of $Mn_2(CO)_9$ also follows first-order kinetics, and the rate constant is determined to be $(2.1 \pm 0.4) \times 10^2\ s^{-1}$. This observed kinetics can be interpreted in terms of the reaction of $Mn_2(CO)_9$ with the CCl_4 and/or CCl_3 radical formed by the reaction of $\cdot Mn(CO)_5$ with CCl_4. The increase in absorbance in the spectral region of 430–500 nm is observed after the disappearance of $Mn_2(CO)_9$. Although the explanation for this observation is not yet clear, the generation of $Mn_2(CO)_9$ even in CCl_4 also supports the nonradical nature of its origin.

The decay of the transient absorption intensity at 825 nm observed for $Mn_2(CO)_{10}$ in $CHCl_3$ follows second-order kinetics. Therefore the reaction rate of $\cdot Mn(CO)_5$ with $CHCl_3$ is much smaller than the recombination rate of the radicals. This is consistent with the report that the reaction rate constant of CCl_4 to the metal radical $(\eta^5\text{-}C_5H_5)W(CO)_3$ is larger than that of $CHCl_3$ by 3 orders of magnitude.[25]

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn(CO)_5$, 15651-51-1; $Mn_2(CO)_9$, 86728-79-2; $Mn_2(CO)_9(t\text{-}BuNC)$, 57956-57-7; $Mn_2(CO)_9(MeCN)$, 14837-20-8; $Mn_2(CO)_9[P(n\text{-}Bu)_3]$, 24476-71-9; $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$, 15609-33-3; EtCN, 107-12-0; $P(n\text{-}Bu)_3$, 998-40-3; CCl_4, 56-23-5; $CHCl_3$, 67-66-3.

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(24) Because the molar absorptivity of $Mn(CO)_5Cl$ is very small in wavelengths longer than 400 nm, the increase in absorbance in that region could not be observed: Bamford, C. H.; Burley, J. W.; Coldbeck, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1846.

(25) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388.

Highly Reduced Organometallics. 15.[1] Coordinatively Unsaturated Tetranuclear Hydrido Carbonyl Clusters of Molybdenum and Tungsten. Structural Characterization of $[(n\text{-}C_3H_7)_4N]_4[HMo(CO)_3]_4$

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Abstract: Treatment of $M(CO)_3(PMTA)$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine; M = Mo, W) with $K[sec\text{-}Bu_3BH]$ in refluxing THF, followed by cation exchange, provides 50–60% yields of deep purple $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ and 25–40% yields of deep blue-violet $[R_4N]_4[HW(CO)_3]_4$ (R = Et, *n*-Pr, *n*-Bu). Similar reactions of $Mo(CO)_4(TMED)$ (TMED = *N,N,N',N'*-tetramethylethylenediamine) with $K[sec\text{-}Bu_3BH]$ give 18–27% yields of $[R_4N]_4[HMo(CO)_3]_4$. While excess $K[sec\text{-}Bu_3BH]$ reacts with $[Et_4N]_2[H_2Mo_2(CO)_8]$ to provide a 12% yield of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$, substantially lower yields (ca. 4%) of $[Et_4N]_4[HMo(CO)_3]_4$ are obtained from the reactions of $Na_4[Mo(CO)_4]$ with excess CH_3CN or $Mo(CO)_6$ with $NaBH_4$ in refluxing THF, followed by cation exchange. Treatment of $K_2[H_2W(CO)_4]$ with aqueous $[Et_4N]Br$ or $[Me_3O][BF_4]$ in CH_3CN, followed by cation exchange, provides a 19% or 38% yield of $[Et_4N]_4[HW(CO)_3]_4$. These initial examples of hydrido carbonyl clusters of molybdenum and tungsten are coordinatively unsaturated 56-electron tetramers and are characterized on the basis of elemental analyses and IR and ^1H NMR spectra. Analysis of the latter for $[HW(CO)_3]_4^{4-}$ establishes this cluster to be stereochemically nonrigid where there is equivalent coupling of each hydride to all four tungsten atoms from +20 to −40 °C in acetonitrile. Although these clusters are quite resistant to attack by basic reagents, they do readily interact with CO to give initially unsaturated dimers, $H_2M_2(CO)_8^{2-}$, which are then converted in high yields to $M_2(CO)_{10}^{2-}$. A single-crystal X-ray structural determination of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ shows the presence of an essentially tetrahedral anion in which the carbonyl groups are eclipsed with respect to the M–M edges. The latter structural feature strongly suggests the presence of four face-bridging hydrogen atoms, which were not located directly. The crystals were monoclinic (space group $P2_1$) with cell parameters $a = 15.467\ (6)$ Å, $b = 15.540\ (14)$ Å, $c = 15.143\ (4)$ Å, $\beta = 92.37\ (3)°$, $V = 3637\ (6)\ Å^3$, and $z = 2$.

The chemistry and syntheses of polynuclear transition-metal compounds have become an area of great interest due to the possible involvement of such species, especially carbonyl clusters, in the catalyzed hydrogenation of carbon monoxide and related important processes.[2] Although homonuclear carbonyl clusters of metals of groups 7 and 8 are well established and structurally characterized in many cases, corresponding clusters containing the group 6 transition elements are much less common.[3] To our knowledge, $[Cp_3Mo_3(CO)_6S]^+$ is the only previously established homonuclear group 6 carbonyl cluster.[4] Several polynuclear complexes of Cr, Mo, and W are known, but the metals in these species appear to be held together by bridging ligands and at most one metal–metal bond. For example, the unusual $[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$ is best considered to contain only one W–W bond,[5] while $[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}OCH_3)]^-$,[6] $[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}O)]^{2-}$,[6] and $[HW(CO)_3(OH)(PPh_3O)]_4$[7] are formulated to contain no significant metal–metal interactions. While trinuclear carbonylmetallates, $M_3(CO)_{14}^{2-}$ (M = Cr, Mo, W), were reported many years ago and formulated on the basis of elemental and gas analyses,[8] no further information has been presented on these mysterious materials.

In this paper we report on the synthesis and characterization of the initial examples of tetranuclear carbonyl clusters of mo-

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(1) Part 14: Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Organometallics* **1983**, *2*, 1145.

(2) Masters, C. *Adv. Organomet. Chem.* **1979**, *18*, 61. Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(3) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225 and references cited therein.

(4) Curtis, M. D.; Butler, W. M. *J. Chem. Soc., Chem. Commun.* **1980**, 998.

(5) Ellis, J. E.; Rochfort, G. L. *Organometallics* **1982**, *1*, 682.

(6) Kirtley, S. W.; Chanton, J. P.; Love, R. A.; Tipton, D. L.; Sorel, T. N.; Bau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3451.

(7) Albano, V. G.; Ciani, G.; Manassero, M.; Sansoni, M. *J. Organometal. Chem.* **1972**, *34*, 353.

(8) Behrens, H.; Haag, W. *Chem. Ber.* **1961**, *94*, 320. Behrens, H.; Yogl, J. *Ibid.* **1963**, *96*, 2220.

0002-7863/83/1505-6252$01.50/0

lybdenum and tungsten. These are formally electron deficient and related to the previously established 56-electron clusters, including $[HRe(CO)_3]_4$,[9] $[HRh(1,5\text{-cyclooctadiene})]_4$,[10] and $[HRh((MeO)_2PCH_2CH_2P(OMe)_2)]_4$.[11] The molecular structure of the molybdenum cluster $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ has been determined and will be described.

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 cannulae 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 to 2 h before use. Published procedures were followed for the preparation of $(TMED)M(CO)_4$ (M = Mo and W; TMED = *N,N,N',N'*-tetramethylethylenediamine),[12] $(PMTA)M(CO)_3$ (M = Mo and W; PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine),[5] $[Et_4N]_2[H_2Mo_2(CO)_8]$,[13] and $K_2[H_2W(CO)_4]$.[13] 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 Corporation 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 Labortorien.

