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Synthesis and Characterization of Zerovalent Polynuclear Metal Carbonyl Compounds of Cr, Mo, and W. X-ray Crystal Structure of $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$

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Compounds of the general formula $[NR_4]_n[M(CO)_3(XR)]_n$ (*n* = 3 or 4) (M = Cr, Mo, W; XR = OMe, OEt, SPh) have been prepared by refluxing the corresponding $M(CO)_3$PMTA (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with the appropriate NaXR in THF, followed by metathesis with tetramethyl- or tetraethylammonium halides. Treatment of $W(CO)_3$PMTA or $W(CO)_3(CH_3CN)_3$ with NaOPh provides after cation exchange a substance formulated as $[Et_4N]_3[W_2(CO)_6(\mu\text{-}OPh)_3]$. These complexes have been characterized by infrared and ^1H NMR spectra and elemental analyses. Also, the product obtained from the reaction of NaOEt with $W(CO)_3$PMTA followed by metathesis with Me_4NBr has been characterized by a single-crystal X-ray structure determination. This material has the formula $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}OEt)_2]$. The anion contains a highly unsymmetrical metal triangle which is best considered to contain only one W–W bond. The molecule crystallizes in space group *Cc* (No. 9) with two crystallographically independent molecules in the unit cell. Crystal data: $a = 14.831$ (4) Å, $b = 41.686$ (14) Å, $c = 12.905$ (3) Å, $\beta = 90.74$ (4)°, $Z = 4$, $V = 7978$ (7) Å^3, and ρ(calcd) = 1.848 g/cm^3.

Introduction

The chemistry and syntheses of polynuclear transition-metal compounds has become an area of great interest due to the possible involvement of such species, especially carbonyl clusters, in catalyzed hydrogenation of carbon monoxide and related important processes.[1] Although homonuclear carbonyl clusters of group 7 and 8 metals are well established and structurally characterized in many cases, corresponding clusters and polynuclear species of group 6 metals are much less common. To our knowledge, $[Cp_3Mo_3(CO)_6S]^+$ is the only previously established homonuclear group 6 carbonyl cluster;[2] however, several mixed-metal clusters containing these metals have been structurally characterized. Several other polynuclear carbonyl complexes of Cr, Mo, and W are known, but the metals in these species appear to be held together by bridging ligands rather than metal–metal bonds; e.g., $[HW(CO)_3OH(PPh_3O)]_4$ contains a tetrahedral array of $W(CO)_3$ units held together by triply bridging OH groups. Its rather long W–W distances (3.48 Å) are consistent with the presence of little direct metal–metal bonding.[3] More recently, Bau et al., reported on the structural characterization of $[PPN]_3\{Na[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}O)]_2\}$ and $[Me_4N][Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}OCH_3)]$ which were also suggested to contain no significant metal–metal bonding.[4]

In the course of our investigation on the reduction of $M(CO)_3$PMTA (M = Cr, Mo, W; PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) we had occasion to treat these PMTA complexes with sodium alkoxides and thiophenoxide. This general reaction provided low to moderate yields of new polynuclear complexes of Cr, Mo, and W. In this paper we report on the X-ray structural characterization of one compound in this series: $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}OEt)_2]$. The syntheses of related compounds containing Cr, Mo, and W are also discussed. Comparisons between these polynuclear species and those reported by Bau et al (vide supra) and electronically equivalent complexes of the type $[Mn(CO)_3(OR)]_n$ (*n* = 3, 4)[5] are also presented.

Experimental Section

All synthesis, transfers, and workups were carried out under an atmosphere of rigorously purified N_2 or Ar using standard Schlenk techniques. Infrared spectra were obtained on a Perkin-Elmer 283 grating instrument as Nujol mulls on NaCl plates or as solutions in 0.1-mm path length amalgam sealed cells fitted with stainless-stell stopcocks. ^1H NMR spectra were determined in CD_3CN (Aldrich, 99 atom%) degassed by at least three freeze–thaw cycles on a Varian Associates HFT-80 spectrometer at 79.5 MHz. Elemental analyses were performed by Galbraith Laboratories, Inc., Spang Microanalytical Laboratories, or Analystiche Laboratorien. Melting points were determined in N_2-filled capillaries using a Thomas Hoover "Unimelt" apparatus and are uncorrected. All solvents were reagent grade from commercial sources. THF and diethyl ether were distilled from blue Na or K benzophenone ketyl solutions and stored under N_2 or Ar. Acetonitrile was purged thoroughly with dry N_2, refluxed over CaH_2, and distilled under N_2 or Ar. All other solvents were stored over molecular sieves and purged with N_2 before use. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were purchased from Pressure Chemical Co. and used as received. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMTA) was purchased from Eastman or PCR and freed from oxygen before use. Tetramethylammonium chloride (J.T. Baker) and tetraethylammonium bromide (Aldrich) were dried at 100 °C in vacuo prior to use.

Infrared spectra are tabulated in Table I, ^1H NMR in Table II, elemental analyses, melting points, and yields in Table III for all compounds.

Synthesis of Compounds. $M(CO)_3$PMTA (M = Cr, Mo, W). Details are given for $W(CO)_3$PMTA. Corresponding syntheses of $Cr(CO)_3$PMTA and $Mo(CO)_3$PMTA are essentially identical. Typically, 20.0 g (52.4 mmol) of $W(CO)_6$ was refluxed in 250 mL of CH_3CN for several days to form $W(CO)_3(CH_3CN)_3$ according to the method of King et al.[6] Neat PMTA (14 mL, 11.6 g, 66.7 mmol) is added at once, and reflux continued for 4–6 h to give an orange yellow solution which is filtered hot and then reduced in volume. Yellow crystalline $W(CO)_3$PMTA separates out in spectroscopically and analytically pure form in 75–80% yield. The use of colorless, freshly distilled PMTA instead of the pale yellow

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Table I. Infrared Spectra of the Complexes in the Carbonyl Stretching Region (cm^{-1})[a,b]

