spectrum (EI), *m/e* 740 (100), 741 (41), 742 (80), 743 (45), 744 (44), 745 (13); mass spectrum (FD), *m/e* 740 (100), 741 (36), 742 (94), 743 (47), 744 (73), 745 (26).

Anal. Calcd for $C_{30}H_{48}N_4S_4O_2Ni_2$: C, 48.43; H, 6.52; N, 7.55; Ni, 15.81. Found: C, 48.32; H, 6.58; N, 7.54; Ni, 15.58.

$Ni_2BB(N_3)$. $Ni(acetate)_2{\cdot}4H_2O$ (1.55 g, 6.2 mmol), H_3BB (1.75 g, 3.0 mmol), and NaN_3 (0.325, 5.0 mmol) were combined in 50 mL of acetone. After the mixture was stirred 2 days, the acetone was evaporated and the solid was extracted with 60 mL of toluene at 50–60 °C. Slow evaporation of the toluene resulted in the isolation of brown needle-like crystals: yield, 80%; M_r = 739.38. mass spectrum (FD), *m/e* 737 (100), 738 (57), 739 (90), 740 (43), 741 (71), 742 (29).

Anal. Calcd for $C_{28}H_{43}N_7S_4ONi_2$: C, 45.48; H, 5.86; N, 13.26; Ni, 15.88. Found: C, 45.76; H, 5.75; N, 13.66; Ni, 15.50.

Ni_2BB(pyrazolate). $Ni_2BB(OEt)$ (250 mg, 0.337 mmol) was combined with pyrazole (25 mg, 0.35 mmol) (Aldrich) in 20 mL of THF. The solution was stirred at room temperature for 2 days. The dark red solution was rotovapped to dryness. The dark red–brown crystals were dried at 100 °C under vacuum: yield, 95%; M_r = 764.45. mass spectrum (FD), *m/e* 762 (100), 763 (57), 764 (100), 765 (66), 766 (62), 767 (29), 768 (22), 679 (15).

Anal. Calcd for $C_{31}H_{46}N_6S_4ONi_2$: C, 48.71; H, 6.07; N, 10.99; Ni, 15.36. Found: C, 49.00; H, 6.11; N, 10.89; Ni, 15.18.

$Zn_2BB(OEt)$. $Zn(acetate)_2{\cdot}2H_2O$ (461 mg, 2.1 mmol) and H_3BB (583 mg, 1.0 mmol) were combined with 20 mL of ethanol and stirred for 2 days. The solution was rotovapped to dryness and the solid residue extracted with toluene. The toluene was slowly evaporated yielding a bright yellow solid. The solid was dried under vacuum at 100 °C: yield, 80%; M_r = 755.74. mass spectrum (FD) (no molecular ion group was found; however, a manifold of bands fitting a Zn_2 molecule was found 15 mass units below the expected molecular ion, perhaps indicating loss of a methyl group) *m/e* 737 (100), 738 (30), 739 (90), 740 (70), 741 (100), 742 (55).

Anal. Calcd for $C_{30}H_{48}N_4S_4O_2Zn_2$: C, 47.68; H, 6.40; N, 7.41; Zn, 17.30. Found: C, 47.88; H, 6.24; N, 7.36; Zn, 17.59.

$Zn_2BB(OH)$. $Zn(acetate)_2{\cdot}2H_2O$ (461 mg, 2.1 mmol) and H_3BB (583 mg, 1.0 mmol) were combined in a solution of 20 mL of THF and 0.5 mL of H_2O. The mixture was stirred for 3 days and the clear orange solution rotovapped to dryness. The residue was extracted with toluene, and the solution was filtered and rotovapped, yielding an orange-yellow powder. The product was dried under vacuum at 100 °C: yield, 80%; M_r = 727.68.

Anal. Calcd for $C_{28}H_{44}N_4S_4O_2Zn_2$: C, 46.22; H, 6.09; N, 7.70; Zn, 17.97. Found: C, 46.66; H, 5.97; N, 7.43; Zn, 17.30.

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Registry No. $Cu_2BB(OEt)$, 84895-77-2; $Cu_2BB(OH)$, 84895-78-3; $Cu_2BB(N_3)$, 84895-79-4; $Cu_2BB(Br)$, 84895-80-7; $Cu_2BB(CN)$, 84895-81-8; Cu_2BB(pyr), 84895-82-9; $Ni_2BB(OEt)$, 84895-83-0; $Ni_2BB(N_3)$, 84895-84-1; NiBB(pyr), 84895-85-2; $Zn_2BB(OEt)$, 84895-86-3; $Zn_2BB(OH)$, 84895-87-4; CuZnBB(OEt), 84895-88-5; CuHBB(OH), 84895-89-6; CuHBB(OEt), 84895-90-9; $CuHBB(N_3)$, 84895-91-0; CuHBB(pyr), 84895-92-1; H_3BB, 84895-76-1; CS_2, 75-15-0; 4-*tert*-butyl-6-formylsalicylaldehyde, 84501-28-0; *S*-heptyl dithiocarbazate, 66528-20-9; 4-*tert*-butylphenol, 98-54-4; formaldehyde, 50-00-0; 4-*tert*-butyl-2,6-bis(hydroxymethyl)phenol, 2203-14-7; hydrazine, 302-01-2; potassium dithiocarbazate, 26648-11-3; 1-iodoheptane, 4282-40-0.

Highly Reduced Organometallics. 9.[1] Synthesis and Characterization of the Tetrasodium Tetracarbonylmetalates(4−) of Chromium, Molybdenum, and Tungsten, $Na_4M(CO)_4$: Their Reactions with Weak Acids To Generate $H_2M_2(CO)_8^{2-}$ (M = Cr, Mo, and W)

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Abstract: Alkali metal reductions of $M(CO)_4(TMED)$, TMED = *N,N,N′,N′*-tetramethylethylenediamine, in liquid ammonia provide high yields of the "super-reduced" species $Na_4M(CO)_4$ which contain chromium, molybdenum, and tungsten in their lowest known formal oxidation states. These substances have been isolated as somewhat shock-sensitive yellow to orange solids which give acceptable elemental analyses for the proposed formulations. Treatment of liquid ammonia slurries of $Na_4M(CO)_4$ with 4 equiv of NH_4Cl produces good yields (50–80%) of the corresponding $M(CO)_4(NH_3)_2$, while 2.5 equiv of NH_4Cl or excess acetonitrile gives 20–50% yields of $H_2M_2(CO)_8^{2-}$ which have been isolated as Et_4N^+ or $(Ph_3P)_2N^+$ salts. The chromium and molybdenum dianions are new species and are characterized by their elemental compositions and infrared and ^1H NMR spectra. The first well-defined reactions of $H_2W_2(CO)_8^{2-}$ with nucleophiles are reported. New compounds formed in these reactions are $[Et_4N]_2[W_2(CO)_8(PMe_3)_2]$, $[Et_4N]_2[W_2(CO)_8(PMe_2Ph)_2]$, $[Et_4N]_2[W_2(CO)_8(P(OMe)_3)_2]$, and $K_2H_2W(CO)_4$. The former are the first reported bisphosphine-substituted derivatives of $M_2(CO)_{10}^{2-}$ dianions, while $H_2W(CO)_4^{2-}$ is formally a diprotonated derivative of $W(CO)_4^{4-}$. High yields (70%) of $H_2W(CO)_4^{2-}$ are also obtained by the reaction of $W(CO)_4(TMED)$ with excess K[*sec*-Bu_3BH] in THF. Treatment of $W_2(CO)_8L_2^{2-}$ with water provides the hydride anions, $HW_2(CO)_8L_2^-$, which are isolated as Et_4N^+ salts and characterized by elemental analyses and infrared and ^1H NMR spectra.

During the past several years our research group has established that the reduction of various carbonylmetalate monoanions leads to a new class of highly reduced species which have been characterized as carbonylmetalate trianions.[2-5]

$$AM(CO)_n + 3A \rightarrow A_3M(CO)_{n-1} + 0.5[A_2(CO)_2] \quad (1)$$

A = alkali metals;

M = V,[2] Nb,[3] Ta,[3] Mn,[4] Re,[4] Co,[5] Rh,[5] Ir[5]

These materials are extremely useful precursors to a variety of new compounds which are unavailable from other reactants.[2-6] Attempts to extend this method to the preparation of previously unknown carbonylmetalate tetraanions by the reduction of cor-

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responding carbonylmetalate dianions were unsuccessful:

$$A_2M(CO)_n + 3A \nrightarrow A_4M(CO)_{n-1} + 0.5[A_2(CO)_2] \quad (2)$$

$$A = \text{alkali metals; } M = \text{Cr, Mo, W, Fe}$$

For this reason a new synthetic approach to such highly reduced organometallics was explored which involved the reduction of substituted carbonyls containing poor or non-π-acceptor ligands. It was hoped that the reduction of such species would preferentially labilize the substituent ligands, thus producing a binary anionic metal carbonyl:

$$M(CO)_xL_y + 2yA \rightarrow A_{2y}M(CO)_x + yL \quad (3)$$

$$A = \text{alkali metals}$$

$$L = 2 \text{ electron donors which are poorer } \pi \text{ acceptors than CO}$$

This "reductive labilization" method has proven to be remarkably successful in the synthesis of a new class of organometallic compounds which have the composition $Na_4M(CO)_4$ and chemically behave like carbonylmetalate tetraanions. Formally these materials contain transition metals in their lowest known oxidation state.