$K_4[HMo(CO)_3]_4$ (1). Method 1. One equivalent of $K[sec\text{-}Bu_3BH]$ (7.84 mL of a 1.0 M solution in THF) in 30 mL of THF at room temperature was added dropwise over a 20-min period to a refluxing solution of $(TMED)Mo(CO)_4$ (2.56 g, 7.84 mmol) in 80 mL of THF. Refluxing was continued for 3 h. After the solution cooled to room temperature, a dark purple precipitate was removed by filtration, washed with THF (4 × 25 mL), and dried in vacuo. A yield of 0.68 g of purple powder was thereby obtained. ^1H NMR spectra of 1, Table I, prepared in this way indicated that a variable amount of TMED was associated with the product. For this reason, efforts to obtain reproducible elemental analyses were unsuccessful. Infrared spectra (Table I) of 1, however, indicated that the product was spectroscopically free of other carbonylmetallates.

Method 2. By exactly the same procedure indicated above, dropwise addition of a solution of $K[sec\text{-}Bu_3BH]$ (3.70 mmol) to 1.30 g (3.68 mmol) of $(PMTA)Mo(CO)_3$ in refluxing THF (60 mL) provided, after a 2.0 h reflux period, a 0.64-g quantity of 1, contaminated by PMTA. Infrared spectra in the ν(CO) region and ^1H NMR spectra in the metal-hydride region of 1 prepared by Methods 1 and 2 were identical. Compound 1 must not be handled in air as a solid or solution as it oxidizes completely within minutes.

$[Et_4N]_4[HMo(CO)_3]_4$ (2). Method 1. Acetonitrile (25 mL) was added to a mixture of 0.45 g of $K_4[HMo(CO)_3]_4 \cdot x TMED$ and excess $[Et_4N]Br$ (0.63 g). After the mixture was stirred at room temperature for 12 h, a purple precipitate was removed by filtration, washed with acetonitrile (3 × 15 mL) and water (2 × 5 mL), and dried in vacuo. This purple powder (0.30 g, 18% yield based on $(TMED)Mo(CO)_4$) gave satisfactory analyses for unsolvated 2 without further treatment.

Anal. Calcd for $C_{44}H_{84}Mo_4N_4O_{12}$: C, 42.25; H, 6.80; N, 4.50. Found: C, 42.28; H, 6.36; N, 4.27.

Compound 2 is insoluble to very slightly soluble in most solvents. It appears to be most soluble in dimethyl sulfoxide (Me_2SO), providing an air-sensitive purple solution. But even as a saturated solution in Me_2SO, the concentration of 2 was sufficiently low that no hydride signal could be observed by NMR. As a solid, compound 2 is the most air-stable salt containing $[HMo(CO)_3]_4^{4-}$ and may be handled for up to 6 h in air without obvious deterioration. Compound 2 is very thermally stable and decomposes above 185 °C to give a white substance of unknown nature.

Method 2 (Obtained as a Byproduct from the Synthesis of $[Et_4N]_2[H_2Mo_2(CO)_8]$[13]). Addition of anhydrous acetonitrile (200 mL) to a slurry of $Na_4Mo(CO)_4$ (prepared in situ from 3.84 g (11.8 mmol) of $(TMED)Mo(CO)_4$) followed by stirring at room temperature for 15 h provides, after workup and cation exchange, principally $[Et_4N]_2[H_2Mo_2(CO)_8]$ (1.20 g, 28% yield). However, from this reaction, which has been reported in detail previously,[13] an acetone-insoluble purple solid (0.15 g, 4.1% yield based on $(TMED)Mo(CO)_4$) was also obtained. This substance was spectroscopically identical with bona fide 2.

Method 3 (Obtained as a Byproduct from the Synthesis of $[Et_4N][HMo_2(CO)_{10}]$[14]). A mixture of $Mo(CO)_6$ (6.0 g, 22.7 mmol) and $NaBH_4$ (0.50 g, 13.2 mmol) was refluxed in THF (100 mL) for 4.5 h. The procedure used in isolating the major product was identical with that of Hayter[14] and provided yellow $[Et_4N][HMo_2(CO)_{10}]$ as a THF-soluble product. The THF-insoluble component was washed with water (2 × 5 mL) and acetonitrile (3 × 3 mL) to provide a purple solid (0.25 g, 3.5% based on $Mo(CO)_6$) that was spectroscopically identical with analytically pure 2.

$[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ (3). Method 1. Water (25 mL) was added to a mixture of 0.48 g of 1, prepared by Method 2, and 0.8 g of $[n\text{-}Pr_4N]Br$. The resulting purple slurry was stirred at room temperature for 12 h. Subsequently, it was filtered, washed with water (3 × 10 mL) and ether (3 × 10 mL), and dried in vacuo to provide 0.50 g (50% based on $(PMTA)Mo(CO)_3$) of product which analyzed satisfactorily for compound 3. In other preparations, up to 62% yields of 3 have been obtained starting from $(PMTA)Mo(CO)_3$.

Anal. Calcd for $C_{60}H_{116}Mo_4N_4O_{12}$: C, 49.05; H, 7.96; N, 3.81. Found: C, 48.90; H, 7.78; N, 3.89.

Compound 3 is an air-sensitive solid which dissolves in polar solvents such as acetone or acetonitrile to provide very air sensitive purple solutions. It is insoluble in alkanes, arenes, diethyl ether, tetrahydrofuran, and water. Compound 3 decomposes above 161 °C to a brown substance.

In an essentially identical procedure, 0.60 g of 1, prepared by Method 1, was converted to 0.57 g of 3, which represents a 23% yield based on $(TMED)Mo(CO)_4$. Compound 3 prepared in this manner was identical with the analytical sample.

Method 2. Six equivalents of $K[sec\text{-}Bu_3BH]$ (4.42 mL of a 1.0 M solution in THF) was added to a slurry of $[Et_4N]_2[H_2Mo_2(CO)_8]$[13] (0.50 g, 0.74 mmol) and the mixture was refluxed for 24 h. After the mixture was cooled to room temperature, an uncharacterized purple-brown precipitate was washed with THF until the washings were colorless. Then 0.2 g of $[n\text{-}Pr_4N]Br$ dissolved in 20 mL of H_2O was added to the solid and the mixture was stirred at room temperature for 12 h. Subsequently, the product was purified as in Method 1 to provide 0.065 g (12% yield) of bona fide 3.

Reaction of 3 with Carbon Monoxide. Synthesis of $[n\text{-}Pr_4N]_2[Mo_2(CO)_{10}]$. Carbon monoxide, predried by being passed through a trap charged with 4 Å molecular sieves, was bubbled at atmospheric pressure through an acetonitrile solution at room temperature containing 0.40 g of 3. After 20 min an infrared solution spectrum showed the presence of only $[H_2Mo_2(CO)_8]^{2-}$ and $[Mo_2(CO)_{10}]^{2-}$. After 2 h, only $[Mo_2(CO)_{10}]^{2-}$ was present in solution. The solvent was then removed under reduced pressure. The residue was recrystallized from CH_3CN–THF to provide 0.31 g (67% yield) of orange-yellow $[n\text{-}Pr_4N]_2[Mo_2(CO)_{10}]$ of satisfactory purity.

Anal. Calcd for $C_{34}H_{56}Mo_2N_2O_{10}$: C, 48.34; H, 6.68. Found: C, 48.28; H, 6.49. This material has essentially the same properties as the previously characterized $[Et_4N]_2[Mo_2(CO)_{10}]$[14] and decomposes above 173 °C. IR data: ν(CO) (CH_3CN) 1935 (m), 1893 (vs), 1793 cm^{-1} (m s); (Nujol) 1931 (s), 1891 (sh), 1863 (vs), 1795 (m), 1781 cm^{-1} (vs).

$[n\text{-}Bu_4N]_4[HMo(CO)_3]_4$ (4). Water (30 mL) was added to a mixture of 0.77 g of 1, prepared by Method 1, and 1.5 g of $[n\text{-}Bu_4N]Br$. The same procedure for the purification of compound 3 in Method 1 was followed and provided 0.85 g (27% yield based on $(TMED)Mo(CO)_4$) of purple powder which analyzed satisfactorily for unsolvated 4.