$\mathrm{Cr(CO)_3PMTA}$	mull	1901 s, 1896 s, 1764 s, 1741 sh
	$\mathrm{CH_3CN}$	1906 s, 1768 s, 1750 sh
$\mathrm{Mo(CO)_3PMTA}$	mull	1895 s, 1766 s, 1743 s
	$\mathrm{CH_3CN}$	1909 s, 1774 s, 1759 sh
$\mathrm{W(CO)_3PMTA}$	mull	1890 s, 1752 s, 1728 s
	$\mathrm{CH_3CN}$	1902 s, 1767 s, 1753 sh
$\mathrm{[Me_4N]_3[W(CO)_3(OEt)]_3}$ (1)	mull	1902 m, 1863 s, 1736 sh
	$\mathrm{CH_3CN}$	1900 w, 1870 s, 1759 ms, 1732 ms
$\mathrm{[Me_4N]_3[Mo(CO)_3(OEt)]_3}$ (2)	mull	1903 m, 1862 s, 1721 br
	$\mathrm{CH_3CN}$	1903 w, 1870 s, 1759 ms, 1732 m
$\mathrm{[Me_4N]_{\mathit{n}}[Cr(CO)_3(OEt)]_{\mathit{n}}}$ (3)	$\mathrm{CH_3CN}$	1899 w, 1858 s, 1748 s, 1724 m, 1716 m
$\mathrm{[Et_4N]_{\mathit{n}}[Cr(CO)_3(OMe)]_{\mathit{n}}}$ (4)	mull	1856 s, 1705 br
	$\mathrm{CH_3CN}$	1864 s, 1718 s
$\mathrm{[Et_4N]_{\mathit{n}}[Mo(CO)_3(OMe)]_{\mathit{n}}}$ (5)	mull	1991 w, 1864 s, 1695 br
	$\mathrm{CH_3CN}$	1871 s, 1739 sh, 1729 s
$\mathrm{[Et_4N]_{\mathit{n}}[W(CO)_3(OMe)]_{\mathit{n}}}$ (6)	$\mathrm{CH_3CN}$	1905 w, 1866 m, 1857 m, 1747 sh, 1727 s
$\mathrm{[Me_4N]_{\mathit{n}}[Mo(CO)_3(SPh)]_{\mathit{n}}\cdot CH_3CN}$ (7)[c]	mull	1909 w, 1875 vs, 1739 s, 1705 s
	$\mathrm{CH_3CN}$	1882 vs, 1754 s
$\mathrm{[Me_4N]_{\mathit{n}}[W(CO)_3(SPh)]_{\mathit{n}}}$ (8)	mull	1872 s, 1732 s
	$\mathrm{CH_3CN}$	1880 s, 1755 s
$\mathrm{[Ph_4P]_{\mathit{n}}[Cr(CO)_3(SPh)]_{\mathit{n}}}$ (9)	$\mathrm{CH_3CN}$	1917 m, 1891 s, 1859 sh, 1843 sh, 1797 m
$\mathrm{[Et_4N]_3[W_2(CO)_6(OPh)_3]}$ (10)	$\mathrm{CH_3CN}$	1860 s, 1719 s

[a] Compounds 3, 6, and 9 were not isolated as pure substances. See Discussion. [b] The value of n may be 3 and/or 4 for compounds **3-9**. [c] ν(CN) = 2140 vw cm^{-1} for Nujol mull.

Table II. ^{1}H NMR Data (δ, Ppm) for the Complexes[a,b]

$\mathrm{Cr(CO)_3PMTA}$	2.63 (m, 15 H, N-$\mathrm{CH_3}$), 2.92 (s, 8 H, N-$\mathrm{CH_2}$)
$\mathrm{Mo(CO)_3PMTA}$	2.51 (s, 12 H, $\mathrm{N(CH_3)_2}$), 2.65 (m, 3 H, $\mathrm{N(CH_3)}$), 2.85 (s, 8 H, N-$\mathrm{CH_2}$)
$\mathrm{W(CO)_3PMTA}$	2.81 (m, N-$\mathrm{CH_3}$, N-$\mathrm{CH_2}$)
1	1.22 (br t, 9 H, -$\mathrm{CH_3}$), 3.54 (m, 4 H, μ_3-$\mathrm{OCH_2}$-), 4.11 (m, 2 H, μ-$\mathrm{OCH_2}$-)
2	1.20 (br t, 9 H, -$\mathrm{CH_3}$), 3.38 (q, 4 H, μ_3-$\mathrm{OCH_2}$-), 4.00 (q, 2 H, μ-$\mathrm{OCH_2}$-)
4	4.15 (s, 3 H, -$\mathrm{OCH_3}$)
5	4.07 (s, 3 H, -$\mathrm{OCH_3}$)
7[c]	1.96 (s, $\mathrm{CH_3CN}$), 6.98-8.40 (m, -$\mathrm{SC_6H_5}$)
8	7.21-8.37 (m, 5 H, -$\mathrm{SC_6H_5}$)
10	6.41-7.69 (m, 15 H, -$\mathrm{OC_6H_5}$)

[a] Solvent = $\mathrm{CD_3CN}$; $\mathrm{Me_4Si}$ reference. Values of chemical shifts are in ppm. Tetramethylammonium cations in compounds **1**, **2**, **7**, and **8** have very similar resonance positions: δ 3.00-3.14 (s). Tetraethylammonium cations in **4**, **5**, and **10** also have similar ^{1}H NMR spectra: e.g., δ 1.22 (t of t, -$\mathrm{CH_3}$), 3.23 (q, -$\mathrm{CH_2}$-). [b] ^{1}H NMR spectra are only reported for compounds isolated as pure substances. See Table I for formulation of salts. Integrations of proton resonances for compounds 4, 5, and 8 are arbitrarily defined for $n = 1$. [c] Integration of proton resonance signals was not sufficiently precise to determine whether n = 3 or 4.

commercial product has no effect on product yields. Orange $\mathrm{Cr(CO)_3PMTA}$ and yellow $\mathrm{Mo(CO)_3PMTA}$ form air-stable crystals (no observable change after several hours in air at room temperature) that dissolve in $\mathrm{CH_3CN}$, acetone, $\mathrm{CH_2Cl_2}$, and THF to provide quite air sensitive solutions. They are insoluble in ethyl ether and cold hydrocarbon solvents.

$\mathrm{[Me_4N]_{\mathit{n}}[M(CO)_3(OC_2H_5)]_{\mathit{n}}}$ (M = W (1), Mo (2), Cr (3); n = 3). Sodium ethoxide was generated by stirring 0.22 g (9.7 mmol) of Na in absolute ethanol (7.0 mL). This was added to a slurry of 4.28 g (9.7 mmol) of $\mathrm{W(CO)_3PMTA}$ in 100 mL of THF. The mixture was refluxed for 3 h and yielded an orange slightly cloudy solution. The solution was pumped to a dark oil and treated with 1.06 g (9.7 mmol) of $\mathrm{Me_4NCl}$ in 20 mL of ethanol. Recrystallization of the resulting yellow powder from $\mathrm{CH_3CN}$-EtOH yielded 2.47 g (66% yield) of spectroscopically pure 1 which was characterized by standard methods as well as single-crystal X-ray crystallography. Reaction of $\mathrm{Mo(CO)_3PMTA}$ or $\mathrm{Mo(CO)_3(CH_3CN)_3}$ with 1 equiv of NaOEt and $\mathrm{Me_4NCl}$ metathesis provides modest (45-50%) yields of yellow, crystalline $\mathrm{[Me_4N]_3[Mo_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}OEt)_2]}$ (2).