Although the reactions of these substances with chlorotriphenylstannane have been the subject of a preliminary report,[7] more recently we have discovered that they also readily react with weak acids in liquid ammonia. Significant amounts of the previously unknown $H_2Cr_2(CO)_8^{2-}$ and $H_2Mo_2(CO)_8^{2-}$ as well as the known $H_2W_2(CO)_8^{2-}$[8-10] are obtained in these reactions. These materials are of considerable interest in that they contain very reactive and formally unsaturated atoms connected by three-center-two-electron bonds analogous to those in diborane, $H_2Os_3(CO)_{10}$,[11a] and related species.[11b] In addition, the former species are anionic and thus might be expected to be more reactive toward electrophilic reagents than their neutral bonding analogues. The latter have been studied extensively for several years, while the chemistry of $H_2W_2(CO)_8^{2-}$ has been the subject of only one previous report.[10a]

In this paper, the synthesis and characterization of $Na_4M(CO)_4$ are described. In addition, their reactions with weak acids in liquid ammonia to generate $M(CO)_4(NH_3)_2$ and $H_2M_2(CO)_8^{2-}$ are considered along with some representative reactions of $H_2W_2(CO)_8^{2-}$ and nucleophiles.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulas and syringes; otherwise reactions were generally performed by using standard Schlenk apparatus with a double manifold vacuum line. Ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade acetonitrile was dried with CaH_2, freed of oxygen by a nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran and diethyl ether were distilled from alkali metal benzophenone ketyls before use. Reagent grade acetone, heptane, absolute ethanol, and isopentane were freed of oxygen by bubbling nitrogen through the solvents for 1–2 h before use. A published procedure was followed for the preparation of (TMED)M(CO)$_4$ (M = Cr, Mo, W; TMED = *N,N,N',N'*-tetramethylethylenediamine).[12] All other reactants and solvents were obtained from commercial sources.

Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1-mm sealed NaCl cells, equipped with Becton-Dickinson steel stopcocks to permit filling outside of the drybox. Nujol mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox under continuously recirculating nitrogen. NMR samples sealed into 5-mm Pyrex tubes were run on a Varian FT-80 or XL-100 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by Galbraith Laboratories or H. Malissa and G. Reuter Analytische Laboratorien.

$Na_4W(CO)_4$ (1). Liquid ammonia (100 mL) was distilled into a flask containing a glass stir bar, (TMED)W(CO)$_4$ (1.00 g, 2.42 mmol), and sodium metal (0.222 g, 9.67 mmol) at −70 °C. Within 30 min after the reaction mixture was warmed to −33 °C, a finely divided orange solid had formed. Only after the mixture stirred for 8 h at reflux was the blue color of the sodium metal in liquid ammonia completely discharged. The orange slurry was filtered at −70 °C, washed with liquid ammonia (2 × 50 mL), and dried under vacuum. In this manner 0.74 g (97%) of a pale orange, extremely pyrophoric solid was obtained which analyzed satisfactorily for **1** without further treatment.

Anal. Calcd for $C_4Na_4O_4W$: C, 12.39; H, 0.00; Na, 23.71; W, 47.40. Found: C, 12.48; H, 0.12; Na, 23.47; W, 47.25.

Compound **1** reacts explosively with fluorolube, water, and air but is insoluble in dry THF, HMPA, and liquid ammonia. Compound **1**, like the previously reported $K_3V(CO)_5$[2], will often rapidly deflagrate when scratched or hit with a metal spatula against a ground- or fritted-glass surface and thus must be handled with extreme caution.

$Na_4Mo(CO)_4$ (2) and $Na_4Cr(CO)_4$ (3). Essentially identical procedures were used to prepare samples of **2** and **3** of satisfactory purity. From 1.00 g (3.06 mmol) of (TMED)Mo(CO)$_4$ and 0.281 g (12.2 mmol) of sodium metal was obtained 0.87 g (95%) of orange-yellow, powdery **2**, and from 1.00 g (3.56 mmol) of (TMED)Cr(CO)$_4$ and 0.328 g (14.2 mmol) of sodium metal was obtained 0.84 g (93%) of yellow and powdery **3**.

Anal. Calcd for **2**, $C_4MoNa_4O_4$: C, 16.02; H, 0.0; Mo, 31.99; Na, 30.66. Found: C, 15.75; H, 0.08; Mo, 32.23; Na, 31.03.

Anal. Calcd for **3**, $C_4CrNa_4O_4$: C, 18.77; H, 0.00; Cr, 20.31; Na, 35.92. Found: C, 18.53; H, 0.24; Cr, 20.42; Na, 35.56.

Compounds **2** and **3** have very similar properties to those of **1** and may also explode or rapidly deflagrate if exposed to moisture or air or if scratched with a metal spatula, especially on a rough glass surface. In general **1**, **2**, and **3** are used in situ and not isolated because of their extreme sensitivities.

$W(CO)_4(NH_3)_2$ (4). Ammonium chloride (1.24 g, 22 mmol) was added all at once with a bent Schlenk tube into a liquid ammonia slurry at −40 °C of $Na_4W(CO)_4$, prepared in situ from 2.34 g (5.5 mmol) of (TMED)W(CO)$_4$ and 0.53 g (23 mmol) of sodium metal at −78 °C in 60 mL of liquid ammonia. Within seconds after the addition, the solution turned yellow with simultaneous evolution of gas. The solution was stirred for 2 h at reflux and filtered (medium frit) at −60 °C. After all ammonia evaporated, a bright yellow solid was obtained. Recrystallization from ammonia–water yielded 0.99 g (53% based on (TMED)W(CO)$_4$) of bright yellow and crystalline **4**.

Anal. Calcd for $C_4H_6N_2O_4W$: C, 14.56; H, 1.83; N, 8.49. Found: C, 15.05; H, 2.00; N, 8.30. Compound **4** decomposes above 131 °C. This substance has apparently not been reported previously in the scientific literature, although the Cr and Mo analogues have been noted.

$Mo(CO)_4(NH_3)_2$ (5). The same procedure for **5** was used as reported for **4** above. By this method 0.70 g of $Mo(CO)_4(NH_3)_2$ was obtained which represents a 74% yield based on the use of 1.28 g of (TMED)Mo(CO)$_4$ as the original reactant. The properties of **5** are identical with those of bona fide $Mo(CO)_4(NH_3)_2$, prepared originally by the reaction of (norbornadiene)Mo(CO)$_4$ and liquid ammonia (for which no yield was reported).[13]

$Cr(CO)_4(NH_3)_2$ (6). Compound **6** was prepared by the same procedure used for **4**. By this method 0.50 g (65%) of **6** was obtained from 1.10 g of (TMED)Cr(CO)$_4$. The properties of **6** are extremely similar to those of **4** and **5**. Compound **6** was previously reported to form by the reaction of $Cr(CO)_5NH_3$ with NH_3, but no yield or confirming spectroscopic data were given.[14]

$[Et_4N]_2[H_2W_2(CO)_8]$ (7). Method A. Ammonium chloride (0.52 g, 9.8 mmol) at room temperature was added slowly via a Schlenck tube into a liquid ammonia slurry of $Na_4W(CO)_4$ at −78 °C, prepared in situ from the reaction of (TMED)W(CO)$_4$ (1.62 g, 3.9 mmol) and sodium metal (0.36 g, 15.7 mmol) in 60 mL of liquid ammonia at −78 °C. Gas evolution was observed during the addition of NH_4Cl. The solution was refluxed for 1 h at −33 °C. Then, with minimal agitation, the slightly