Anal. Calcd for $C_{76}H_{148}Mo_4N_4O_{12}$: C, 53.89; H, 8.81; N, 3.30. Found: C, 53.61; H, 8.63; N, 3.27.

Compound 4 is very air sensitive as a solid and can be crystallized from acetone–ether. It is the most soluble of salts containing $[HMo(CO)_3]_4^{4-}$ prepared thus far and darkens above 142 °C.

$[Et_4N]_4[HW(CO)_3]_4$ (5). Method 1. Water (30 mL) was added to a mixture of $K_2[H_2W(CO)_4]$[13] (0.50 g, 1.33 mmol) and $[Et_4N]Br$ (0.28 g, 1.33 mmol). The resulting slurry was stirred at room temperature for

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[9] (a) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687. (b) Saillant, R.; Barcelo, G.; Kaesz, H. D. *Ibid.* **1970**, *92*, 5739.

[10] Kulzick, M.; Price, R. T.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 1256.

[11] Fryzuk, M. *Organometallics* **1982**, *1*, 408.

[12] King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

[13] Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

[14] Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

Table I. IR Spectra in the ν(CO) Region and ^{1}H NMR Spectra of $[HM(CO)_3]_4^{4-}$

compound	medium	ν(CO), cm^{-1}	δ^b
$K_4[HMo(CO)_3]_4$[a] (**1**)	Nujol mull	1863 (vs, b), 1692 (vs, vb)	−6.62 (CD_3CN)
	CH_3CN	1871 (vs), 1775 (s)	
$[Et_4N]_4[HMo(CO)_3]_4$ (**2**)	Nujol mull	1863 (vs), 1758 (vs, b)	*c*
$[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ (**3**)	Nujol mull	1861 (vs), 1758 (vs, b)	−6.56 (CD_3CN)
	CH_3CN	1869 (vs), 1769 (s)	
$[n\text{-}Bu_4N]_4[HMo(CO)_3]_4$ (**4**)	Nujol mull	1859 (vs), 1752 (vs)	−6.59 (CD_3CN)
	CH_3CN	1867 (vs), 1767 (s)	
$[Et_4N]_4[HW(CO)_3]_4$ (**5**)	Nujol mull	1861 (vs), 1767 (vs, b)	*c*
	Me_2SO	1863 (vs), 1765 (s)	
$[n\text{-}Pr_4N]_4[HW(CO)_3]_4$ (**6**)	Nujol mull	1857 (vs), 1771 (vs, b)	−5.8 (1:3.3:1 triplet,
	CH_3CN	1867 (vs), 1769 (s)	J_{H-W} = 44.5 Hz) (CD_3CN)
$[n\text{-}Bu_4N]_4[HW(CO)_3]_4$ (**7**)	Nujol mull	1855 (vs, b), 1765 (s, b)	−5.5 (1:3.3:1 triplet,
	CH_3CN	1865 (vs), 1771 (s)	J_{H-W} = 44.5 Hz) (CD_3CN)

[a] Not isolated as a pure substance, see Experimental Section. [b] Resonance positions of cation signals are not given: δ for $n\text{-}Pr_4N^+$: 3.2–3.0 (m), 1.9–1.6 (m), 1.0–0.9 (t, J_{H-H} = 7 Hz). δ for $n\text{-}Bu_4N^+$: 3.4–3.0 (m), 1.8–1.5 (m), 1.3–1.2 (m). [c] Compound was insufficiently soluble to observe the metal-hydride signal.

15 h. After filtration, the solid was washed with water (3 × 15 mL), dried in vacuo, washed with acetone until the washings were colorless, and again dried in vacuo to provide 0.10 g (19% yield based on $K_2[H_2W(CO)_4]$) of violet solid which analyzed satisfactorily for **5**.

Anal. Calcd for $C_{44}H_{84}N_4O_{12}W_4$: C, 33.10; H, 5.32; N, 3.51. Found: C, 33.38; H, 5.23; N, 3.29.

From the acetone washings, a 9% yield of the previously characterized $[Et_4N]_2[H_2W_2(CO)_8]$[13] was also isolated. Compound **5** has essentially the same properties as the Mo analogue **2**, but decomposes at a higher temperature (>208 °C) to a white substance.

Method 2. Methyl iodide (0.165 mL, 2.66 mmol) in CH_3CN (20 mL) was cooled to 0 °C and added dropwise to a mixture of $K_2[H_2W(CO)_4]$ (1.00 g, 2.66 mmol) and $[Et_4N]Br$ (1.89 g, 9.0 mmol) prechilled to 0 °C. After the addition was complete, the solution was warmed to room temperature and stirred for 20 h. A reddish supernatant was removed from a purple solid via cannula. The solid was then washed with CH_3CN (3 × 20 mL) to provide 0.40 g (38% yield) of product which was identical with bona fide **5** made by Method 1.

In a similar reaction, equivalent amounts of $[Me_3O][BF_4]$ and $K_2[H_2W(CO)_4]$ provided a 20% yield of compound **5**. Other soluble products from this reaction and that with CH_3I remain uncharacterized.

Method 3. One equivalent of K[*sec*-Bu_3BH] (3.4 mL of a 1.0 M solution in THF) in 25 mL of THF was added dropwise to a refluxing slurry of $(PMTA)W(CO)_3$ (1.5 g, 3.4 mmol) in 100 mL of THF. The mixture was refluxed for 10 h and cooled to room temperature. Filtration provided an impure purple brown solid (0.85 g) which appears to be mainly $K_4[HW(CO)_3]_4$ (see Discussion). This was washed with THF (3 × 15 mL), dried, and subsequently stirred with a solution of $[Et_4N]Br$ (0.80 g, 3.8 mmol) in 35 mL of water of 6 h at room temperature. The resulting violet precipitate was washed with water (2 × 10 mL) and CH_3CN (2 × 5 mL) and dried to provide 0.59 g (43% based on $(PMTA)W(CO)_3$) of solid which was spectroscopically identical with bona fide **5**.

$[n\text{-}Pr_4N]_4[HW(CO)_3]_4$ (6). The same procedure (Method 3) for the preparation of compound **5** was followed except $[n\text{-}Pr_4N]Br$ was used in the cation exchange step. In one reaction 1.55 g of $(PMTA)W(CO)_3$ was converted to solid violet **6** in 24% yield (0.38 g) which gave satisfactory analyses.

Anal. Calcd for $C_{60}H_{116}N_4O_{12}W_4$: C, 39.58; H, 6.42. Found: C, 39.31; H, 6.26.

Compound **6** has solubility and spectroscopic properties which are virtually identical with those of the Mo analogue **3**, but it appears to be much more thermally stable. It decomposes above 195 °C to a black substance.

$[n\text{-}Bu_4N]_4[HW(CO)_3]_4$ (7). The same procedure for the preparation of compound **5** was followed except $[n\text{-}Bu_4N]Br$ was used in the cation exchange. By this method 1.1 g of $(PMTA)W(CO)_3$ was converted to a violet solid (0.45 g, 35% yield) which gave satisfactory analyses for unsolvated **7**.

Anal. Calcd for $C_{76}H_{148}N_4O_{12}W_4$: C, 44.63; H, 7.29. Found: C, 44.40; H, 7.09.

Compound **7** has very similar properties to those of the Mo analogue **4** and begins to darken above 132 °C.