The analogous reaction with $\mathrm{Cr(CO)_3PMTA}$ and NaOEt gave a deep orange mixture believed to contain $\mathrm{Cr_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}OEt)_2^{3-}}$ (3) and other, apparently inseparable, metal carbonyl species on the basis of solution IR spectra. All products from these reactions are extremely air and moisture sensitive.

$\mathrm{[Et_4N]_{\mathit{n}}[M(CO)_3(OCH_3)]_{\mathit{n}}}$ (M = Cr (4), Mo (5), W (6)). In a typical preparation 0.030 g (1.5 mmol) of Na was reacted with a slight excess (0.1 mL) of reagent grade methanol in THF. When

Table III. Elemental Analyses, Melting Points, and Yields of the Complexes

		elemental anal.							
		C		H		N			
compd	compositn	calcd	found	calcd	found	calcd	found	mp, °C	yield, %
$\mathrm{Cr(CO)_3PMTA}$	$\mathrm{C_{12}H_{23}CrN_3O_3}$	46.62	46.32	7.44	7.21	13.58	13.75	73 dec	80
$\mathrm{Mo(CO)_3PMTA}$	$\mathrm{C_{12}H_{23}MoN_3O_3}$	40.82	41.23	6.52	6.23	11.90	12.15	160 dec	83
$\mathrm{W(CO)_3PMTA}$	$\mathrm{C_{12}H_{23}N_3O_3W}$	32.66	32.30	5.22	5.05	9.53	9.38	175 dec	80
1	$\mathrm{C_{27}H_{51}N_3O_{12}W_3}$	27.92	28.31	4.44	4.68	3.62	3.88	200 dec	66
2	$\mathrm{C_{27}H_{51}Mo_3N_3O_{12}}$	36.12	36.06	5.74	5.66	4.68	4.78	210 dec	45
4[b]	$\mathrm{[C_{12}H_{23}CrNO_4]_{\mathit{n}}}$	47.94	47.60	7.89	7.63	4.76	4.84	190	59
5	$\mathrm{[C_{12}H_{23}MoNO_4]_{\mathit{n}}}$	42.21	42.01	6.81	6.80	4.10	4.28	220	26
7[c]	$\mathrm{[C_{13}H_{27}MoNO_3S]_{\mathit{n}}\cdot CH_3CN}$	43.41	43.05	4.79	4.84	4.69	4.78	60 dec	36
8	$\mathrm{[C_{13}H_{27}NO_3SW]_{\mathit{n}}}$	34.60	34.54	3.81	3.64	3.10	3.15	130	7
10[d]	$\mathrm{C_{48}H_{75}N_3O_9W_2}$	47.80	47.89	6.28	6.27	3.48	3.46	156 dec	17

[a] See Table I for formulations of tetraalkylammonium salts. The value of n for compounds 4, 5, 7, and 8 may be 3 or 4. [b] Cr analysis: calcd, 17.66; found, 18.05. [c] C, H, and N percentages were calculated by assuming n = 4. For n = 3, the calculated values are very similar: C, 43.55; H, 4.81; N, 4.95. [d] C, H, and N percentages calculated for the formulation $\mathrm{[Et_4N]_{\mathit{n}}[W(CO)_3(OPh)]_{\mathit{n}}}$ are as follows: C, 41.57; H, 5.13; N, 2.85.

all Na had been consumed, the solution was added at once to a rapidly stirred solution of 0.46 g (1.5 mmol) of $Cr(CO)_3PMTA$ in 160 mL of THF. After 16 h of reflux the solvent was removed in vacuo and the pyrophoric yellow powder metathesized with Et_4NCl in CH_3CN. Recrystallization from CH_3CN–diethyl ether gave a modest yield (59%) of crystalline yellow 4. Compound 5, also a yellow crystalline substance, was prepared similarly from $Mo(CO)_3PMTA$. However, it has not been possible to separate the complex mixture of yellow products containing 6 from the reaction of $W(CO)_3PMTA$ with $NaOCH_3$.

$[Me_4N]_n[M(CO)_3(SC_6H_5)]_n$ (M = Mo (7), W (8), Cr (9)). $Mo(CO)_3(CH_3CN)_3$ was prepared by refluxing 2.74 g (10.4 mmol) of $Mo(CO)_6$ in CH_3CN.[6] The solvent was removed in vacuo and the residue redissolved in THF and treated with slurry of NaSPh (prepared by reaction of 1.15 g (10.4 mmol) of benzenethiol (Eastman) with 0.24 g (10.4 mmol) of Na). The orange solution of $Mo(CO)_3(CH_3CN)_3$ immediately turned dark red and was refluxed for 10 h. Removal of the solvent, dissolution in CH_3CN, and treatment with ethanolic Me_4NCl provided 1.30 g (36%) of yellow, crystalline 7. Infrared and ^1H NMR spectroscopy and elemental analysis indicate that 7 contains one acetonitrile of crystallization per formula unit. In a similar preparation, $W(CO)_3(CH_3CN)_3$ was reacted with NaSPh to provide yellow, crystalline 8 in high spectroscopic purity, but isolated yields were low due to partial decomposition in the metathesis step. Unlike 7, there is no evidence for solvent of crystallization in 8. Reaction of $Cr(CO)_3PMTA$ or $Cr(CO)_3(CH_3CN)_3$ with NaSPh gave (as with NaOEt) a dark red inseparable mixture of products containing 9. Products 7, 8, and 9 are air sensitive and rapidly hydrolyze in a moist atmosphere as evidenced by the strong odor of benzenethiol produced when crystalline samples are left standing in air.