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Table I. IR Spectra of Compounds in the Carbonyl Stretching Frequency Region

compd	medium	ν(CO), cm^{-1}
$Na_4W(CO)_4$ (**1**)	silicone fluid mull	1679 w, 1529 s, 1478 s, br
$Na_4Mo(CO)_4$ (2)	silicone fluid mull	1680 w, 1471 s, br
$Na_4Cr(CO)_4$ (3)	silicone fluid mull	1657 w, 1462 s, br
$W(CO)_4(NH_3)_2$^{a,d} (4)	CH_3CN	2002 w, 1874 s, 1806 m
$Mo(CO)_4(NH_3)_2$^{b,d} (**5**)	CH_3CN	2012 w, 1903 s, 1831 s
$Cr(CO)_4(NH_3)_2$^{c,d} (**6**)	CH_3CN	2016 w, 1893 s, 1835 sh, 1825 m
$[Et_4N]_2[H_2W_2(CO)_8]$ (7)	Nujol mull	1964 m, 1833 s, 1789 s
	CH_3CN	1976 w, 1884 s, 1829 m, 1800 m
$[Et_4N]_2[H_2Mo_2(CO)_8]$ (8)	Nujol mull	1970 m, 1843 s, 1793 s
	CH_3CN	1976 w, 1887 s, 1831 m, 1797 m
$[PNP]_2[H_2Mo_2(CO)_8]$ (9)	Nujol mull	1966 m, 1855 sh, 1825 s, 1797 s
	CH_3CN	1977 w, 1893 s, 1833 w, 1799 m
$[PNP]_2[H_2Cr_2(CO)_8]$ (**10**)	Nujol mull	1948 w, 1851 s, 1823 m, 1789 m-s
	CH_3CN	1958 w, 1899 s, 1823 s, 1795 m
$[Et_4N]_2[H_2Cr_2(CO)_8]$ (**11**)	Nujol mull	1948 w, 1835 s, 1783 s
	CH_3CN	1958 w, 1877 s, 1825 m, 1789 m-s
$[Et_4N]_2[W_2(CO)_8(PMe_3)_2]$ (**12**)	Nujol mull	1939 w, 1863 m, 1819 s, 1783 m, 1706 s, br
	CH_3CN	1939 w, 1865 s, 1833 vs, 1730 s
$[Et_4N]_2[HW_2(CO)_8(PMe_3)_2]$ (13)	Nujol mull	2000 m, 1982 m, 1941 sh, 1867 s, 1843 s, 1799 s
	CH_3CN	1998 w, 1980 m, 1887 vs, 1867 sh, 1827 s
$[Et_4N]_2[W_2(CO)_8(PMe_2Ph)_2]$ (**14**)	Nujol mull	1941 m, 1863 m, 1819 s, 1794 sh, 1769 m, 1714 s
	CH_3CN	1944 w, 1867 s, 1835 vs, 1732 s
$[Et_4N][HW_2(CO)_8(PMe_2Ph)_2]$ (15)	Nujol mull	2000 w, 1982 w, 1937 sh, 1915 sh, 1895 m, 1875 m, 1849 m, 1823 m, 1795 m
	THF	2000 w, 1984 w, 1897 s, 1873 sh, 1823 m
$[Et_4N]_2[W_2(CO)_8(P(OMe)_3)_2$ (16)	Nujol mull	1994 sh, 1966 w, 1887 s, 1837 s, 1817 sh, 1793 sh, 1712 s
	CH_3CN	1964 w, 1905 sh, 1895 s, 1855 vs, 1754 s
$[Et_4N][HW_2(CO)_8(P(OMe)_3)_2]$ (17)	Nujol mull	2024 w, 2004 w, 1901 s, 1877 s, 1817 s
	THF	2008 w, 1990 w, 1907 s, 1883 sh, 1829 m
$K_2[H_2W(CO)_4]$^{e} (18)	Nujol mull	1843 s, 1783 s, 1732 s
	HMPA	1851 sh, 1837 m, 1729 s, 1704 vs

[a] Nujol mull: ν(N-H) 3348 w, 3282 w; ν(CO) 2005 w, 1874 sh, 1839 s, br, 1773 s, br; $\delta(NH_2)$ 1601 w cm^{-1}. [b] Nujol mull: ν(N-H) 3366 w, 3296 w; ν(CO) 2012 w, 1889 s, br, 1843 s, br, 1779 s, br; $\delta(NH_2)$ 1600 w cm^{-1}. [c] Nujol mull: ν(N-H) 3457 w, 3301 w; ν(CO) 1879 s, br, 1853 s, 1783 s, $\delta(NH_2)$ 1602 m cm^{-1}. [d] The Nujol mull infrared spectrum of 5 has been previously reported[13] and agrees well with ours, with the exception of a ν(CO) band at 1915 cm^{-1} for which we have assigned a value of 1889 cm^{-1}. However, due to the great breadth of all these low-energy ν(CO) bands, their maxima are probably uncertain to ±20 cm^{-1}. These comments also apply to the Nujol mull spectra of compounds 4 and 6. The apparent differences in the band positions of compounds 4 and 5 in CH_3CN are not understood. We note that compounds 5 and 6 are not very stable in CH_3CN, so these values may be due to decomposition products. [e] $Li_2[H_2W(CO)_4]$ generated by the reaction of $W(CO)_4(TMED)$ with excess Li[*sec*-Bu_3BH] in refluxing THF has the following IR spectrum in CH_3CN: 1842 m, 1744 sh, 1730 s cm^{-1}. The shoulder at 1851 cm^{-1} in the HMPA solution spectrum of $K_2[H_2W(CO)_4]$ may be due to an oxidation product.

turbid red supernatant was filtered (medium porosity frit) at −60 to −78 °C. The filtrate proceeded directly into a flask containing 0.41 g (1.96 mmol) of Et_4NBr. After all of the ammonia evaporated, 50 mL of acetonitrile was added to the mixture. After the mixture was stirred for 12 h at room temperature, the solution was filtered. Removal of solvent in vacuo left orange-yellow crystals which were washed with THF (3 × 15 mL) and recrystallized from acetone–THF to yield 0.50–0.60 g (30–37% based on $(TMED)W(CO)_4$) of orange-red crystalline **7**. The compound has the same infrared spectrum as that described previously by Davison and co-workers[8] and decomposes above 165 °C.

Anal. Calcd for $C_{24}H_{42}N_2W_2O_8$: C, 33.74; H, 4.96; N, 3.28. Found: C, 33.91; H, 5.06; N, 3.32. For spectroscopic properties, see Tables I and II.

Method B. Anhydrous acetonitrile (150 mL) was added to a slurry of $Na_4W(CO)_4$ (5.85 mmol, prepared in situ as in method A) in 100 mL of liquid ammonia at −78 °C. The solution was then warmed to room temperature while stirring. After 16 h the solution had turned to a red orange color. It was filtered through a cold-jacketed filtration apparatus into a flask containing 1.23 g of Et_4NBr prechilled to −20 °C.. After the mixture was stirred for an additional 8 h at −20 °C the solvent was removed in vacuo to give an orange solid. This residue was carefully washed with H_2O (3 × 10 mL) and then with THF until the washings were colorless. The product was then dried in vacuo to provide 1.3 g (52% yield based on $(TMED)W(CO)_4$) of orange-red crystalline **7**, which had the same spectroscopic properties as samples prepared by method A.

$[Et_4N]_2[H_2Mo_2(CO)_8]$ (8). Anhydrous acetonitrile (200 mL) was added to a slurry of $Na_4Mo(CO)_4$ (prepared in situ from 3.84 g (11.8 mmol) of $(TMED)Mo(CO)_4$ and 1.08 g (47.0 mmol) of Na in 100 mL of liquid ammonia). The resulting mixture was stirred at room temperature for 15 h during which time the solution turned a deep red. The solution was then filtered through a low-temperature filtration apparatus into a vessel containing 2.47 g of solid Et_4NBr, prechilled to −20 °C. After the mixture was stirred for an additional 8 h at −20 °C, the solvent was removed to give an orange residue. This solid was carefully washed with water (3 × 20 mL) and acetone (3 × 3 mL) and dried. Recrystallization from acetone–THF provided 1.20 g (28% based on $(TMED)Mo(CO)_4$) of orange crystalline **8**. Compound **8** decomposes above 128 °C to give a maroon substance.

Table II. ^1H NMR Spectra of Anionic Derivatives

compd	medium	δ, ppm
7^a	$(CD_3)_2CO$	−4.5 (t, J_{W-H} = 30.4 Hz)
8^a	CD_3CN	−7.7 (s, μ-H)
9^b	CD_3CN	−7.7 (s, μ-H)
10^b	CD_3CN	−14.6 (s, μ-H)
11^a	CD_3CN	−14.6 (s, μ-H)
12^a	CD_3CN	1.5 (d, PMe_3, J_{H-P} = 6.8 Hz)
13^a	CD_3CN	1.6 (d, PMe_3, J_{H-P} = 7.1 Hz), −11.2 (t, μ-H, J_{H-P} = 16 Hz, J_{W-H} = 40.8 Hz)
14^a	CD_3CN	7.5–7.7 (m, $C_6H_5PMe_2$), 1.8 (d, $C_6H_5PMe_2$, J_{P-H} = 7.5 Hz)
15^a	CD_3CN	7.3–7.7 (m, $C_6H_5PMe_2$), 1.8 (d, $C_6H_5PMe_2$, J_{P-H} = 6.8 Hz), −10.8 (t, μ-H, J_{H-P} = 15.6 Hz, J_{H-W} = 44.0 Hz)
16^a	CD_3CN	3.5 (d, P(OMe)$_3$, J_{H-P} = 11.4 Hz)
17^a	CD_3CN	3.6 (d, P(OMe)$_3$, J_{H-P} = 11.2 Hz), −11.9 (t, μ-H, J_{H-P} = 21.3 Hz, J_{W-H} = 45.2 Hz)
18	CD_3CN	−3.4 (t, J_{W-H} = 33.6 Hz)

[a] Signals of cation Et_4N^+ are very similar for all salts and are at the following approximate δ: 3.0–3.6 (q, $-CH_2-$, J_{H-H} = 7.2 Hz), 1.1–1.5 (tt, CH_3, J_{H-H} = 7.2 Hz, J_{N-H} = 1.9 Hz). All integrations are satisfactory. [b] Signals of cation PNP^+ are nearly anion independent and are at δ 7.7 (m, C_6H_5).