Collection and Reduction of X-ray Data for 3. Purple needles of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ were grown by slow diffusion of diethyl ether into a nearly saturated solution of compound **3** in acetonitrile at room temperature. A crystal cut to dimensions 0.3 × 0.3 × 0.5 mm under Nujol to protect it from air oxidation was wedged inside a 0.2-mm glass capillary tube which was then flame sealed and mounted on a goniometer head. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs and by a Delauney reduction calculation. Systematic absences (0*k*0; *k* = 2*n* + 1) showed the space group to be either $P2_1$ (No. 4) or $P2_1/m$ (No. 11). The former was shown to be correct by the eventual solution of the structure, vide infra. Data were collected on a CAD 4 Nonius diffractometer. Background counts were measured at both ends of the scan range, with the use of an ω-2θ scan equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of measuring backgrounds is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure and no decay with time was noted. The intensities of 6641 (+*h*, +*k*, ±*l*) unique reflections were measured at 23 °C out to 2θ = 50° by using monochromatized Mo Kα radiation. The data were corrected for Lorentz, polarization, and background effects, using a value of 0.03 for *p*.[16] ψ scans were made rotating the crystal about the needle axis; since the maximum variation

Table II. Summary of Crystal and Intensity Collection Data for $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$

(A) Crystal Parameters at 23 °C

space group: $P2_1$
a = 15.467 (6) Å
b = 15.540 (14) Å
c = 15.143 (4) Å
β = 92.37 (3)°
V = 3637 (6) Å^3
Z = 2
mol wt 1469.37
ρ(calcd) = 1.342 g cm^{-3}
cryst dimens: 0.3 × 0.3 × 0.5 mm

(B) Measurement of Intensity Data

radiation: λ(Mo Kα) = 0.710 73 Å
monochromator: graphite
abs coeff = 7.176 cm^{-1}
2θ limits = 0–50
final number of variables: 253
unique data used: 4675, $F_o^2 \geqslant 2.00(F_o^2)$
R^a = 0.053
$R_w{}^a$ = 0.072
error in observn of unit wt: 2.48

[a] The function minimized was $\Sigma w(F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$; $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $Rw = [(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o)^2)]^{1/2}$.

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(15) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsvele, J., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71; and "CAD 4 and SDP Users Manual", Enraf-Nonius; Delft, Holland, 1978.

(16) The intensity data were processed as described: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where $K = 2.1166x$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

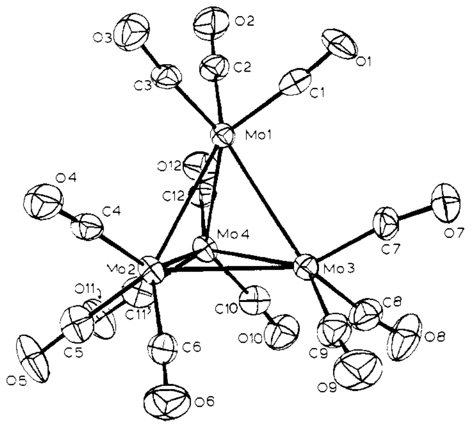

Figure 1. ORTEP view of $[HMo(CO)_3]_4^{4-}$ showing the labeling scheme for all non-hydrogen atoms. The ellipsoids are drawn with 30% probability boundaries.

of intensity was less than 5%, no absorption corrections were made. Of the 6641 unique reflections, 4675 have $F_o^2 \geq 2.0\sigma(F_o^2)$ and were used for the final solution and refinement of the structure. A summary of crystal and intensity collection data is shown in Table II.

Solution and Refinement of the Structure for 3. Conventional heavy-atom techniques were used in solving the structure of 3. The Mo atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining non-hydrogen atoms.[17] The atomic scattering factors were taken from the usual tabulation.[18] A table of observed and calculated structure factors for 3 is available.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the cations were included at idealized positions (and not refined) for those carbon atoms whose $\bar{B}$ values were less than 12. The hydrogen atoms were assigned B's 1.0 unit larger than the $\bar{B}$ value of the carbon to which they were attached. Hydrogen atoms in the anions were not located in the final difference Fourier maps and therefore were not included. The final positional parameters of the atoms in the anion are in Table III. The ORTEP drawing of the anionic unit in 3 is shown in Figure 1, and the ellipsoids are drawn with 30% probability boundaries. The final positional and thermal parameters of the atoms in the cations are available as supplementary data.[19]

Results and Discussion

We recently reported that the treatment of $(TMED)W(CO)_4$ with excess K[*sec*-Bu_3BH] in THF under reflux provided good yields of $K_2[H_2W(CO)_4]$.[13] It was of interest to determine whether the molybdenum analogue could be prepared by the same procedure. Surprisingly, however, one or more equivalents of K[*sec*-Bu_3BH] reacted with $(TMED)Mo(CO)_4$ to give, instead, appreciable amounts of a slightly soluble purple solid (**1**). Reproducible carbon and hydrogen analyses could not be obtained for **1** due to contamination of this material with variable amounts of TMED, which could clearly be seen in its ^1H NMR spectrum. However, the K:Mo ratio was established to be very close to 1:1. Subsequently, homogeneous and relatively pure, unsolvated tetraalkylammonium salts containing the same anion were obtained. On the basis of preliminary analytical data and ^1H NMR spectra, the anion was initially formulated to be $[HMo(CO)_4]_3^{3-}$,[20] which is electronically equivalent with the known $[HRe(CO)_4]_3$.[21] However, IR spectra of these salts were not compatible with this formulation and carbon analyses were not entirely satisfactory. It was clearly necessary to establish the structure of the anion by single-crystal X-ray analysis. Attempts to prepare suitable crystals from Et_4N^+ and PPN^+ salts were unsuccessful. A preliminary study was done on the tetrabutylammonium salt **4** which established that the anion consisted of a tetrameric cluster, but the cations were badly disordered.[22] A more recent X-ray analysis of the tetrapropylammonium salt **3** proved to be far more satisfactory. Analytical, spectroscopic, and X-ray data are all entirely consistent with the presence of $[HMo(CO)_3]_4^{4-}$ units in these salts.

Table III. Final Positional Parameters and Their Esd's for the Nonhydrogen Atoms of $[HMo(CO)_3]_4^{4-}$ [a]

atom	x	y	z
Mo1	0.31575 (7)	−0.09300 (0)	0.17953 (7)
Mo2	0.34169 (7)	0.06477 (10)	0.30443 (7)
Mo3	0.17985 (8)	−0.05285 (9)	0.31938 (8)
Mo4	0.19792 (7)	0.06977 (10)	0.15894 (7)
O1	0.3015 (9)	−0.2910 (7)	0.2135 (9)
O2	0.3247 (8)	−0.1516 (9)	−0.0136 (7)
O3	0.5084 (7)	−0.1398 (8)	0.1680 (8)
O4	0.5412 (6)	0.0376 (8)	0.3360 (7)
O5	0.3744 (7)	0.2632 (7)	0.2944 (9)
O6	0.3384 (7)	0.1052 (9)	0.5041 (7)
O7	0.1210 (8)	−0.2383 (8)	0.3540 (8)
O8	−0.0187 (7)	−0.0389 (11)	0.3258 (9)
O9	0.1852 (9)	−0.0608 (10)	0.5241 (7)
O10	0.0046 (7)	0.1209 (9)	0.1685 (8)
O11	0.2212 (9)	0.2649 (7)	0.1223 (9)
O12	0.1600 (7)	0.0495 (8)	−0.0429 (6)
C1	0.3033 (9)	−0.2138 (11)	0.2010 (9)
C2	0.3183 (10)	−0.1241 (10)	0.0585 (9)
C3	0.4348 (8)	−0.1183 (9)	0.1762 (9)
C4	0.4650 (8)	0.0463 (9)	0.3213 (8)
C5	0.3612 (9)	0.1878 (12)	0.2955 (10)
C6	0.3391 (8)	0.0870 (10)	0.4292 (9)
C7	0.1525 (10)	−0.1678 (10)	0.3372 (9)
C8	0.0555 (11)	−0.0387 (12)	0.3229 (11)
C9	0.1846 (9)	−0.0536 (12)	0.4462 (10)
C10	0.0771 (10)	0.0995 (10)	0.1639 (9)
C11	0.2137 (10)	0.1889 (11)	0.1375 (10)
C12	0.1761 (8)	0.0549 (10)	0.0338 (8)

[a] Final positional parameters for the cations and anisotropic thermal parameters of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ are available as supplementary data.[19]

Interestingly, after our characterization of $[HMo(CO)_3]_4^{4-}$, we discovered that this purple substance has been observed previously by other research groups. Many years ago Hayter mentioned that the reaction of $NaBH_4$ and $Mo(CO)_6$ provided, after cation exchange, mainly soluble, yellow $[Et_4N][HMo_2(CO)_{10}]$ "contaminated by a small amount of unidentified, insoluble, intensely purple material".[14] Subsequently, we determined that Hayter's unidentified material was bona fide $[Et_4N]_4[HMo(CO)_3]_4$. Also, after this work was completed, we were informed that Kirtley, Tipton, and Bau had isolated a crystalline purple product from a 3-day reaction of $NaBH_4$ and $Mo(CO)_6$ in refluxing THF. This material was formulated as $Na_4[HMo(CO)_3]_4 \cdot x(C_2H_5OH)$ on the basis of IR and ^1H NMR spectra and a single-crystal X-ray structure determination.[22b] The conditions used by Kirtley et al. appear to be very similar to those reported by Behrens and Haag in 1961 in the preparation of a "deep violet"

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[17] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $Rw = [(\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

[18] Cromers, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromers, D. T. *Ibid.*, Table 2.3.1.

