 75.14° (mean) in **1**-W to 104.20° in **2**-W and an increase in the W–P bond lengths from 2.481 (5) Å (av) in **1**-W to 2.599 (16) Å (av) in **2**-W. As in the iron complexes $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^n$,[18,19] there is a marked contraction of the P···P distance, which changes from 3.933 (2) Å in **1**-W to 3.193 (3) Å in **2**-W. However, at variance with the proposal for the iron complexes,[41] the P···P distances in **1**-W and **2**-W are too long for net attractive bonding interactions to exist.

The lithium ion possesses an almost regular tetrahedral oxygen environment (av Li–O 1.90(1) Å), similar to that found in $[Li(THF)_3][(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_2(C(O)Ph)]$,[42] where a tight Li–O(acyl) interaction is present (Li–O 1.902 (25) Å). The Li–O(4)–C(4) bond angle of 148.9 (7)° in $[Li(THF)_3{}^+]_2$**2**-W is essentially identical with the Li–O–C angle of 149° in the iron benzoyl complex. These similarities suggest that, as proposed for the latter complex,[42] a strong electrostatic interaction exists between the lithium ion and the polarized carbonyl oxygen atom.

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Conclusions

Chemical reduction of the molybdenum and tungsten complexes $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (**1**) and reactions of various new binuclear anions generated therefrom are summarized in Scheme I. Particularly noteworthy features of these reactions are the remarkably facile scission and formation of the M–M and M–(μ-PPh$_2$) bonds. Cleavage of the M–M bond occurs especially readily in $[(CO)_4\overline{M(\mu\text{-}PPh_2)M}(CO)_4(PPh_2H)]^-$ (**3**) and is attributed to the donor–acceptor nature of this linkage. Rupture of M–(μ-PPh$_2$) bonds takes place easily by the combination of a bridging phosphido with hydrogen to afford terminal PPh$_2$H. This latter process can result in a fragmentation of the binuclear unit to mononuclear species. The foregoing reactions may serve as models for analogous processes in phosphido-bridged polynuclear complexes, including those that occur under catalytic conditions.

The structures of $W_2(CO)_8(\mu\text{-}PPh_2)_2$ (**1**-W) and $[Li(THF)_3]_2[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ ($[Li(THF)_3{}^+]_2$**2**-W) reveal the effect of the addition of 2 valence electrons on various molecular parameters. Both molecules possess a planar W$_2$P$_2$ core which is stretched along the W···W axis on going from **1**-W to **2**-W. Thus, the W–W bonding distance of 3.0256 (4) Å in **1**-W dramatically increases to a nonbonding value of 4.1018 (4) Å in **2**-W, and the W–P–W bond angles of 75.14° (mean) in **1**-W markedly widen to 104.20° in **2**-W. The W–P bond lengths increase by 0.118 Å whereas the W–CO bond lengths decrease, W–CO-(equatorial) by ca. 0.066 Å and W–CO(axial) by ca. 0.038 Å, on passing from **1**-W to **2**-W. This crystallographic study provides the first example of structure determinations of geometrically similar binuclear complexes of the type $[M_2L_x(\mu\text{-}PR_2)_2]^n$ where $n = 0$ and 2–. It may be compared with a related study of Dahl and co-workers[18,19] on $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^n$ (n = 0, 2–) where the geometry of the Fe$_2$P$_2$ core changes from folded (n = 0) to planar (n = 2–).

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Registry No. **1**-Mo, 20909-82-4; **1**-W, 80049-82-7; (Li$^+$)$_2$ **2**-Mo, 102982-87-6; (K$^+$)$_2$ **2**-Mo, 89828-34-2; (Li$_+$(THF)$_3$)$_2$ **2**-W, 108060-75-9; (K$^+$)$_2$ **2**-W, 80049-81-6; Li$^+$ **3**-Mo, 89828-31-9; K$^+$ **3**-Mo, 108060-76-0; (Ph$_3$P)$_2$N$^+$ o-Mo, 108036-38-0; Li$^+$ **3**-W, 89828-33-1; K$^+$ **3**-W, 108036-39-1; Li$^+$ **4a**-Mo, 89828-36-4; Li$^+$ **4a**-W, 89828-39-7; Li$^+$ **4b**-Mo, 89828-37-5; Li$^+$ **4b**-W, 89847-94-9; Li$^+$ **4c**-Mo, 89828-38-6; Li$^+$ **4c**-W, 108036-40-4; **5a**-Mo, 89828-40-0; **5a**-W, 89828-41-1; **5c**-Mo, 108036-41-5; **5c**-W, 108036-42-6; Li$^+$ **6**-Mo, 108036-43-7; (Ph$_3$P)$_2$N$^+$ **6**-Mo, 108036-45-9; Li$^+$ **6**-W, 108036-46-0; Mo(CO)5 (PPh$_2$H), 18399-61-6; W(CO)$_5$ (PPh$_2$H), 18399-62-7; *cis*-Mo(CO)$_4$(PPh$_2$H)$_2$, 18399-63-8; *cis*-S(CO)$_4$(PPh$_2$H)$_2$, 70505-43-0; LiBEt$_3$H, 22560-16-3; KB(*s*-Bu)$_3$H, 54575-49-4; LiAlH$_4$, 16853-85-3; Co, 630-08-0; MeLi, 917-54-4; BuLi, 109-72-8; PhLi, 591-51-5; Me$_3$OBF$_4$, 420-37-1; CF$_3$CO$_2$H, 76-05-1; MeI, 74-88-4; EtI, 75-03-6; Mo, 7439-98-7; W, 7440-33-7; acetaldehyde ion (1–), 64723-93-9; benzaldehyde ion (1–), 78944-74-8.

Supplementary Material Available: Listing of temperature factors and hydrogen atom coordinates for complexes **1**-W and $[Li(THF)_3{}^+]_2$**2**-W (5 pages); listing of structure factors (37 pages). Ordering information is given on any current masthead page.

Transient Formation of *N*-Alkylhemins during Hemin-Catalyzed Epoxidation of Norbornene. Evidence Concerning the Mechanism of Epoxidation

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Abstract: During the course of hemin-catalyzed epoxidation of norbornene and other alkenes, the hemin catalyst is converted to *N*-alkylhemin by addition to the alkene. This transient species is a catalyst for epoxidation but is not an intermediate. As the oxidant disappears, the *N*-alkylhemin reverts to the original hemin. Proposed mechanisms that require the accumulation of other transients can be excluded because the *N*-alkylhemin is the only species that accumulates.

Cytochromes P-450 have been under intense investigation for many years.[1-3] These enzymes carry out hydroxylations, epoxidations, and other oxidation reactions by using dioxygen and electrons from electron-transfer proteins to produce a high-valent intermediate which is now considered to be similar to horseradish peroxidase compound I, i.e., an oxo iron(IV) porphyrin cation radical.[4,5] We symbolized this species as Hm$^+$=O derived from Hm$^+$ which represents the Fe(III) porphyrin, or resting state (eq 1). Direct formation of Hm$^+$=O in the enzyme and with model

$$Hm^+ \xrightarrow{e^-} Hm \xrightarrow{O_2} Hm\text{–}O_2 \xrightarrow[H^+]{e^-} Hm^+{=}O \xrightarrow{S} SO \qquad (1)$$

systems has been accomplished with several other oxidizing agents including hypochlorite,[6] peracids,[4,7,8] hydroperoxides,[9,10] and io-

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