Anal. Calcd for $C_{24}H_{42}N_2Mo_2O_8$: C, 42.49; H, 6.24; N, 4.13; Mo, 28.28. Found: C, 42.57; H, 6.17; N, 4.30; Mo, 28.13. For spectroscopic data, see Tables I and II. When the same procedure for preparing compound **7** (method A) was used in the synthesis of **8**, much smaller yields (9–10%) were obtained.

$[PNP]_2[H_2Mo_2(CO)_8]$ (9). Essentially the same procedure for the synthesis of **8** was used. Anhydrous acetonitrile (150 mL) was added to $Na_4Mo(CO)_4$ (13.7 mmol) prepared in situ in 60 mL of of liquid ammonia. After a low-temperature metathesis (at −20 °C) with [PNP]Cl (7.68 g) and a CH_3CN–THF recrystallization, 3.0 g (29% yield based on $(TMED)Mo(CO)_4$) of analytically pure, red crystalline **9** was obtained.

Anal. Calcd for $C_{80}H_{62}Mo_2N_2O_8P_4$: C, 64.27; H, 4.18; N, 1.87. Found: C, 64.21; H, 4.22; N, 1.92. Compound **9** decomposes above 165 °C to a maroon substance.

$[PNP]_2[H_2Cr_2(CO)_8]$ (10). The same procedure for the synthesis of **8** was used except the reaction time of $Na_4Cr(CO)_4$ with acetonitrile was only 5 h. From 1.10 g of $Cr(CO)_4(TMED)$ a 0.99 g (18% yield) sample of analytically pure, burgundy, crystalline **10** was obtained. This represents an unoptimized yield. Longer reaction times should improve the yield (see below).

Anal. Calcd for $C_{80}H_{62}Cr_2N_2O_8P_4$: C, 68.28; H, 4.44. Found: C, 68.02; H, 4.53. Compound **10** decomposes above 135 °C.

$[Et_4N]_2[H_2Cr_2(CO)_8]$ (11). The same procedure for the synthesis of **8** was used except the reaction time was 16 h. From 3.30 g of $Cr(CO)_4(TMED)$, 2.10 g (52% yield) of burgundy, crystalline **11** was obtained which was of satisfactory purity.

Anal. Calcd for $C_{24}H_{42}Cr_2N_2O_8$: C, 48.81; H, 7.17; N, 4.74. Found: C, 48.75; H, 7.19; N, 4.78. Compound **11** decomposes to a black material above 115 °C.

Reaction of 7 with Carbon Monoxide. Synthesis of $[Et_4N]_2[W_2(CO)_{10}]$. Carbon monoxide, predried by passing through a trap at −78 °C charged with 13X molecular sieves, was bubbled at atmospheric pressure through an acetonitrile solution (50 mL) containing 0.50 g of **7**. After 48 h at room temperature the solvent was removed under reduced pressure. The residue was crystallized from acetonitrile–THF to provide orange $[Et_4N]_2[W_2(CO)_{10}]$ in 75% yield (0.40 g) which was identical with that prepared by Hayter's original procedure.[15a] The infrared solution spectrum of $[Et_4N]_2[W_2(CO)_{10}]$ in acetonitrile has $\nu(CO)$ bands at 1941 (s), 1893 (vs), and 1793 (s) cm^{-1}. No evidence for the formation of $HW_2(CO)_{10}^{-}$[15a] or $HW(CO)_5^{-}$[15b] was observed in this reaction (e.g., no absorptions were present in the $\nu(CO)$ region above 2000 cm^{-1}). However, when the CP grade carbon monoxide was not passed through molecular sieves at −78 °C, $HW_2(CO)_{10}^{-}$ and $W(CO)_6$ were produced.

$[Et_4N]_2[W_2(CO)_8(PMe_3)_2]$ (12). A 5-fold excess of PMe_3 (ca. 1.0 mL) was added to an anhydrous acetonitrile solution (50 mL) containing 0.90 g of **7**. After 20 h at room temperature, the solvent and excess PMe_3 were removed under reduced pressure. The residue was recrystallized from acetonitrile–THF to give 0.63 g (59% yield) of orange crystalline and analytically pure **12**.

Anal. Calcd for $C_{30}H_{58}N_2W_2P_2O_8$: C, 35.81; H, 5.82; N, 2.79. Found: C, 35.94; H, 5.29; N, 2.97. The compound was slightly soluble in THF to form very oxygen- and moisture-sensitive solutions. Compound **12** melts at 120 °C.

$[Et_4N][HW_2(CO)_8(PMe_3)_2]$ (13). Excess oxygen-free water (25 mL) was added to 0.30 g of solid **12**. The slurry was stirred for 24 h at room temperature. The yellow precipitate which formed was washed with water (3 × 15 mL) and recrystallized from acetone–ether to provide 0.15 g (58% yield) of bright yellow crystalline **13** which gave satisfactory analysis.

Anal. Calcd for $C_{22}H_{39}NW_2P_2O_8$: C, 30.19; H, 4.97; N, 1.60. Found: C, 30.25; H, 4.66; N, 1.59. Compound **13** melts with decomposition at 147 °C.

$[Et_4N]_2[W_2(CO)_8(PMe_2Ph)_2]$ (14). A 10-fold excess of PMe_2Ph (ca. 2.0 mL) was added to an anhydrous acetonitrile solution (50 mL) containing 0.60 g of **7**. After the mixture was stirred 40 h at room temperature, the solvent was removed under reduced pressure. The residue was precipitated from acetonitrile–THF to give 0.42 g (54%) of analytically pure powdery orange **14**.

Anal. Calcd for $C_{40}H_{62}N_2P_2O_8W_2$: C, 42.57; H, 5.54; N, 2.48. Found: C, 42.71; H, 5.63; N, 2.64. Compound **14** melts at 113 °C.

$[Et_4N][HW_2(CO)_8(PMe_2Ph)_2]$ (15). Treatment of 0.30 g of solid **14** with 25 mL of oxygen-free water provided a yellow precipitate after 24 h of vigorous stirring at room temperature. The solid was washed with water (3 × 15 mL) and then recrystallized from acetone–ether to provide 0.17 g (64% yield) of yellow crystalline **15**.

Anal. Calcd for $C_{32}H_{43}NP_2O_8W_2$: C, 38.46; H, 4.34; N, 1.40. Found: C, 38.63; H, 4.18; N, 1.60. Compound **15** decomposes above 109 °C to a green substance.

$[Et_4N]_2[W_2(CO)_8(P(OMe)_3)_2]$ (16). A 5-fold excess of $P(OMe)_3$ (ca. 4.5 mL) was added to an anhydrous acetonitrile solution (50 mL) containing 2.95 g of **7**. The solution bubbled vigorously after addition of the trimethyl phosphite. After 24 h at room temperature the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile–THF to give 3.10 g (82% yield) of analytically pure orange microcrystalline **16**.

Anal. Calcd for $C_{30}H_{58}N_2P_2O_{14}W_2$: C, 32.74; H, 5.31; N, 2.55. Found: C, 32.65; H, 5.23; N, 2.55. Compound **16** decomposed above 96 °C to a red substance.

$[Et_4N][HW_2(CO)_8(P(OMe)_3)_2]$ (17). Treatment of 0.45 g of solid **16** with excess (25 mL) of oxygen-free water provided a yellow precipitate after 24 h of vigorous stirring. The solid was washed with water (3 × 15 mL) and then recrystallized from acetone–ether to provide 0.20 g (46% yield) of yellow crystalline and analytically pure **17**.

Anal. Calcd for $C_{22}H_{39}O_{14}NP_2W_2$: C, 27.21; H, 4.05; N, 1.44. Found: C, 27.27; H, 4.15; N, 1.48. Compound **17** melts at 84 °C.

$K_2[H_2W(CO)_4]$ (18). Method A. A 10-fold excess of K[*sec*-Bu_3BH] (1.0 M solution in THF) was added to a slurry containing 0.30 g (0.35 mmol) of **7** in 30 mL of THF. After the solution was refluxed for 24 h and cooled to room temperature, the supernatant was removed via cannula and the orange-yellow precipitate was washed with THF (3 × 15 mL) to provide a nearly quantitative yield (0.13 g) of analytically pure **18**.