[19] See paragraph at end of paper pertaining to supplementary material.

[20] Lin, J. T.; Ellis, J. E. *Abstr. Pap.-Am. Chem. Soc.* **1982**, 184th, INOR 207.

[21] Higgins, D. K.; Fellman, W.; Smith, J. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 4841.

[22] (a) Summary of crystal data for $[n\text{-}Bu_4N]_4[HMo(CO)_3]_4$: space group $C2/c$, a = 21.377 (5) Å, b = 16.295 (6) Å, c = 25.901 (10) Å, β = 93.12 (3)°, z = 4, V = 9009 (9) Å^3, ρ(calcd) = 1.249 g/cm^3. R = 0.099; R_w = 0.119. The solution and refinement of this structure were carried out following the procedure described in this paper for the tetrapropylammonium salt. No significant differences were observed in the structures of the $[HMo(CO)_3]_4^{4-}$ units in both salts. A list of positional and thermal parameters determined when refinement of the structure was discontinued is available as supplementary data.[19] The Mo–Mo distances in this structure analysis ranged from 3.10 to 3.13 Å, with an average value of 3.12 (1) Å. (b) Kirtley, S. W.; Tipton, D. L.; Bau, R.; unpublished results, 1979–1981. In a private communication, Professor Bau indicated that the structure analysis of this sodium salt was never published because of disorder problems involving the ethanol molecules of crystallization, which led to a poor agreement factor of R = 13.6%. However, as in the case of our structural analysis of $[n\text{-}Bu_4N]_4[HMo(CO)_3]_4$ mentioned earlier (ref 22a), the geometry of the anion was not disordered and is essentially the same as that described in this paper.

Table IV. Bond Distances and Angles with esd's for $[HMo(CO)_3]_4{}^{4-}$ [a,b]

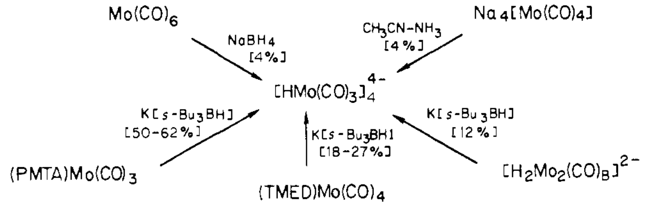
	(a) Distances (Å)		
Mo(1)-Mo(2)	3.112 (1)	Mo(4)-C(10)	1.93 (1)
Mo(1)-Mo(3)	3.108 (1)	Mo(4)-C(11)	1.90 (1)
Mo(1)-Mo(4)	3.126 (1)	Mo(4)-C(12)	1.92 (1)
Mo(2)-Mo(3)	3.115 (1)	C(1)-O(1)	1.21 (1)
Mo(2)-Mo(4)	3.066 (1)	C(2)-O(2)	1.18 (1)
Mo(3)-Mo(4)	3.109 (1)	C(3)-O(3)	1.20 (1)
Mo(1)-C(1)	1.92 (1)	C(4)-O(4)	1.20 (1)
Mo(1)-C(2)	1.90 (1)	C(5)-O(5)	1.19 (1)
Mo(1)-C(3)	1.88 (1)	C(6)-O(6)	1.17 (1)
Mo(2)-C(4)	1.94 (1)	C(7)-O(7)	1.23 (1)
Mo(2)-C(5)	1.94 (1)	C(8)-O(8)	1.15 (1)
Mo(2)-C(6)	1.92 (1)	C(9)-O(9)	1.18 (1)
Mo(3)-C(7)	1.86 (1)	C(10)-O(10)	1.18 (1)
Mo(3)-C(8)	1.94 (1)	C(11)-O(11)	1.21 (1)
Mo(3)-C(9)	1.92 (1)	C(12)-O(12)	1.18 (1)
	Angles (deg)		
Mo(2)-Mo(1)-Mo(3)	60.1 (2)	Mo(1)-C(1)-O(1)	175.4 (9)
Mo(2)-Mo(1)-Mo(4)	58.9 (2)	Mo(1)-C(2)-O(2)	172.5 (10)
Mo(3)-Mo(1)-Mo(4)	59.8 (2)	Mo(1)-C(3)-O(3)	173.9 (9)
Mo(1)-Mo(2)-Mo(3)	59.9 (2)	Mo(2)-C(4)-O(4)	176.4 (8)
Mo(1)-Mo(2)-Mo(4)	60.8 (3)	Mo(2)-C(5)-O(5)	176.8 (10)
Mo(3)-Mo(2)-Mo(4)	60.4 (2)	Mo(2)-C(6)-O(6)	176.3 (10)
Mo(1)-Mo(3)-Mo(2)	60.0 (2)	Mo(3)-C(7)-O(7)	168.8 (10)
Mo(1)-Mo(3)-Mo(4)	60.4 (2)	Mo(3)-C(8)-O(8)	173.3 (12)
Mo(2)-Mo(3)-Mo(4)	59.0 (2)	Mo(3)-C(9)-O(9)	174.6 (12)
Mo(1)-Mo(4)-Mo(2)	60.4 (2)	Mo(4)-C(10)-O(10)	177.1 (10)
Mo(1)-Mo(4)-Mo(3)	59.8 (2)	Mo(4)-C(11)-O(11)	177.8 (10)
Mo(2)-Mo(4)-Mo(3)	60.6 (2)	Mo(4)-C(12)-O(12)	176.6 (9)
C(1)-Mo(1)-C(2)	85.5 (4)	Mo(2)-Mo(1)-C(1)	132.8 (3)
C(1)-Mo(1)-C(3)	84.6 (4)	Mo(4)-Mo(1)-C(1)	138.4 (3)
C(2)-Mo(1)-C(3)	82.0 (4)	Mo(2)-Mo(1)-C(2)	141.3 (3)
C(4)-Mo(2)-C(5)	90.0 (4)	Mo(3)-Mo(1)-C(2)	138.7 (3)
C(4)-Mo(2)-C(6)	87.5 (4)	Mo(3)-Mo(1)-C(3)	138.5 (3)
C(5)-Mo(2)-C(6)	84.3 (5)	Mo(4)-Mo(1)-C(3)	137.1 (3)
C(7)-Mo(3)-C(8)	82.7 (5)	Mo(3)-Mo(2)-C(4)	133.9 (3)
C(7)-Mo(3)-C(9)	81.3 (5)	Mo(4)-Mo(2)-C(4)	141.3 (3)
C(8)-Mo(3)-C(9)	88.3 (4)	Mo(1)-Mo(2)-C(5)	138.6 (3)
C(10)-Mo(4)-C(11)	84.6 (5)	Mo(3)-Mo(2)-C(5)	135.3 (3)
C(10)-Mo(4)-C(12)	86.4 (4)	Mo(1)-Mo(2)-C(6)	137.0 (3)
C(11)-Mo(4)-C(12)	88.2 (5)	Mo(4)-Mo(2)-C(6)	131.1 (3)
Mo(3)-Mo(1)-C(1)	90.3 (3)	Mo(2)-Mo(3)-C(7)	139.7 (4)
Mo(4)-Mo(1)-C(2)	98.4 (3)	Mo(4)-Mo(3)-C(7)	137.0 (3)
Mo(2)-Mo(1)-C(3)	94.5 (3)	Mo(1)-Mo(3)-C(8)	137.8 (4)
Mo(1)-Mo(2)-C(4)	93.8 (3)	Mo(2)-Mo(3)-C(8)	137.4 (4)
Mo(4)-Mo(2)-C(5)	92.0 (3)	Mo(1)-Mo(3)-C(9)	133.0 (3)
Mo(3)-Mo(2)-C(6)	89.1 (3)	Mo(4)-Mo(3)-C(9)	141.7 (4)
Mo(1)-Mo(3)-C(7)	94.0 (3)	Mo(1)-Mo(4)-C(10)	138.7 (3)
Mo(4)-Mo(3)-C(8)	94.2 (4)	Mo(2)-Mo(4)-C(10)	130.8 (3)
Mo(2)-Mo(3)-C(9)	94.5 (3)	Mo(1)-Mo(4)-C(11)	136.7 (3)
Mo(3)-Mo(4)-C(10)	89.9 (3)	Mo(3)-Mo(4)-C(11)	138.4 (3)
Mo(2)-Mo(4)-C(11)	93.0 (3)	Mo(2)-Mo(4)-C(12)	142.8 (2)
Mo(1)-Mo(4)-C(12)	94.5 (3)	Mo(3)-Mo(4)-C(12)	132.6 (4)