$[Et_4N]_3[W_2(CO)_6(\mu\text{-}OC_6H_5)_3]$ (10). Sodium phenoxide was generated by the action of excess sodium sand on 0.49 g (5.14 mmol) of phenol in refluxing THF. Tris(acetonitrile)tricarbonyltungsten was prepared by refluxing $W(CO)_6$ (1.81 g, 5.14 mmol) in acetonitrile.[6] The NaOPh solution was then added to the dry $W(CO)_3(CH_3CN)_3$ and brought to reflux for ca. 3 h. After metathesis with an ethanol solution of Et_4NBr, 0.54 g (17% yield) of yellow, crystalline $[Et_4N]_3[W_2(CO)_6(\mu\text{-}OPh)_3]$ was obtained. Infrared and ^1H NMR spectra and elemental analyses support this formulation. The same compound has also been isolated from the reaction of $W(CO)_3PMTA$ with NaOPh.

Reaction of $M(CO)_3PMTA$ with KOH (M = Cr, W). Numerous attempts to prepare bridging hydroxide complexes similar to 1–10 by reaction of $M(CO)_3PMTA$ with ethanolic or mixed THF–ethanol solutions of KOH led to dark red solutions containing inseparable complex mixtures of metal carbonyl containing materials. Similar attempts with $M(CO)_3(CH_3CN)_3$ were likewise unfruitful.

Collection and Reduction of X-ray Data. A summary of crystal data is presented in Table IV. An acceptable crystal of 1 was mounted under N_2 in a glass capillary. The crystal was found to belong to the C-centered monoclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing program and by a Dulaney reduction calculation.[7] Systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) showed the space group to be either Cc (No. 9) or $C2/c$ (No. 15). The former was shown to be correct by the eventual solution of the structure, vide infra. 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 7040 ($\pm h$, $+k$, $+l$) unique reflections were measured at 23 °C out to $2\theta = 50°$ by using monochromatized Mo Kα radiation.[8] The data were corrected for Lorentz, polarization, absorption, and background effects, using a value of 0.06 for p.[7] Of the 7040 unique reflections, 3794 have $F_o^2 \geq 2.5\sigma(F_o)^2$ and were used for final solution and refinement of the structure.

Table IV. Summary of Crystal Data and Intensity Collection

formula	$C_{27}H_{51}N_3O_{12}W_3$
fw	1161.33
a, Å	14.831 (4)
b, Å	41.686 (14)
c, Å	12.905 (3)
β, deg	90.74 (2)
V, Å^3	7978 (7)
Z	4
d(calcd)	1.848 g/cm^3
space group	Cc (no. 9)
cryst dimens, mm	0.036 × 0.126 × 0.250
temp, °C	23
radiation	Mo Kα (0.710 69 Å) from monochromator
linear abs faction, cm^{-1}	91.976
2θ limits, deg	0–50
final no. of variables	389
unique data used	3794
R[a]	0.049
R_w[a]	0.055
error in an observn of unit weight	1.17

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

Solution and Refinement of the Structure. The structure was solved by conventional heavy atom techniques. The Patterson map could be interpreted on the assumption that the space group was $C2/c$, with two independent molecules, each lying on a twofold axis. Further work, however, indicated that the molecules had only approximately twofold symmetry and that they were either ordered in space group Cc or disordered in space group $C2/c$. Refinement using the 2973 most intense reflections and with only the W atoms included led to parameters near those given in Table V with a conventional $R = 0.105$ and weighted $R_w = 0.156$ when ordered molecules in Cc were used. The corresponding refinement for disordered molecules in $C2/c$ (with W1A and W2A averaged, with W2B and W3B averaged, and with W3A and W1B having occupancy factors of one-half) converged with parameters similar to the starting parameters but with $R = 0.190$ and $R_w = 0.275$. All correlation coefficients in either refinement that were larger than 0.5 involved only thermal parameters and the scale factor. The results clearly indicate the ordered structure in Cc to be the correct choice. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining nonhydrogen atoms with no further difficulties.[9] The atomic scattering factors were taken from the usual source,[10] and the effects of anomalous dispersion were included in F_c for all atoms by using Cromers and Ibers[11] values of $\Delta f'$ and $\Delta f''$. Tables of weighted least-square planes and the distances of the atoms from their respective planes,

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(7) 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 Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978.

(8) 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 $K = 20.1166x$ (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 $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (\rho I)^2]$, where ρ 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 $\sigma(F_o) = {}^1/_2(\sigma(I)/I)F_o$.

(9) 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 $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ where NO and NV are the number of observations and variables, respectively.

(10) Cromers, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. Ibid., Table 2.3.1.