Anal. Calcd for $C_4H_2O_4K_2W$: C, 12.77; H, 0.54; K, 20.79; W, 48.88; O, 17.02. Found: C, 12.68; H, 0.66; K, 20.94; W, 49.10; O (by difference), 16.62. Compound **18** decomposes at 110 °C to a gray tar.

Method B. A 10-fold excess of K[*sec*-Bu_3BH] (ca. 40 mL of a 1.0 M solution in THF) was added to a solution of $(TMED)W(CO)_4$ (1.62 g, 3.92 mmol) in 50 mL of THF. The solution was refluxed for 24 h and then cooled to room temperature. The supernatant was then removed and rejected. The resulting precipitate was washed with THF (3 × 30 mL) to provide 1.03 g (70% yield) of orange-yellow microcrystalline **18** which had identical properties to that prepared by method A.

Results and Discussion

Reductive Labilization Method for the Synthesis of Highly Reduced Organometallics. For several years it has been recognized by our group that the reduction of a non-cluster-metal complex containing both good and poor π-acceptor ligands often causes preferential loss of the weaker or non-π-acceptors.[7] For example, $ClCr(CO)_5^-$ undergoes reduction by sodium in HMPA to provide $Cr(CO)_5^{2-}$, i.e., eq 4.[16] Cooper and co-workers have recently used

$$Cr(CO)_5Cl^- \xrightarrow{\text{Na-HMPA}} Cr(CO)_5^{2-} + Cl^- \qquad (4)$$

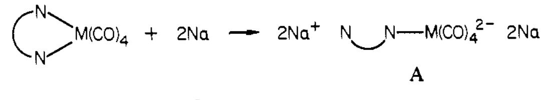
this same method to synthesize the first phosphine substituted carbonyl dianion of tungsten by reduction, i.e., eq 5.[17] Our

$$W(CO)_4(NH_3)(i\text{-}Pr_3P) \xrightarrow{\text{2Na-Np}} W(CO_4)(i\text{-}Pr_3P)^{2-} + NH_3 \qquad (5)$$

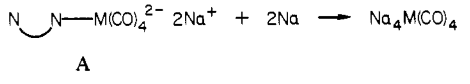
discovery that this reductive labilization method could be extended to carbonyl complexes bearing two poor π-acceptor groups was particularly gratifying. In this process *N,N,N′,N′*-tetramethylethylenediamine is effectively replaced by four electrons in the sodium metal reduction of $M(CO)_4(TMED)$ to produce the first examples of $Na_4M(CO)_x$ species, i.e., eq 6. The reduction process

$$M(CO)_4(TMED) + 4Na \xrightarrow{NH_3} Na_4M(CO)_4 + TMED \qquad (6)$$

may proceed stepwise and thus resemble initially that reaction depicted above in eq 5, i.e., eq 7 and 8. Although we have



(7)



(8)

attempted to prepare the postulated intermediate A by the reaction of $M(CO)_4(TMED)$ with 2 equiv of alkali metal in liquid ammonia, the results of these experiments are not yet conclusive. It is noteworthy, however, that this synthesis of $Na_4M(CO)_4$ establishes the importance of the reductive labilization method as

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(15) (a) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376. (b) Darensbourg, M. Y.; Slater, S. *Ibid.* **1981**, *103*, 5914.

(16) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7825.

(17) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1982**, *1*, 215.

a route to novel organometallic anions. Certainly, other extensions of this general procedure to new families of transition-metal complexes are anticipated.

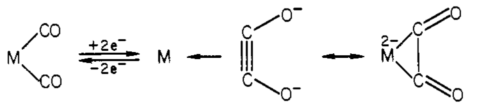
One very important and obvious limitation of this reductive labilization method is that the ligand to be expelled should not be susceptible to reduction either in a coordinated or free state. For this reason, complexes of the type $M(CO)_4L_2$ containing the preformed tetracarbonylmetal unit and bearing ligands which are not attacked by sodium in liquid ammonia were initially examined. Our best results (yields >90% of $Na_4M(CO)_4$) have been obtained by the reduction of $M(CO)_4(TMED)$ in liquid ammonia. These reductions are remarkably clean compared to those of other systems we have examined, where acetylenediolate dianion, $C_2O_2^{2-}$, and small amounts of $NaNH_2$ invariably contaminate the final product unless they can be removed by filtration.[2-5] It was observed that the reduction of $M(CO)_4$(norbornadiene) gives very poor yields (2–3% for M = W) of $Na_4M(CO)_4$. It is known that free norbornadiene reacts with $Na-NH_3$, but the presence of the complexed ligand may also complicate the reduction. Also, reductions of $M(CO)_4$(ethylenediamine) generally give substantially lower yields of $Na_4M(CO)_4$ than $M(CO)_4(TMED)$. Although, free ethylenediamine is inert to $Na-NH_3$ at −33 °C, the coordinated ligand may be attacked (e.g., deprotonated) under these conditions.

Properties of $Na_4M(CO)_4$ (M = Cr, Mo, W). From the reductions of $M(CO)_4(TMED)$, high yields of brightly colored yellow to orange precipitates are obtained which have elemental compositions closely corresponding to the formulations $Na_4M(CO)_4$. As noted in the Experimental Section, these dry substances are extremely reactive and may decompose explosively if not handled with care.

Infrared spectra of $Na_4M(CO)_4$ in the carbonyl stretching frequency region show bands at exceedingly low energies for terminal carbonyl groups (Table I). These values are almost 200 cm^{-1} lower than those reported previously for $Na_3M(CO)_4$ (M = Mn and Re)[4] and $Cs_3V(CO)_5$[2] and thus are consistent with a metal center bearing more negative charge than that present on the metals in the carbonyl trianions. We presently believe that these insoluble "tetraanions" are most reasonably formulated as $[M(CONa)_4]_x$, where extensive and strong sodium ion–carbonyl oxygen interactions may be responsible for the very low ν(CO) values. It should be emphasized however that reductively coupled carbon monoxide units may also be present in these highly reduced species. Free carbon monoxide rapidly reacts with $Na-NH_3$ in the following fashion:[18a]

$$2Na + 2CO \rightarrow NaOC{\equiv}CONa \qquad (9)$$

As suggested previously,[7] it is very possible that bound CO could also undergo reductive coupling to produce coordinated acetylenediolate dianion or condensation products thereof (e.g., coordinated $C_4O_4^{4-}$ containing a cyclobutadiene group);[18b] i.e.[36]

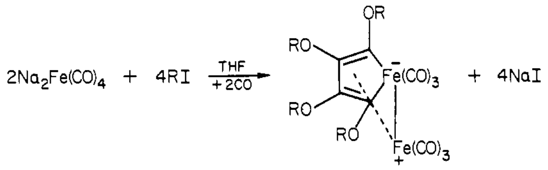


(10)

The broad and intense absorptions observed in the 1400–1500-cm^{-1} region for $Na_4M(CO)_4$ are in the range expected for CO stretching frequencies corresponding to a CO bond order between one and two. Although it is tempting to attribute these bands to coordinated acetylenediolate or related units, there is presently no chemical or other spectroscopic evidence to justify this assignment. Indeed, all reactions of $Na_4M(CO)_4$ investigated to date give rise to derivatives containing only terminal carbonyls. As depicted in eq 10, however, it is possible that reductive coupling of CO can be reversed on addition of an electrophile to yield the observed products. Indeed, we have shown that $K_2C_2O_2$ does react with certain metal halides to give low to moderate yields of metal carbonyls; e.g., eq 11.[33] Coupling of coordinated carbon monoxide

$$(Ph_3P)_2NiBr_2 + K_2C_2O_2 \rightarrow \underset{\text{yield} \sim 40\%}{(Ph_3P)_2Ni(CO)_2} + 2KBr \qquad (11)$$

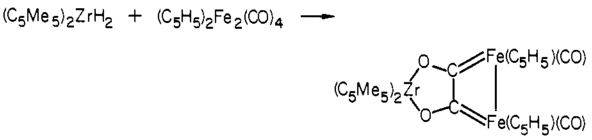
has been established to occur in the following interesting reaction of $Na_2Fe(CO)_4$ with Me_3SiI: eq 12.[19]



(12)

R = Me_3Si

More recently, $(C_5Me_5)_2ZrH_2$ has been shown to react with $[C_5H_5Fe(CO)_2]_2$ to provide a novel product containing coordinated $C_2O_2^{2-}$:[20]



(13)

On the basis of these precedents for "noninnocent" behavior of carbon monoxide in complexes, it would clearly be inappropriate at this time to suggest that $Na_4M(CO)_4$ really do contain monomeric "tetracarbonylmetalate tetraanion" units, despite the fact that they react with various electrophiles to provide bona fide derivatives of $M(CO)_4^{4-}$.