[a] Bond distances and angles of $[n\text{-}Pr_4N]^+$ are given in the supplementary material.[19] [b] See Results and Discussion for average values of bond distances and angles.

compound suggested to be $Na_2[Mo_3(CO)_{14}]$ on the basis of elemental analysis.[8] In this connection it is worth noting that a solid containing approximately a 4:1 ratio of $Na[HMo_2(CO)_{10}]$ to $Na_4[HMo(CO)_3]_4$ would provide elemental analyses close to those calculated for "$Na_2[Mo_3(CO)_{14}]$".

Molecular Structure of $[n\text{-}Pr_4N]_4[HMo(CO)_3]_4$ (3). An ORTEP drawing of the anionic unit in compound **3** is shown in Figure 1. Compound **3** consists of discrete cations and anions with no unusually short interionic contacts. The anions are comprised of essentially tetrahedral $[Mo(CO)_3]_4{}^{4-}$ units which are structurally identical with those in $[HRe(CO)_3]_4$.[9a] Although we were not able to directly observe hydrogen atoms in the anion, ^1H NMR spectra of **3** (vide infra) indicate that the cluster is a metal hydride and contains very nearly one hydrogen per tetrapropylammonium cation. On this basis, the anions are formulated to contain $[HMo(CO)_3]_4{}^{4-}$ units. Further, the presence of eclipsed carbonyl groups in **3** strongly suggests that the four hydrogens are face bridging. This is a reasonable formulation in terms of the known molecular structure of the isovalent $[HRe(CO)_3]_4$ and electronic structure calculations on such 56-electron species which indicate that the bonding interactions take place primarily over the faces of the tetrahedron.[23]

Scheme I.[a] A Summary of Synthetic Routes to $[HMo(CO)_3]_4{}^{4-}$ [a]



[a] Yields of the tetramer are in brackets.

The individual Mo–Mo bond distances are shown in Table IV and range from 3.066 (1) to 3.126 (1) Å with an average value of 3.11 (2) Å.[24] It is surprising that the average value is not significantly different from the single-bonded Mo–Mo bond distance (3.123 (7) Å) in $Mo_2(CO)_{10}{}^{2-}$,[25] since the average Re–Re bond distance (2.91 (2) Å) in the isovalent $[HRe(CO)_3]_4$[9a] is significantly shorter than the single bond distance in $Re_2(CO)_{10}$ (3.02 Å). The shorter Re–Re distances in $[HRe(CO)_3]_4$ compared to that in $Re_2(CO)_{10}$[26] have been rationalized on the basis of the unsaturated nature of the cluster or geometric considerations.[9a] In $[HMo(CO)_3]_4{}^{4-}$, the electrostatic repulsions of the individual metal atoms possibly play a dominant role in influencing the metal–metal distances.

The average Mo–C and C–O distances are 1.91 (2) and 1.19 (2) Å, respectively, which are very similar to corresponding average values (1.90 and 1.20 Å, respectively) found in $Mo_2(CO)_{10}{}^{2-}$ [25] Thus, all of the interatomic distances in $[HMo(CO)_3]_4{}^{4-}$ and $Mo_2(CO)_{10}{}^{2-}$ are quite similar. Average bond angles (Table IV) are also consistent with the tetrahedral geometry of the anion. Thus, the average Mo–Mo–Mo and Mo–C–O bond angles are 60.0 (6) and 175 (2)°, respectively. Other angles (averaged) in Table IV are as follows: C–Mo–C = 85 (3)°, Mo–Mo–C = 137 (3)° and 93 (2)°. These values are very similar to those reported for the essentially isostructural $[HRe(CO)_3]_4$.[9a]

A comparison of the gross structures of the 56-electron carbonyl clusters, $[HM(CO)_3]_4{}^z$ (M = Re, z = 0; M = Mo, z = 4–), and the recently reported 56-electron rhodium cluster, [HRh(1,5-COD)]$_4$ (COD = cyclooctadiene), reveals substantial and puzzling differences.[10] While the carbonyl clusters are nearly regular tetrahedra and contain six similar, though not identical, metal–metal distances, the rhodium tetramer contains a distorted tetrahedron of idealized D_{2d} symmetry. In this molecule are two long (2.97 Å) and four short (2.80 Å) Rh–Rh bonds, where the latter are characteristic of Rh–H–Rh bridges.

Synthesis of $[HMo(CO)_3]_4{}^{4-}$. Various synthetic routes to $[HMo(CO)_3]_4{}^{4-}$ are summarized in Scheme I. The many different reactions in which the tetramer forms are indicative of its importance in molybdenum carbonyl anion chemistry as well as its surprisingly unreactive nature.

The formation of $[HMo(CO)_3]_4{}^{4-}$ as a byproduct in the reaction of $NaBH_4$ and $Mo(CO)_6$ in refluxing THF is of historical importance and has been discussed previously. About the same yield of tetramer (4%) also was isolated from the protonation of $Na_4[Mo(CO)_4]$ by CH_3CN along with the major isolated product, $[Et_4N]_2[H_2Mo_2(CO)_8]$, obtained in 28–30% yields.[13] A third low-yield synthesis of $[HMo(CO)_3]_4{}^{4-}$ involves the reaction of 6 equiv of K[*sec*-Bu_3BH] with $[Et_4N]_2[H_2Mo_2(CO)_8]$. It was hoped

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(23) Hoffman, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.

(24) Wilson and Bau[9a] have commented earlier on the fact that differences in the M–M bond distances on the order of 0.03 to 0.06 Å are commonly found in related tetrahedral clusters such as $H_4Co_4(C_5H_5)_4$, $Os_4O_4(CO)_{12}$, $H_4Re_4(CO)_{12}$, and $Fe_4(CO)_4(C_5H_5)_4$.

(25) Handy, L. B.; Ruff, J. K.; Dahl, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 7312.

(26) Dahl, L. F.; Ishishi, E.; Rundle, R. E. *J. Chem. Phys.* **1957**, *26*, 1750.

that this procedure would provide the presently unknown $K_2[H_2Mo(CO)_4]$, by analogy to the corresponding reaction of K[*sec*-Bu_3BH] with $[Et_4N]_2[H_2W_2(CO)_8]$.[13] However, no $H_2Mo(CO)_4^{2-}$ appeared to form in this reaction. Instead, a 12% yield of the purple tetramer was isolated as the *n*-Pr_4N^+ salt. Interestingly, in the reaction of $[Et_4N]_2[H_2W_2(CO)_8]$ with excess K[*sec*-Bu_3BH], no evidence for the formation of the corresponding $[HW(CO)_3]_4^{4-}$ (vide infra) was obtained. Thus, $H_2Mo_2(CO)_8^{2-}$ and $H_2W_2(CO)_8^{2-}$ appear to behave much differently in the presence of *sec*-Bu_3BH^-. The only explanation we have for these differences is the suggestion that $H_2Mo(CO)_4^{2-}$ may be unstable with respect to loss of H^-.