(11) Cromers, D. T.; Ibers, J. A., in reference 10.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
W1A	0.060 20 (0)	0.106 07 (3)	0.3409 (0)	2.72 (5)	3.14 (6)	4.50 (6)	0.27 (5)	0.15 (5)	0.40 (6)
W1B	-0.023 32 (12)	0.430 80 (4)	0.2947 (1)	4.71 (7)	3.29 (6)	5.04 (7)	0.48 (6)	0.49 (6)	0.02 (6)
W2A	-0.061 52 (9)	0.100 45 (3)	0.1603 (1)	2.60 (5)	2.48 (5)	4.74 (6)	-0.08 (5)	0.25 (5)	-0.29 (6)
W2B	-0.070 76 (10)	0.363 83 (3)	0.3493 (1)	3.29 (5)	3.16 (6)	4.25 (6)	0.11 (6)	0.33 (5)	0.38 (6)
W3A	-0.023 74 (10)	0.175 60 (3)	0.2202 (1)	2.64 (9)	2.38 (5)	6.53 (8)	0.04 (5)	0.43 (5)	-0.01 (6)
W3B	0.076 46 (10)	0.365 64 (3)	0.1627 (1)	4.08 (6)	3.10 (6)	4.58 (6)	-0.21 (6)	1.35 (5)	-0.29 (6)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O1A	0.181 (2)	0.1451 (7)	0.498 (2)	7.6 (7)	C8A	-0.110 (2)	0.2093 (8)	0.245 (2)	3.6 (7)
O1B	-0.392 (3)	-0.0216 (10)	0.214 (3)	11.0 (10)	C8B	0.057 (2)	0.3466 (9)	0.041 (3)	4.2 (7)
O2A	0.006 (2)	0.0675 (7)	0.544 (2)	7.7 (7)	C9A	0.027 (3)	0.2060 (10)	0.144 (3)	5.9 (9)
O2B	-0.179 (2)	0.4805 (8)	0.257 (2)	9.4 (9)	C9B	0.191 (2)	0.3491 (9)	0.178 (3)	4.3 (7)
O3A	0.231 (2)	0.0629 (7)	0.336 (2)	6.6 (7)	C10A	-0.159 (2)	0.1589 (8)	0.034 (2)	4.3 (7)
O3B	0.007 (2)	0.4731 (8)	0.494 (2)	8.7 (8)	C10B	0.018 (2)	0.2986 (9)	0.286 (3)	5.0 (9)
O4A	-0.009 (2)	0.0323 (6)	0.244 (2)	6.4 (6)	C11A	-0.245 (4)	0.1619 (14)	0.089 (4)	9.3 (14)
O4B	-0.195 (2)	0.4126 (8)	0.468 (2)	8.3 (8)	C11B	0.097 (3)	0.2919 (11)	0.365 (3)	6.6 (10)
O5A	-0.239 (2)	0.0650 (7)	0.153 (2)	6.9 (7)	C12A	-0.134 (3)	0.1292 (10)	0.391 (3)	6.4 (10)
O5B	-0.258 (2)	0.3307 (7)	0.336 (2)	6.7 (7)	C12B	-0.139 (3)	0.3913 (10)	0.140 (3)	5.8 (9)
O6A	-0.008 (2)	0.0668 (6)	-0.037 (2)	5.4 (6)	C13A	-0.217 (3)	0.1394 (11)	0.345 (3)	7.4 (12)
O6B	-0.056 (2)	0.3377 (7)	0.580 (2)	7.4 (7)	C13B	-0.124 (4)	0.4082 (14)	0.059 (4)	9.8 (15)
O7A	0.077 (2)	0.2082 (8)	0.406 (2)	7.8 (7)	C14A	0.140 (2)	0.1312 (8)	0.125 (3)	4.6 (7)
O7B	0.152 (4)	0.4189 (16)	0.016 (5)	5.8 (18)	C14B	0.132 (2)	0.3858 (8)	0.407 (2)	4.0 (7)
O8A	-0.166 (2)	0.2290 (6)	0.261 (2)	5.7 (6)	C15A	0.213 (3)	0.1501 (12)	0.172 (3)	7.7 (12)
O8B	0.051 (2)	0.3339 (7)	-0.043 (2)	7.6 (7)	C15B	0.211 (3)	0.4073 (10)	0.377 (3)	5.8 (9)
O9A	0.066 (3)	0.2248 (9)	0.077 (3)	10.6 (10)	C16	0.190 (3)	0.0366 (10)	0.099 (3)	6.3 (10)
O9B	0.270 (2)	0.3382 (8)	0.176 (2)	8.3 (8)	C17	0.295 (3)	-0.0004 (12)	0.513 (4)	8.5 (13)
O10A	-0.097 (2)	0.1469 (6)	0.110 (2)	4.9 (5)	C18	0.149 (4)	-0.0131 (14)	0.434 (4)	9.7 (15)
O10B	0.002 (2)	0.3318 (5)	0.263 (2)	4.2 (4)	C19	0.143 (6)	0.0144 (21)	0.572 (6)	17.4 (26)
O11A	-0.069 (1)	0.1313 (5)	0.304 (2)	3.6 (4)	C20	0.093 (4)	0.8918 (12)	0.274 (4)	8.5 (13)
O11B	0.446 (1)	-0.1116 (5)	0.202 (2)	4.4 (5)	C21	0.017 (3)	0.8502 (12)	0.356 (4)	7.9 (12)
O12A	0.056 (1)	0.1301 (5)	0.193 (1)	3.2 (4)	C22	-0.063 (3)	0.1156 (13)	-0.252 (4)	8.7 (13)
O12B	0.564 (1)	-0.1130 (4)	0.327 (1)	2.3 (3)	C23	0.021 (4)	0.8490 (14)	0.160 (4)	9.6 (14)
N1	0.202 (2)	-0.0080 (7)	0.529 (2)	4.6 (6)	C24	0.214 (2)	0.7231 (10)	0.495 (3)	5.1 (8)
N2	0.018 (2)	0.8675 (8)	0.262 (3)	6.5 (8)	C25	0.781 (3)	0.7536 (12)	0.148 (4)	8.2 (13)
N3	0.792 (2)	0.7554 (8)	0.041 (2)	6.4 (8)	C26	0.787 (3)	0.7243 (11)	-0.017 (3)	6.6 (10)
N4	-0.211 (3)	-0.0109 (9)	-0.031 (3)	8.3 (10)	C27	0.879 (4)	0.2265 (15)	0.533 (4)	10.4 (16)
N5	-0.013 (3)	0.5777 (9)	0.251 (3)	9.2 (10)	C28	-0.306 (3)	0.0006 (10)	-0.014 (3)	5.6 (9)
N6	-0.172 (2)	0.2831 (8)	0.011 (2)	6.3 (8)	C29	-0.180 (4)	0.0205 (16)	0.575 (4)	11.1 (17)
C1A	0.128 (2)	0.1323 (9)	0.438 (3)	4.4 (7)	C30	-0.203 (3)	0.0370 (12)	0.396 (4)	8.3 (13)
C1B	-0.460 (4)	-0.0427 (16)	0.223 (5)	11.8 (19)	C31	-0.154 (4)	0.0174 (17)	-0.081 (5)	12.2 (19)
C2A	0.028 (3)	0.0847 (10)	0.466 (3)	6.0 (10)	C32	0.939 (6)	0.5722 (20)	0.160 (6)	15.5 (24)
C2B	-0.109 (3)	0.4613 (12)	0.270 (3)	7.8 (12)	C33	-0.043 (7)	0.6023 (21)	0.311 (7)	19.2 (30)
C3A	0.161 (3)	0.0805 (9)	0.332 (3)	5.2 (9)	C34	0.988 (8)	0.5493 (23)	0.331 (8)	21.3 (35)
C3B	-0.011 (3)	0.4577 (11)	0.414 (3)	6.8 (10)	C35	-0.414 (9)	0.0678 (30)	0.245 (9)	24.1 (46)
C4A	-0.024 (2)	0.0592 (7)	0.222 (2)	2.8 (6)	C36	-0.171 (3)	0.3044 (12)	-0.084 (3)	7.7 (12)
C4B	-0.144 (2)	0.3943 (8)	0.423 (3)	4.2 (7)	C37	0.837 (5)	0.3017 (18)	0.116 (6)	14.7 (23)
C5A	-0.173 (2)	0.0791 (8)	0.155 (2)	3.8 (7)	C38	0.768 (6)	0.7469 (25)	0.507 (7)	18.2 (29)
C5B	-0.187 (2)	0.3430 (9)	0.356 (3)	4.9 (8)	C39	-0.070 (4)	0.2675 (17)	0.018 (5)	12.7 (19)
C6A	-0.032 (2)	0.0795 (8)	0.046 (2)	3.9 (7)	CX	0.044 (6)	0.7175 (21)	0.245 (6)	16.3 (31)
C6B	-0.063 (4)	0.3494 (13)	0.484 (4)	9.4 (14)	CX2	-0.035 (6)	0.2408 (21)	-0.220 (7)	17.5 (28)
C7A	0.043 (3)	0.1935 (11)	0.327 (4)	8.0 (12)	CX3	0.107 (6)	0.2876 (21)	-0.294 (6)	19.3 (28)
C7B	0.120 (2)	0.3982 (7)	0.089 (2)	8.2 (7)	CX4	0.042 (5)	0.2570 (18)	-0.244 (5)	14.3 (23)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors are available.[12] The W atoms were refined anisotropically while all others were treated isotropically. Hydrogen atoms were not located in the final difference Fourier maps and therefore were not included.