Reaction of Metal Carbonyl Anions with Brønsted Acids. The protonation of metal carbonyl anions is a fundamentally important reaction in organometallic chemistry.[21] Generally, these reactions give rise to metal carbonyl hydrides which may subsequently decompose to carbonyl dimers, clusters, or other species. For example, most binary carbonyl monoanions and the group 8 carbonyl dianions can be protonated to form isolatable neutral carbonyl mono- and dihydrides:

$$M(CO)_x^- + H^+ \rightarrow HM(CO)_x \qquad (14)$$

$$x = 5,\ M = Mn, Tc, Re;\ x = 4,\ M = Co, Rh, Ir$$

$$M(CO)_4^{2-} + 2H^+ \rightarrow H_2M(CO)_4 \qquad (15)$$

$$M = Fe, Ru, Os$$

By contrast, we have recently observed that protonation of the binary carbonyl trianions of V[2], Nb[3], Ta[3], Mn,[22] and Co[22] in liquid ammonia results in the rapid elimination of molecular hydrogen and the formation of amminecarbonylmetalate monoanions as shown in eq 16 and 17. Thus far, no spectroscopic evidence for

$$M(CO)_x^{3-} + 2H^+ \rightarrow \underset{\text{unstable}}{[H_2M(CO)_x^-]} \qquad (16)$$

$$[H_2M(CO)_x^-] + NH_3 \rightarrow M(CO)_xNH_3^- + H_2 \qquad (17)$$

the formation of the carbonyl dihydride monoanions has been obtained; however, the amminepentacarbonylmetalate ions of vanadium, niobium, and tantalum have been isolated as thermally stable salts.[2,3] Also, in the case of the corresponding diprotonation of $Re(CO)_4^{3-}$,[4] the thermally stable *cis*-$H_2Re(CO)_4^-$ has been isolated as the tetraethylammonium salt in good yield.[22]

It was therefore of interest to extend these protonation studies to the only presently known compounds formally containing

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(22) Ellis, J. E.; Warnock, G. F., unpublished research.

mononuclear metal carbonyl tetraanions, $Na_4M(CO)_4$. The only previously reported reactions of these unusual substances have been with chlorotriphenylstannane which provided moderate to high yields of derivatives containing six- and seven-coordinate chromium, molybdenum, and tungsten:[7]

$$2Ph_3SnCl + Na_4M(CO)_4 \rightarrow Na_2[(Ph_3Sn)_2M(CO)_4] + 2NaCl \quad (18)$$

$$3Ph_3SnCl + Na_4M(CO)_4 \rightarrow Na[(Ph_3Sn)_3M(CO)_4] + 3NaCl \quad (19)$$

By analogy with the Ph_3SnCl reactions, it was hoped that reactions of $Na_4M(CO)_4$ with acids would lead to the formation of the new species $H_2M(CO)_4^{2-}$ and $H_3M(CO)_4^-$. Actually, 4 equiv or an excess of NH_4Cl react with $Na_4M(CO)_4$ in liquid ammonia to provide 50–80% yields of the diammine complexes, $M(CO)_4(NH_3)_2$. Intermediates in this reaction have not been identified yet. Although $Na_4M(CO)_4$ could undergo protonation to form the aforementioned $H_xM(CO)_4^{x-4}$, in view of the very strong reducing nature of $Na_4M(CO)_4$, a process involving radicals may be more likely. Indeed, we have evidence to indicate that $H_2W(CO)_4^{2-}$ is *not* an intermediate in this reaction (vide infra). A significant difficulty in attempting to isolate intermediates from these protonation reactions is that even when fewer than 4 equiv of NH_4Cl are added, the final product contains much $M(CO)_4(NH_3)_2$ in addition to unreacted $Na_4M(CO)_4$. Evidently the insoluble tetrasodium compound is converted to soluble intermediates which react more rapidly with NH_4Cl than $Na_4M(CO)_4$. Attempts to trap potential intermediates such as $HM(CO)_4^-$ with phosphines and other nucleophiles have been unsuccessful thus far.

While $Mo(CO)_4(NH_3)_2$[13] and $Cr(CO)_4(NH_3)_2$[14] have been reported previously, apparently $W(CO)_4(NH_3)_2$ is a new species. It is worth pointing out, however, that the yields of the molybdenum and chromium diammine complexes were not reported, so our synthesis, which provides 50–70% yields of $M(CO)_4(NH_3)_2$, may be the method of choice for the preparation of these materials. Significantly, there is no evidence for the presence of $M(CO)_5NH_3$ or $M(CO)_3(NH_3)_3$ in these samples.

The properties of these substances are very similar and they have infrared spectra in the ν(CO) region (Table I) which are consistent with those expected for species of *cis*-$M(CO)_4L_2$ geometry. The ^1H NMR spectrum of *cis*-$W(CO)_4(NH_3)_2$ in CD_3CN shows a broad signal at about 2.8 ppm attributable to the NH_3 groups. Attempts to obtain the ^1H NMR spectra of the Cr and Mo analogues in CD_3CN at room temperature were thwarted by slow decomposition. The only unusual property of these materials appears to be their moderate solubility in water. Few other neutral metal carbonyls dissolve appreciably in water without reaction.

Formation of $H_2M_2(CO)_8^{2-}$ from $Na_4M(CO)_4$. Treatment of $Na_4W(CO)_4$ in liquid ammonia with about 2.5 equiv of ammonium chloride or excess acetonitrile provides, after treatment with Et_4NBr, 30–50% yields of pure crystalline $[Et_4N]_2[H_2W_2(CO)_8]$. The reaction with NH_4Cl is fairly rapid and can be scaled up to yield about 5 g of product per preparation. Previously, salts containing $H_2W_2(CO)_8^{2-}$ were available only in very low yield by refluxing solutions of $W(CO)_6$ and $[Et_4N][BH_4]$ in THF.[8,9] However, after our work described herein was completed, Bau, Kirtley, and co-workers reported the synthesis of $[PNP]_2[H_2W_2(CO)_8]$ in 65% yield by the treatment of $[PNP][W(CO)_5I]$ with $[PNP][BH_4]$ in THF.[10a] The spectroscopic properties of the PNP^+ and Et_4N^+ salts prepared by both methods are virtually identical (Tables I and II). Interestingly, although the tungsten salts are very reactive in solution, as crystalline solids they may be handled for hours in air without deterioration.

As in the case of the tungsten system, the best yields of the previously unknown $H_2Mo_2(CO)_8^{2-}$ and $H_2Cr_2(CO)_8^{2-}$ are obtained by the reaction of excess anhydrous acetonitrile with $Na_4M(CO)_4$ (M = Cr, Mo) generated in situ in liquid ammonia. In this reaction, the acetonitrile ($pK_a \approx 25$) functions as a Brønsted acid.[23-26] By monitoring the reactions with infrared spectra, it has been shown that the principal soluble metal carbonyl species is $H_2M_2(CO)_8^{2-}$, while even after 24 h significant amounts of insoluble $Na_4M(CO)_4$ are still present. The lowest yield (18%) of $H_2Cr_2(CO)_8^{2-}$, isolated as the PNP^+ salt, was obtained from a 5-hour reaction time, while the Et_4N^+ salt of this anion was obtained in 52% yield from an essentially identical reaction conducted for 16 h. At ambient temperatures it appears that $H_2Mo_2(CO)_8^{2-}$ and $H_2Cr_2(CO)_8^{2-}$ react with halide ions in solution. For this reason to obtain reasonable yields of the Et_4N^+ and PNP^+ salts, the metatheses had to be carried out at −20 °C or lower. By contrast, $H_2W_2(CO)_8^{2-}$ is significantly less reactive in solution. It may be that the apparent failure to prepare $H_2Mo_2(CO)_8^{2-}$ and $H_2Cr_2(CO)_8^{2-}$ by the reaction of the corresponding $IM(CO)_5^-$ and BH_4^- is due to the presence of the iodide ion generated in this process.[10b]

The infrared and ^1H NMR spectra of $H_2Mo_2(CO)_8^{2-}$ and $H_2Cr_2(CO)_8^{2-}$ are analogous to those of $H_2W_2(CO)_8^{2-}$ and are shown in Tables I and II. The orange $[Et_4N]_2[H_2Mo_2(CO)_8]$ and red $[PNP]_2[H_2Mo_2(CO)_8]$ have IR spectra in the ν(CO) region which are nearly superimposable on the corresponding bands of $H_2W_2(CO)_8^{2-}$. The corresponding ν(CO) bands of the burgundy $[Et_4N]_2[H_2Cr_2(CO)_8]$ and $[PNP]_2[H_2Cr_2(CO)_8]$ are shifted to somewhat lower energy, but the relative shapes and intensities are essentially the same as those of the Mo and W analogues and are consistent with the presence of *cis*-$(\mu\text{-}H)_2M(CO)_4$ units. The ^1H NMR spectra of the Et_4N^+ and PNP^+ salts of $H_2Mo_2(CO)_8^{2-}$ are essentially identical in the metal hydride region and show one sharp signal at −7.65 ppm. The chromium analogue exhibits a sharp signal at significantly higher field, −14.55 ppm. The higher field chemical shift observed for $H_2Cr_2(CO)_8^{2-}$ vs. that of the molybdenum and tungsten analogues is consistent with the similar trend noted for the $(\mu\text{-}H)(M(CO)_5)_2^-$ anions, where δ is −19.2 for Cr, while the δ's for Mo and W are −12.2 and −12.6, respectively.[15a] It should be noted that none of our data rule out the possibility that the molybdenum and chromium hydrides are, in fact, trimers, $[HM(CO)_4]_3^{3-}$. However, we presently favor the dimeric formulation for these species on the basis of their very similar infrared spectra to that of $H_2W_2(CO)_8^{2-}$, for which the structure is known.