In view of our observation that Ph_3SnLi reacts with (TMED)$Mo(CO)_4$ to provide good yields of $(Ph_3Sn)_2Mo(CO)_4^{2-}$,[1] it was considered that (TMED)$Mo(CO)_4$ would also be a good precursor to the unknown $H_2Mo(CO)_4^{2-}$. However, treatment of (TMED)$Mo(CO)_4$ with one or more equivalents of K[*sec*-Bu_3BH] in refluxing THF provided instead 18–27% yields of $[HMo(CO)_3]_4^{4-}$. Before the cation exchange, infrared and ^1H NMR spectra have established that the principle material present is $K_4[HMo(CO)_3]_4$. The general type of reaction used in this synthesis essentially involves the replacement of a poor or non-π-acceptor group by hydride ion. Although this procedure has been used previously to prepare metal carbonyl hydrides,[27] we believe it is important to emphasize the unusual efficacy of trialkylborohydrides, and especially tri-*sec*-butylborohydride, in these type of syntheses.

No intermediates in this or related (vide infra) reactions have been identified. Nevertheless, the formation of $[HMo(CO)_3]_4^{4-}$ in these syntheses can be rationalized on the basis of established reactions of metal carbonyls. The reaction of (TMED)$Mo(CO)_4$ with R_3BH^- may initially involve a reversible ring opening (i.e., a Mo–N bond scission) followed by nucleophilic attack of the R_3BH^-. Such a mechanism has been proposed in the reaction of the similar (TMDP)$Mo(CO)_4$ (TMDP = 1,3-(tetramethyldiamino)propane) with phosphines and phosphites.[28] Alternatively, attack of R_3BH^- at a coordinated carbonyl to give a formyl anion followed by loss of the amine could occur. Although apparently no reactions of R_3BH^- with amine-substituted metal carbonyls have been reported in the literature previously, corresponding reactions with phosphine- or phosphite-substituted neutral carbonyls do result in the formation of anionic metal formyl complexes.[29] It is generally recognized that nucleophilic attack at a coordinated carbonyl is favorable only if the metal carbonyl reactant has at least one IR-active ν(CO) band approximately at or above 2000 cm^{-1}.[30] This condition is met for (TMED)$Mo(CO)_4$ for which the maximum ν(CO) value is about 2000 cm^{-1}. (However, this is not the case for (PMTA)$Mo(CO)_3$, vide infra, which has a maximum ν(CO) value of 1910 cm^{-1}.)

After the nature of this purple substance was established, it was felt that a compound containing a *preformed* $Mo(CO)_3$ unit of the formula $L_3Mo(CO)_3$, where L is a poor or non-π-acceptor and a relatively good leaving group, could be an especially effective precursor to $[HMo(CO)_3]_4^{4-}$. In fact, the highest yields of this tetramer have been obtained from the reaction of (PMTA)$Mo(CO)_3$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with one or more equivalents of K[*sec*-Bu_3BH]. It should be noted that this reaction has been carried out thus far only with (PMTA)$Mo(CO)_3$, which was available from an unrelated project.[5,31] Other $L_3Mo(CO)_3$ (L_3 = arene, triene, diethylenetriamine, diglyme, etc.) may also prove to be effective precursors to $[HMo(CO)_3]_4^{4-}$.

Synthesis of $[HW(CO)_3]_4^{4-}$. One equivalent of K[*sec*-Bu_3BH] also reacts with (PMTA)$W(CO)_3$ in refluxing THF, although more slowly than in the corresponding molybdenum reaction.[32] Substantially impure $K_4[HW(CO)_3]_4$, mixed with uncharacterized carbonyltungstates, precipitates in this reaction as a purple-brown material. Treatment of this solid with aqueous solutions of $[R_4N]Br$ provides 25–43% of $[R_4N][HW(CO)_3]_4$, compared to the 50–60% yields of the corresponding molybdenum complexes (eq 1). When 3 equiv of K[*sec*-Bu_3BH] are reacted with

$$\text{(PMTA)W(CO)}_3 \xrightarrow[\text{(2) }[R_4N]Br]{\text{(1) K}[\textit{sec}\text{-}Bu_3BH]} \underset{25\text{–}43\%}{[R_4N]_4[HW(CO)_3]_4} \qquad (1)$$

(PMTA)$W(CO)_3$, under the same conditions, a much darker brown solid forms. This material still appears to contain mostly $K_4[HW(CO)_3]_4$ (Nujol mull ν(CO) 1851 (s), 1781 (sh), 1700 (vs b) cm^{-1}), but treatment with aqueous [*n*-Pr_4N]Br provided only a 17% yield of [*n*-$Pr_4N]_4[HW(CO)_3]_4$.

By contrast, when one or more equivalents of K[*sec*-Bu_3BH] react with (TMED)$W(CO)_4$ in refluxing THF only orange-yellow $H_2W(CO)_4^{2-}$ is observed to form.[13] When 1 equiv of K[*sec*-Bu_3BH] is used, considerable amounts of unreacted (TMED)$W(CO)_4$ remain. Treatment of the solid $K_2[H_2W(CO)_4]$ with aqueous $[Et_4N]Br$ provides low yields of both violet $[Et_4N]_4[HW(CO)_3]_4$ and orange-red $[Et_4N]_2[H_2W_2(CO)_8]$ which are easily separated (eq 2). Better yields of $[HW(CO)_3]_4^{4-}$ are

$$\text{(TMED)W(CO)}_4 \xrightarrow[\text{THF, }\Delta]{\text{K}[\textit{sec}\text{-}Bu_3BH]} K_2[H_2W(CO)_4]\downarrow \xrightarrow[H_2O]{[Et_4N]Br} \underset{19\%}{[Et_4N]_4[HW(CO)_3]_4} + \underset{9\%}{[Et_4N]_2[H_2W_2(CO)_8]} \qquad (2)$$

obtained from the reaction of $K_2[H_2W(CO)_4]$ and 1 equiv of CH_3I followed by cation exchange. Although up to 38% yields of $[Et_4N]_4[HW(CO)_3]_4$ have been obtained by this procedure, this represents only about a 27% yield based on (TMED)$W(CO)_4$, since the latter provides about 70% yields of $K_2[H_2W(CO)_4]$ under optimum conditions.[13] On this basis (PMTA)$W(CO)_3$ is presently the best precursor to $[HW(CO)_3]_4^{4-}$. Presumably other $L_3W(CO)_3$ complexes would also work in this reaction, provided the substituents are not attacked by R_3BH^-.

Chemical Properties of $[HM(CO)_3]_4^{4-}$ (M = Mo, W). Very little is presently known about the physical or chemical properties of $[HM(CO)_3]_4^{4-}$. Crystalline salts of the purple Mo tetramer are generally less thermally stable than the corresponding blue-violet tungsten complexes, although the differences are not marked. For example, the decomposition points of crystalline $[Et_4N]_4[HMo(CO)_3]_4$ are approximately 185 °C for M = Mo and 208 °C for M = W. These substances also are remarkably robust in solution. They do not degrade markedly after 24 h in refluxing acetonitrile. At room temperature in this solvent they are stable indefinitely under an inert atmosphere. However, within 1 or 2 min at atmospheric pressure and room temperature, carbon monoxide reacts with [*n*-$Pr_4N]_4[HMo(CO)_3]_4$ in CH_3CN to give a mixture of $H_2Mo_2(CO)_8^{2-}$ and $Mo_2(CO)_{10}^{2-}$. After 2 h, all $H_2Mo_2(CO)_8^{2-}$ was converted to $Mo_2(CO)_{10}^{2-}$. Infrared solution spectra taken during these conversions indicated that no other products were formed. Analytically pure [*n*-$Pr_4N]_2[Mo_2(CO)_{10}]$ was isolated from one of these reactions in 67% yield (see Experimental Section). Under essentially identical conditions, the tungsten tetramer appears to react slightly slower with CO than the molybdenum analogue, to provide only $H_2W_2(CO)_8^{2-}$, which has been isolated as pure [*n*-$Pr_4N]_2[H_2W_2(CO)_8]_2$ in 41% yield in a small-scale reaction. The dianion then reacts more slowly than the reactant (or $H_2Mo_2(CO)_8^{2-}$) to provide essentially quantitative yields (by IR spectra) of $W_2(CO)_{10}^{2-}$, as reported previously.[13] Thus, in the present of CO, both tetramers react according to eq 3.