In addition to the peaks corresponding to atoms of the compound, four peaks higher than the noise level were found in an otherwise empty region of the unit cell. These atoms are included in Table V with the labels CX1-4. One molecule of solvent is apparently present per two formula units. The most likely solvent molecule is ethanol where only three peaks would be expected. The presence of solvent could not be corroborated by elemental analysis nor by infrared or ^{1}H NMR spectra. It was not possible to obtain an experimental density of sufficient accuracy to help resolve the issue. The question was not pursued further since the presence or absence of the solvent has no important effect on the structural results presented herein. Atoms corresponding to these peaks are included in the final calculations. The final positional and thermal parameters appear in Table V. The labeling scheme for the two independent molecules **1a** and **1b** are presented in parts a and b of Figure 1 and stereoviews in parts a and b of Figure 2. Selected bond distances and angles are collected in Table VI.

Results and Discussion

Molecular Structure of $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$ (1). Compound **1** forms crystals containing two crystallographically independent anions, **1a** and **1b**, in the unit cell. The gross structures of **1a** and **1b** are the same. They consist of a scalene triangle of tungsten atoms, each of which is bound to three terminal carbonyl groups. One doubly bridging ethoxy group spans one edge of the triangle while two triply bridging ethoxy groups lie above and below the plane defined by the three

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

Table VI. Selected Distances and Angles with Esds for 1a and 1b

	1a	1b		1a	1b
		a. Distances (Å)			
W(1)-W(2)	2.939 (2)	2.966 (2)	W(2)-C(6)	1.78 (4)	1.84 (6)
W(2)-W(3)	3.273 (2)	3.272 (2)	W(3)-C(7)	1.85 (5)	1.78 (3)
W(3)-W(1)	3.511 (2)	3.541 (2)	W(3)-C(8)	1.93 (3)	1.78 (4)
W(1)-O(12)	2.15 (2)	2.27 (2)	W(3)-C(9)	1.78 (4)	1.84 (4)
W(1)-O(11)	2.24 (2)	2.18 (2)	C(1)-O(1)	1.22 (4)	1.34 (7)
W(2)-O(12)	2.17 (2)	2.24 (2)	C(2)-O(2)	1.28 (5)	1.32 (5)
W(2)-O(11)	2.26 (2)	2.18 (2)	C(3)-O(3)	1.28 (4)	1.24 (5)
W(3)-O(12)	2.26 (2)	2.26 (2)	C(4)-O(4)	1.18 (3)	1.23 (4)
W(3)-O(11)	2.25 (2)	2.25 (2)	C(5)-O(5)	1.13 (4)	1.20 (4)
W(2)-O(10)	2.11 (2)	2.05 (2)	C(6)-O(6)	1.24 (4)	1.34 (6)
W(3)-O(10)	2.14 (2)	2.22 (2)	C(7)-O(7)	1.28 (5)	1.37 (7)
W(1)-C(1)	1.93 (4)	1.72 (7)	C(8)-O(8)	1.20 (4)	1.21 (4)
W(1)-C(2)	1.91 (5)	1.82 (5)	C(9)-O(9)	1.30 (5)	1.25 (4)
W(1)-C(3)	1.84 (4)	1.91 (5)	C(10)-O(10)	1.43 (4)	1.43 (4)
W(2)-C(4)	1.97 (3)	1.93 (4)	C(12)-O(11)	1.49 (5)	1.49 (4)
W(2)-C(5)	1.88 (4)	1.93 (4)	C(14)-O(12)	1.53 (4)	1.45 (4)
		b. Angles (Deg)			
W(1)-O(12)-C(14)	120 (2)	124 (12)	W(2)-O(10)-W(3)	99.9 (8)	100.8 (9)
W(1)-O(11)-C(12)	112 (2)	113 (2)	W(3)-W(2)-O(10)	41.9 (6)	40.0 (6)
W(2)-O(12)-C(14)	124 (2)	121 (2)	W(2)-W(3)-O(10)	38.2 (6)	39.2 (6)
W(2)-O(11)-C(12)	129 (2)	113 (2)	W(1)-C(1)-O(1)	170 (3)	151 (5)
W(3)-O(12)-C(14)	119 (2)	125 (2)	W(1)-C(2)-O(2)	176 (4)	172 (4)
W(3)-O(11)-C(12)	128 (2)	127 (2)	W(1)-C(3)-O(3)	174 (4)	172 (4)
W(2)-O(10)-C(10)	134 (2)	127 (2)	W(2)-C(4)-O(4)	169 (3)	176 (3)
W(2)-O(10)-W(3)	100.8 (9)	99.9 (8)	W(2)-C(5)-O(5)	177 (3)	164 (3)
W(3)-O(10)-C(10)	125 (2)	131 (2)	W(2)-C(6)-O(6)	176 (3)	178 (5)
W(1)-O(12)-W(2)	85.8 (7)	82.3 (6)	W(3)-C(7)-O(7)	170 (4)	168 (4)
W(2)-O(12)-W(3)	95.2 (8)	92.2 (7)	W(3)-C(8)-O(8)	176 (3)	175 (3)
W(1)-O(12)-W(3)	105.4 (9)	101.3 (7)	W(3)-C(9)-O(9)	171 (4)	173 (3)
W(1)-O(11)-W(2)	81.5 (7)	85.7 (8)	W(1)-W(2)-W(3)	68.59 (5)	68.96 (5)
W(2)-O(11)-W(3)	92.9 (8)	96.3 (9)	W(1)-W(3)-W(2)	51.20 (4)	51.43 (4)
W(1)-O(11)-W(3)	102.9 (9)	107.3 (9)	W(2)-W(1)-W(3)	60.21 (4)	59.61 (4)