Although it is presently not known how $H_2M_2(CO)_8^{2-}$ form in these protonation reactions, it is possible that they arise via dimerization of the postulated intermediate $HM(CO)_4^-$ mentioned earlier. The chemical reactivity patterns of $H_2Cr_2(CO)_8^{2-}$ and $H_2Mo_2(CO)_8^{2-}$ are largely unexplored and should provide some very interesting comparisons with those of $H_2W_2(CO)_8^{2-}$, $H_2Os_3(CO)_{10}$, and related species.[11] Some initial results on the chemical properties of $H_2W_2(CO)_8^{2-}$ will now be described.

Reactions of $H_2W_2(CO)_8^{2-}$ with Nucleophiles. In principle, $H_2W_2(CO)_8^{2-}$ could react with nucleophiles in various ways resulting in either retention or scission of the ditungsten center. Thus far, the reactions we have observed are of two types and are summarized in eq 20 and 21. Both reactions result in removal

$$H_2W_2(CO)_8^{2-} \xrightarrow{+2L} H_2 + W_2(CO)_8L_2^{2-} \quad (20)$$

$$H_2W_2(CO)_8^{2-} \xrightarrow{+2L} 2HW(CO)_4L^- \quad (21)$$

of the formal unsaturation at the metal centers. When L is a π-acceptor ligand (specifically for L = CO, PMe_3, PMe_2Ph, and $P(OMe)_3$), hydrogen evolution occurs (except for isocyanides)[27]

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(23) Only a few other metal carbonyl anions react with CH_3CN. These include $K_2[Fe(CO)_3PR_3]$[24] and $Na_3V(CO)_5$.[2] An apparently identical deprotonation product, which is characterized by a strong absorption in the infrared region at ca. 2130 cm^{-1}, is obtained from the reaction of potassium metal or $Na_4M(CO)_4$ with excess CH_3CN. The exact nature of this product is not known, but it has been reported that CH_2CN^-[25] adds to CH_3CN to provide $CH_3(CN)CH_2CN^-$.[26] Infrared spectra of these latter anions have apparently not been reported.

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and the corresponding $W_2(CO)_8L_2^{2-}$ forms in high yields. Isolated yields of $W_2(CO)_{10}^{2-}$, $W_2(CO)_8(PMe_3)_2^{2-}$, $W_2(CO)_8(PMe_2Ph)_2^{2-}$, and $W_2(CO)_8(P(OMe)_3)_2^{2-}$ as Et_4N^+ salts are 54–82%. Although infrared monitoring of the reactions show that these materials are formed almost quantitatively, they are very sensitive to traces of moisture and other impurities in solvents used during the purification steps. For example, small amounts of moisture will rapidly convert these dianions to $HW_2(CO)_8L_2^-$. Undoubtedly, the presence of moisture during reaction or workup is responsible for the previous incorrect report that $H_2W_2(CO)_8^{2-}$ reacts directly with CO to form $HW_2(CO)_{10}^-$ and "H^-".[10] Pure samples of the new species $[Et_4N][HW_2(CO)_8L_2]$ (L = PMe_3, PMe_2Ph, and $P(OMe)_3$) were also prepared in 46–64% yield by reacting crystalline samples of $[Et_4N]_2[W_2(CO)_8L_2]$ with water. These reactions were done with small quantities of reactants. The low to moderate yields reported for them are undoubtedly due to handling losses since infrared monitoring indicated that these protonation reactions proceed quantitatively. Although $HW_2(CO)_8L_2^-$ are new species, similar molybdenum compounds have been prepared previously by the thermal substitution of $HMo_2(CO)_{10}^-$ by appropriate ligands.[28,36]

In contrast to the π-acceptor ligand reactions, treatment of $H_2W_2(CO)_8^{2-}$ with 2 equiv of *sec*-Bu_3BH^- causes scission of the ditungsten unit as the potassium salt, i.e., eq 22. Interestingly,

$$H_2W_2(CO)_8^{2-} + 2HBR_3^- \rightarrow 2H_2W(CO)_4^{2-} + 2BR_3 \qquad (22)$$

the only other well-characterized reaction previously reported for $H_2W_2(CO)_8^{2-}$, shown in eq 23, also involves a W–W bond cleavage.[10]

$$H_2W_2(CO)_8^{2-} + 2BH_3{\cdot}THF \rightarrow 2W(CO)_4BH_4^- \qquad (23)$$

Infrared spectra of $HW_2(CO)_8L_2^-$ are extremely similar in the ν(CO) region, where corresponding bands are in approximately the same position and of about the same relative intensity. Additionally, for a corresponding ν(CO) band the energy of the vibration increases as L becomes a weaker donor which is in the expected order: $PMe_3 < PMe_2Ph < P(OMe)_3$. On the basis of these comparisons it seems very likely that these three anions have quite similar structures. The IR spectral bands of these species are also very similar in number, positions, and relative intensities to those reported previously for $HMo_2(CO)_8(PMePh_2)_2^-$ (ν(CO) in THF: 2021 w, 1989 w, 1906 s, 1875 sh, 1822 m cm^{-1}), for which the structure has been determined by a single-crystal X-ray study.[28] The latter study showed that the phosphines are substituted diequatorially (i.e., cis to the hydride bridge) with a P(1)–Mo(1)–Mo(2)–P(2) torsion angle of about 40°. By contrast, both diequatorially and diaxially substituted structures of the neutral $Mn_2(CO)_8L_2$ are known. For L = $PMePh_2$, PPh_3, $AsPh_3$, and PEt_3, the substituents are attached diaxially,[29] while for L = $AsMe_2Ph$, $AsEt_3$ and $AsMe_3$, diequatorial substitution is observed.[30] Structural characterization of $Mn_2(CO)_8(AsMe_2Ph)_2$ showed an As(1)–Mn(1)–Mn(2)–As(2) torsion angle of 180° confirming the diequatorial assignment.[30a] Also, $Mn_2(CO)_8L_2$, where L_2 = diphenylphosphinomethane, has been prepared and has been assigned a syn-diequatorial structure on the basis of its IR spectrum, which is considerably more complex than that of the diaxially or anti-diequatorially substituted $Mn_2(CO)_8L_2$ species.[31]

Infrared spectra of the $W_2(CO)_8L_2^{2-}$ anions are shown in Table I. Their solution spectra consist of four bands and are somewhat similar in complexity to those of $HW_2(CO)_8L_2^-$ but much different than spectra of the diaxially substituted $Mn_2(CO)_8L_2$ for which only one strong and two weak bands are present in the ν(CO) region.[31] However, the relative intensities of the bands in the infrared spectra of $W_2(CO)_8L_2^{2-}$ are so similar to those reported for *eq,eq*-$Mn_2(CO)_8(AsMe_2Ph)_2$[30b] that there is little doubt that $W_2(CO)_8L_2^{2-}$ are also diequatorially substituted, where each tungsten unit has *cis*-$W(CO)_4XY$ geometry. Proton NMR spectra data for $W_2(CO)_8L_2^{2-}$ species shown in Table II are consistent with the presence of two phosphine ligands occupying the same average environment. The ^1H NMR spectral data for the three $HW_2(CO)_8L_2^-$ species are also consistent with one another; e.g., δ values for the bridging hydrogen range from −10.8 to −11.9 ppm while corresponding ^{31}P–^1H and ^{183}W–H coupling constants are 15.6–21 Hz and 40.8–45.2 Hz, respectively.