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(27) (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 146. (b) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (c) Saillant, R. B.; Kaesz, H. D. *Chem. Rev.* **1972**, *72*, 231. (d) Schunn, R. A. In "Transition Metal Hydrides"; Meutterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 203–269. (e) Ginsberg, A. P. *Transition Met. Chem. (N.Y.)* **1965**, *1*, 111.

(28) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113 and references cited therein.

(29) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1 and references cited therein.

(30) In terms of CO force constants, reactions of strong nucleophiles and coordinated CO are generally unfavorable if $k \leq 15.3$ mdyn/Å. (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (b) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

(31) Rochfort, G. L.; Ellis, J. E. *J. Organomet. Chem.* **1983**, *250*, 265.

(32) The corresponding reaction with (PMTA)$Cr(CO)_3$ that proceeds at room temperature to give a brown substance is under investigation.

$$[HM(CO)_3]_4{}^{4-} \xrightarrow{2CO} 2[HM(CO)_4]_2{}^{2-} \xrightarrow[-H_2]{2CO} 2M_2(CO)_{10}{}^{2-} \quad (3)$$

Clearly, additional studies on the chemistry of $[HM(CO)_3]_4{}^{4-}$ will be essential to properly define the reactivity patterns of these novel materials. However, it is already evident that these formally unsaturated molecules are much more resistant to base or nucleophilic attack than $[HRe(CO)_3]_4$. The latter readily degrades in polar solvents including acetonitrile at room temperature.[9b] Also, whereas $[HM(CO)_3]_4{}^{4-}$ reacts with CO to provide only dimeric dianions, the rhenium analogue reportedly yields $H_3Re_3(CO)_{12}$ and $HRe(CO)_5$ as the principle products.[9b] On this basis, it appears that the large amount of negative charge on $[HM(CO)_3]_4{}^{4-}$ does play an important role in defining their reactivities and should make them unusually susceptible to electrophilic attack, despite their formally unsaturated character.

Spectroscopic Properties of $[HM(CO)_3]_4{}^{4-}$ (M = Mo, W). Nujol mull and solution spectra of $[R_4N]_4[HM(CO)_3]_4$ in the ν(CO) region are very similar (Table I) and consist of two intense bands, as expected for a tetrahedral cluster containing four identical $M(CO)_3$ units of local C_{3v} geometry. The bands are fairly sharp and have approximately the same relative intensities as the corresponding bands reported for $[HRe(CO)_3]_4$ (ν(CO) ca. 2040 (vs), 1990 (s), in cyclohexane),[9b] but the positions are about 200 cm^{-1} lower in energy. The ^1H NMR spectrum of $[HMo(CO)_3]_4{}^{4-}$ shows only one singlet at about −6.6 ppm for all isolated salts of this substance (Table I). While this spectrum is fully consistent with a tetrahedral cluster containing static face-bridging hydrogens, other possibilities are not ruled out, including that of a stereochemically non-rigid cluster. The corresponding ^1H NMR spectrum of $[HW(CO)_3]_4{}^{4-}$ is substantially more informative due to additional information provided by $^{183}W-H$ coupling. Davison et al.[33] and later Hayter[14] calculated ^1H NMR spectra expected of various structures for tungsten hydride complexes of the type $HW_2L_n{}^z$. We have extended these calculations, including Hayter's simplification that long-range $^{183}W-H$ coupling is assumed to be zero, to two classes of tetramer structures which are compatible with the X-ray structural results. For class A, each hydrogen interacts with three equivalent tungstens. This class could correspond to a rigid structure with face-bridging hydrogens or one in which a terminal or edge-bridging hydrogen shifts to another identical position rapidly on the NMR time scale[34] such that it is coupled to three equivalent tungsten atoms. For this class structure a 1:4.1:1 triplet is expected.[35] For class B, each hydrogen interacts with four equivalent tungsten atoms. In this case a 1:3.2:1 triplet is expected.[36] This latter situation is that of a stereochemically nonrigid cluster and is equivalent to that recently observed for the related, but structurally quite different, 56-electron cluster, $[(\mu-H)Rh(COD)]_4$, at room temperature.[10] In fact, careful integrations of the hydride signal of $[n-Pr_4N]_4[HW(CO)_3]_4$ in CD_3CN at room temperature have shown the presence of 1:3.2:1 to 1:3.3:1 triplets which strongly suggests that $[HW(CO)_3]_4{}^{4-}$ is stereochemically nonrigid. Since IR spectra of $[n-Pr_4N]_4[HW(CO)_3]_4$ in the solid state (as Nujol mulls) and in CH_3CN are virtually identical, there is no reason to believe that the solid state and solution structures of the cluster are different. Also, ^1H NMR spectra of the same salt down to −40 °C showed no substantial difference, but its solubility was sufficiently low at this temperature that peak integration was also less certain. However, it may be significant that the value of $J_{H-^{183}W}$ remained essentially temperature independent from 25 to −40 °C. By contrast, while the high-field hydride resonance of $[HRh(COD)]_4$ at 30 °C was a binomial quintet with J_{Rh-H} = 14 Hz, at −50 °C it had changed to a binomial quartet with J_{Rh-H} = 19 Hz.[10]

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Registry No. 1, 86854-86-6; **2**, 86854-88-8; **3**, 86854-89-9; **4**, 86854-90-2; **5**, 86854-92-4; **6**, 86854-93-5; **7**, 86854-94-6; $K_4[HW(CO)_3]_4$, 86854-96-8; $(TMED)Mo(CO)_4$, 14971-45-0; $(PMTA)Mo(CO)_3$, 29256-73-3; $(PMTA)W(CO)_3$, 81097-61-2; $Na_4Mo(CO)_4$, 67202-63-5; $Mo(CO)_6$, 13939-06-5; $[n-Pr_4N]_2[Mo_2(CO)_{10}]$, 86854-95-7; $K_2[H_2W(CO)_4]$, 84850-85-1; $[Et_4N]_2[H_2Mo_2(CO)_8]$, 84850-68-0; $[Et_4N]_2[H_2W_2(CO)_8]$, 52032-34-5; $K[sec-Bu_3BH]$, 54575-49-4; $NaBH_4$, 16940-66-2.

Supplementary Material Available: Tables of bond distances and angles and positional and thermal parameters for $(n-C_3H_7)_4N^+$, a table of thermal parameters for $[HMo(CO)_3]_4{}^{4-}$, tables of weighted least-squares planes and the distances of the atoms from their respective planes for $[HMo(CO)_3]_4{}^{4-}$, and observed and calculated structure factors for the structure of $[n-Pr_4N]_4[HMo(CO)_3]_4$ are available; also included is a table of positional and thermal parameters for the incompletely refined structure of $[n-Bu_4N]_4[HMo(CO)_3]_4$, mentioned in ref 22 (40 pages). Ordering information is given on any current masthead page.

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[33] Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.*, **1962**, 3653.

[34] Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 769.

[35] In principle a 0.0002:0.083:1:4.14:1:0.083:0.0002 heptet (separation = $1/2J_{H-^{183}W}$) could be observed, but the natural abundance of ^{183}W ($I = 1/2$) is sufficiently low (ca. 14.3%) that only the three strongest signals would normally be seen. Unsuccessful attempts to observe all signals of the quintet expected for $HW_2(CO)_{10}{}^-$ have been reported.[14]

[36] A 0.0001:0.007:0.12:1.0:3.2:1.0:0.12:0.007:0.0001 nonet (separation = $1/2J_{H-^{183}W}$) is calculated for this situation. Due to the low solubility of salts containing $[HW(CO)_3]_4{}^{4-}$, only a triplet has been definitely observed in our spectra.