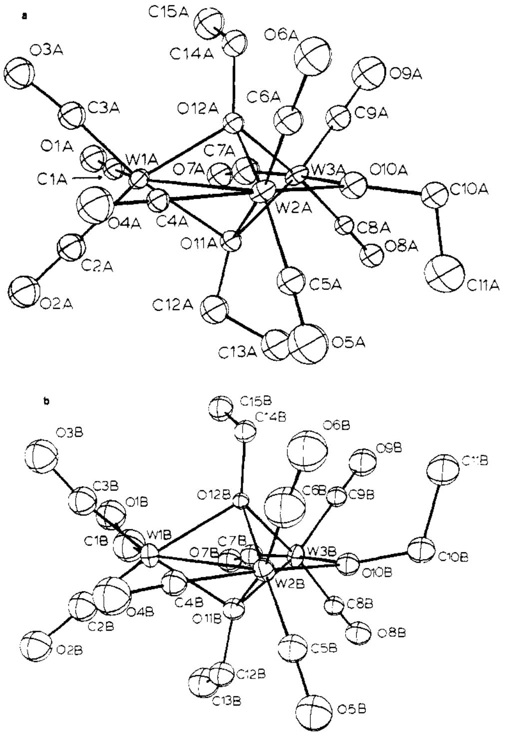

Figure 1. ORTEP view of the independent trianions **1a** (a) and **1b** (b) showing the labeling scheme (50% probability thermal ellipsoids).

tungsten atoms. Cations and anions are well separated, and no unusually short interatomic contacts are observed.

Examination of the data shown in Table VI reveals substantial differences in the W(1)-W(2) and W(1)-W(3) distances in the independent anions. The anions also differ in the orientation of their ethyl groups. Otherwise, they are structurally very similar and are best considered to be lattice stabilized conformational isomers of the same molecule. In solution, these anions appear to be indistinguishable.

Metal-Metal Interactions in 1. The observed W(1)-W(2) distances in **1a** (2.939 (2) Å) and **1b** (2.966 (2) Å) are compatible with the presence of W-W single bonds. Previously reported bond distances, for several tungsten carbonyl derivatives which are considered to correspond to W-W single bonds, are as follows: $[C_5H_5W(CO)_3]_2$ (3.222 (1) Å),[13] $(C_5H_5)_2W_2(CO)_4(C_2H_2)$ (2.987 (1) Å),[14] $(\mu\text{-}Ph_2AsCH_2AsPh_2)(\mu\text{-}Me_2C_2)(\mu\text{-}Br)W_2(CO)_5Br$ (2.937 (1) Å),[15] $[(\mu\text{-}Et_2P)W(CO)_4]_2$ (3.05 (1) Å),[16] and $I_2W_2(CO)_4$ (3.155 Å).[17] Clearly, the W(1)-W(2) distances in **1a** and **1b** fall within the range observed for W-W single bonds.

By contrast, in the following molecules the valence requirements of the tungsten atoms may be satisfied without invoking metal-metal bonds. The W-W distances are shown in parentheses: $K_3[W_2(CO)_6(\mu\text{-}OH)_3]\cdot 2H_2O$ (3.230 (5) Å)[18] and $[HW(CO)_3(\mu_3\text{-}OH)Ph_3PO]_4$ (average value of 3.48 Å).[3] These values are similar to the W(1)-W(3) and W(2)-W(3) distances in **1a** (3.511 (2) and 3.273 (2) Å, respectively) and **1b** (3.541 (2) and 3.272 (2) Å, respectively). Accordingly, **1a** and **1b** are formulated to contain

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[13] Cotton, F. A.; Adams, R. D.; Collins, D. M. *Inorg. Chem.* **1974**, *13*, 1086.

[14] Grinley, D. S.; Bock, C. R.; Wrighton, M. S.; Fisher, B. F.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

[15] Fischer, E. O.; Rahs, A.; Friedrich, P.; Huttner, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 465.

[16] Linck, M. H. *Cryst. Struct. Commun.* **1973**, *2*, 379.

[17] Couldwell, M. C.; Simpson, J.; Robinson, W. R. *J. Organomet. Chem.* **1976**, *107*, 323.

[18] Albano, V. G.; Ciani, G.; Mannassero, M. *J. Organomet. Chem.* **1970**, *25*, C55.

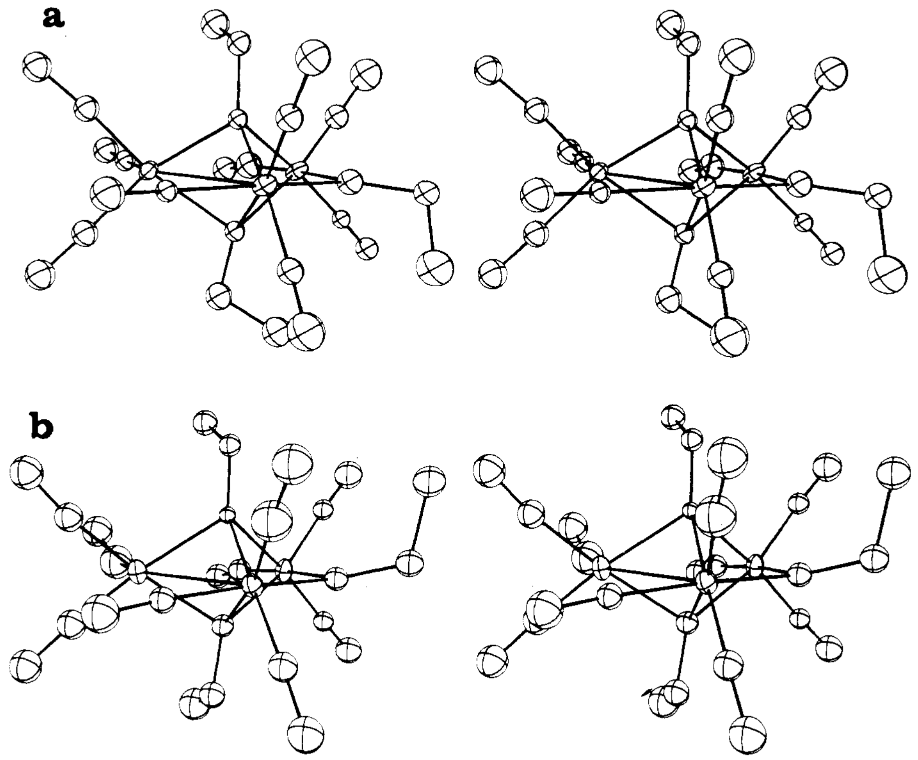

Figure 2. Stereoview of the independent trianions **1a** (a) and **1b** (b).

only one W–W single bond each. This interpretation also formally satisfies the 18-electron requirement of each tungsten atom, where the μ-OC$_2$H$_5$ and μ_3-OC$_2$H$_5$ groups are normally considered to be three- and five-electron donors, respectively. An analogous neutral manganese complex, Mn$_3$(CO)$_9$(μ-OC$_2$H$_5$)(μ_3-OC$_2$H$_5$)$_2$ has been structurally characterized as a dimethylphenylphosphine derivative, Mn$_3$(CO)$_8$(PMe$_2$Ph)(μ-OC$_2$H$_5$)(μ_3-OC$_2$H$_5$)$_2$ and has essentially the same structural features as **1a** and **1b**.[5] This quite unsymmetrical molecule was also formulated to contain only one metal–metal bond for essentially the same reasons as mentioned earlier.