Synthesis and Properties of $K_2[H_2W(CO)_4]$. Perhaps the most useful reaction of $[Et_4N]_2[H_2W_2(CO)_8]$ examined, thus far, is its conversion to the monomeric $H_2W(CO)_4^{2-}$, isolated as the potassium salt. The availability of this previously unknown highly reactive monomeric hydride dianion should make it a useful precursor to a variety of new organotungsten compounds, including metal clusters. It also occurred to us that this material could be made more readily and directly from the reaction of $W(CO)_4(TMED)$ with 2 equiv of hydride ion since we observed previously that $W(CO)_4(TMED)$ rapidly reacts with Ph_3SnLi to provide good yields of $W(CO)_4(SnPh_3)_2^{2-}$:

$$2Ph_3Sn^- + W(CO)_4(TMED) \xrightarrow[\text{room temp}]{\text{THF}} (Ph_3Sn)_2W(CO)_4^{2-} + TMED \qquad (24)^7$$

In fact, excess K[*sec*-Bu_3BH] in THF reacts under reflux to generate approximately 70% yields of the same $K_2[H_2W(CO)_4]$ according to the reaction:

$$2K[sec\text{-}Bu_3BH] + W(CO)_4(TMED) \rightarrow K_2[H_2W(CO)_4] + 2sec\text{-}Bu_3B + TMED \qquad (25)$$

It should be noted that $Cr(CO)_4(TMED)$ and $Mo(CO)_4(TMED)$ react rapidly with one equivalent of $K[HBR_3]$ in refluxing THF to give completely different products which will be the subject of a future report.[32]

The spectroscopic properties and elemental analyses of this orange-yellow microcrystalline solid are consistent with the formulation $K_2[H_2W(CO)_4]$ (**18**). The ^1H NMR of **18** shows a signal at −3.4 ppm in CD_3CN with satellites due to ^{183}W–H coupling ($J_{W\text{-}H}$ = 33.6 Hz). Its infrared spectrum in CH_3CN consists of two relatively intense bands at 1845 and 1722 cm^{-1}, which are in the range expected for a dianion. For example, $W(CO)_5^{2-}$ exhibits IR-active bands at 1775 and 1731 cm^{-1} in HMPA,[16] while $Fe(CO)_4^{2-}$ has one intense band at 1730 cm^{-1} in HMPA.[33] One would expect a four-band pattern in the ν(CO) region for *cis*-$H_2W(CO)_4^{2-}$ and this is observed for $K_2[H_2W(CO)_4]$ in HMPA: 1851 sh, 1837 m, 1729 s, 1704 vs cm^{-1}. Infrared spectra of *cis*-$H_2Re(CO)_4^-$ (ν(CO): 2020 w, 1995 m, 1930 vs, 1895 s cm^{-1} in THF)[34] and *cis*-$H_2Os(CO)_4$ (ν(CO): 2139 w, 2067 m, 2055 s, 2047 vs cm^{-1} in hexane)[35] are similar except the bands are at significantly higher energies. These latter species also have ^1H NMR spectra which are consistent with the presence of one hydride environment ($H_2Re(CO)_4^-$, δ −7.0;[34] $H_2Os(CO)_4$, δ −8.7[35]).

Earlier we suggested that $H_2W(CO)_4^{2-}$ was *not* an intermediate in the production of $W(CO)_4(NH_3)_2$ and $H_2W_2(CO)_8^{2-}$ from the protonation of $Na_4W(CO)_4$. When $K_2[H_2W(CO)_4]$ is treated with 2 equiv of NH_4Cl in liquid ammonia, there is generated a deep violet solid which we have identified by a preliminary crystal structure and elemental analyses as $K_4[HW(CO)_3]_4$.[32] No evi-

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dence for the formation of $W(CO)_4(NH_3)_2$ in this reaction was obtained.

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Registry No. 1, 67202-46-4; **2**, 67202-63-5; **3**, 67202-62-4; **4**, 84894-06-4; **5**, 23623-69-0; **6**, 84850-66-8; **7**, 51232-76-9; **8**, 84850-68-0; **9**, 84850-69-1; **10**, 84850-71-5; **11**, 84850-72-6; **12**, 84850-74-8; **13**, 84850-76-0; **14**, 84850-78-2; **15**, 84850-80-6; **16**, 84850-82-8; **17**, 84850-84-0; **18**, 84850-85-1; $[Et_4N]_2[W_2(OO)_{10}]$, 15616-71-4; $Li_2[H_2W(CO)_4]$, 84850-86-2; (TMED)$W(CO)_4$, 15024-58-5; (TMED)$Mo(CO)_4$, 14971-45-0; (TMED)$Cr(CO)_4$, 21136-10-7; NH_4Cl, 12125-02-9; CH_3CN, 75-05-8; CO, 630-08-0; K[*sec*-Bu_3BH], 54575-49-4.

Synthesis, Characterization, and Chemistry of Pentacarbonylnitrosylvanadium, V(CO)₅NO, a Remarkably Reactive Relative of Hexacarbonylchromium

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Abstract: Thermally unstable, deep red-violet, and remarkably reactive $V(CO)_5NO$ has been prepared in high yields by the reaction of equimolar amounts of $[Et_4N][V(CO)_6]$ and $[NO][BF_4]$ in methylene chloride at −40 °C. Also, $V(CO)_5NO$ has been isolated and characterized for the first time by mass spectra and derivative chemistry. This volatile material undergoes substitution reactions with a large variety of neutral and anionic bases at −30 to 0 °C to provide 42–95% yields of new products. These include $[V(CO)_4NO(Ph_2PCH_2)]_2$, $V(CO)_4(NO)(PMe_3)$, thermally unstable $V(CO)_4(NO)(NMe_3)$, $[Et_4N][V(CO)_4(NO)I]$, $[Ph_4As][(CO)_5MnV(CO)_4NO]$, which contains a Mn–V bond, and $[Et_4N][C_5H_5V(CO)_2NO]$. The last substance is the first example of a carbonylnitrosylcyclopentadienylmetalate ion and the final member of the isoelectronic series $C_5H_5V(NO)_{3-x}(CO)_x{}^{1-x}$ ($x = 0$–3) to be prepared. Attempts to synthesize $Ta(CO)_5NO$ and derivatives thereof are also described.

Although pentacarbonylnitrosylvanadium was mentioned in the literature over 20 years ago,[1] until very recently no other information on this mysterious material was available.[2] By comparison, the properties of the only other presently known neutral mononuclear carbonylnitrosylmetal species, $Mn(CO)(NO)_3$, $Mn(CO)_4NO$, $Fe(CO)_2(NO)_2$, and $Co(CO)_3NO$ have been well documented.[3] In view of the isoelectronic nature of $Cr(CO)_6$ and $V(CO)_5NO$ and the important status of the former species in the organometallic chemistry of chromium, it was felt that an unambiguous characterization of $V(CO)_5NO$ and an examination of its reactivity patterns could be of considerable importance in the development of organovanadium chemistry. In this paper are described our initial studies in this area. In addition, evidence for the synthesis of $Ta(CO)_5NO$ will be discussed.

Experimental Section

General Procedures and Starting Materials. All operations were performed under an atmosphere of nitrogen further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulas and syringes; otherwise reactions were generally performed by using standard Schlenck apparatus with a double manifold vacuum line. Reagent grade methylene chloride and acetonitrile were dried with CaH_2, freed of oxygen by nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran, diethyl ether, toluene, and hexane were distilled from alkali metal benzophenone ketyls before use. Deionized water and reagent grade acetone, heptane, and absolute ethanol were freed of oxygen by dispersing nitrogen through the solvents for 1–2 h before use.

The following reagents were purchased from commercial sources and freed of oxygen before use: bis(diphenylphosphino)ethane, nitrosonium tetrafluoroborate, tetraethylammonium bromide, trimethylphosphine, and triphenylphosphine. Tetraethylammonium hexacarbonylvanadate,[4] tetraphenylarsonium hexacarbonylvanadate,[5] tetraphenylarsonium pentacarbonylmanganate,[6] tetraphenylphosphonium hexacarbonyltantalate,[7] and (1,2-dimethoxyethane)sodium cyclopentadienide[8] were prepared by known procedures.

Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1-mm sealed NaCl cells, equipped with Becton-Dickinson steel stopcocks to permit filling outside of the drybox. Nujol mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox under continuously recirculating nitrogen. NMR samples sealed into 5-mm Pyrex tubes were run on a Varian FT-80 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by Galbraith Laboratories or H. Malissa and G. Reuter Analytische Laboratorien. Low- and high-resolution mass spectra were recorded at 70 eV on an AEI MS-30 spectrometer where the solid probe was cooled to −10 °C (to minimize thermal decomposition of the sample) and allowed to slowly warm to room temperature. UV–visible spectra were recorded on a Cary 17D spectrophotometer.

Pentacarbonylnitrosylvanadium, $V(CO)_5(NO)$ (1). Tetraethylammonium hexacarbonylvanadate (1.0 g, 2.9 mmol) was dissolved in 20 mL of CH_2Cl_2 and cooled to −50 °C. Solid $[NO][BF_4]$ (0.34 g, 2.9 mmol) was placed in another flask and cooled to −50 °C. The $[Et_4N][V(CO)_6]/CH_2Cl_2$ slurry was transferred into the flask containing $[NO][BF_4]$. An additional 20 mL of CH_2Cl_2 was used to transfer all of the $[Et_4N][V(CO)_6]$ into the reaction flask. The reaction mixture rapidly changed from a yellow slurry into a very dark purple solution with purple precipitate on the sides of the flask. The mixture was stirred for 1.5 h at −40 °C. The CH_2Cl_2 was removed in vacuo at −40 °C to leave a dry brown solid. The flask was warmed to −10 °C. Compound (1) was extracted with 20 mL of hexane at this temperature and transferred into a Schlenck tube. The solution was cooled to −78 °C and nearly all of

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