Metal–Ligand Interactions and the Ligands. The more important bond lengths are given in Table VI together with their standard deviations. Corresponding bond lengths and angles between the two independent molecules are paired. In some cases the differences between the members of the pair would appear to be significant, but we believe they are not. A half-normal probability plot[19] indicates that the esd's should be about 50% larger. If we compare chemically similar bonds, we find W–C(av) = 1.86 (7) Å, C–O(av) = 1.26 (6) Å, W–μ-O(av) = 2.13 (2) Å, and W–μ_3-O(av) = 2.23 (4) Å, the esd's estimated from the set of bond lengths are again about 50% larger than those found in the least-squares analysis. With these larger error estimates the only bonds that seem significantly different are W(1)–W(2) and W(3)–W(1). For both of these the distance in molecule **1a** is about 0.03 Å (approximately 10 standard deviations) shorter than in molecule **1b**. The structure of [W$_2$(CO)$_6$(μ-OH)$_3$]$^{3-}$, a related highly charged anionic tungsten carbonyl complex, has been determined.[18] For this substance similar average bond distances were reported: W–C(av) = 1.87 (2) Å, C–O(av) = 1.21 (3) Å, and W–μ-O(av) = 2.16 (2) Å. The somewhat longer W–μ_3-O distances found in **1a** and **1b** are consistent with those reported for [HW(CO)$_3$(μ_3-OH)(Ph$_3$PO)]$_4$ where W–μ_3-O(av) = 2.21 (2) Å.[3]

Syntheses and Possible Structures of [M(CO)$_3$(XR)]$_n$$^{n-}$. Ethoxy Complexes (1, 2, and 3). The reaction of sodium ethoxide with M(CO)$_3$PMTA (M = Mo, W) provides the best characterized compounds of the general formula [M(CO)$_3$(XR)]$_n$$^{n-}$.[20] On the basis of the crystallographic structure determination for the tungsten derivative and the very similar IR and ^{1}H NMR spectra (Tables I and II) exhibited by the molybdenum and tungsten compounds, it is reasonable to assign both of these substances (**1** and **2**) the formula [Et$_4$N]$_3$[M$_3$(CO)$_9$(μ-OC$_2$H$_5$)(μ_3-OC$_2$H$_5$)$_2$] (M = Mo and W). It is important to note that the ^{1}H NMR spectra of **1** and **2** show two different enviornments for the ethoxy groups in solution. These are assigned to the doubly and triply bridging ethoxy groups. Thus, at room temperature these groups do not rapidly interconvert on the NMR time scale and the unsymmetrical trinuclear structures [M(CO)$_3$(OC$_2$H$_5$)]$_3$$^{3-}$ evidently persist in solution. This situation is similar to that described by Abel et al.,[5] for the structurally similar Mn$_3$(CO)$_9$(μ-OR)(μ_3-OR)$_2$ where R = Me and Et. Major differences are present in the infrared solution spectra of these manganese compounds and [M$_3$(CO)$_9$(μ-OC$_2$H$_5$)μ_3-OC$_2$H$_5$)$_2$]$^{3-}$ (M = Mo, W), however. While the manganese complexes show nine clearly resolved CO stretching modes in hexane, the acetonitrile solution spectra of **1** and **2** are much simpler and contain only four CO stretching frequencies. The latter have bands which are broader than those reported for [Mn(CO)$_3$(OC$_2$H$_5$)]$_3$ and quite possibly envelope more than one stretching mode

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[19] Abrahams, S. C.; Keve, E. T. *Acta. Crystallogr., Sect. A* **1971**, *A27*, 157.

[20] M(CO)$_3$PMTA (M = Cr, Mo, W) rather than M(CO)$_3$(CH$_3$CN)$_3$ have been generally used in the reactions reported in this paper because they are more easily handled and purified than the tris(acetonitrile) complexes. However, in those cases where purified M(CO)$_3$(CH$_3$CN)$_3$ (M = Mo, W) have been used, similar yields of products were obtained. We have not used the previously reported M(CO)$_3$(dien) (dien = diethylenetriamine) in these reactions (Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 2323); however, there is no reason why these species should not work equally well. Our original reason for preparing the PMTA complexes was to examine their reductions by alkali metals in liquid ammonia (Ellis, J. E.; Rochfort, G. L., to be submitted for publication), where coordinated dien or CH$_3$CN groups could be deprotonated.

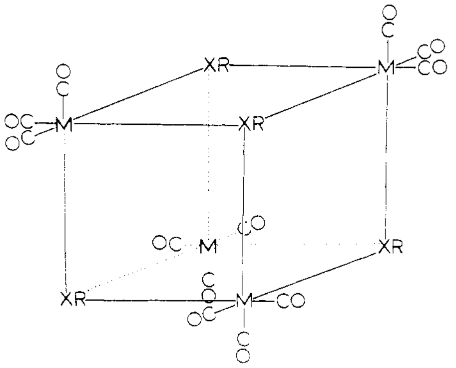

Figure 3. Cubane-type structure proposed for $[M(CO)_3(XR)]_4^{4-}$.

each. As indicated in the Experimental Section, it was not possible to isolate pure samples of the corresponding chromium complex, 3. Infrared spectra of impure $[Me_4N]_n[Cr(CO)_3(OEt)]_n$ in acetonitrile (Table I) contain one more band than do corresponding spectra of 1 and 2. This difference is likely to be due to the presence of an impurity since attempted recrystallizations of this air-sensitive orange substance result in changes in the intensity ratios of certain ν(CO) bands. The similarities in the infrared spectra of 1, and 2, and 3, however, suggest that the unsymmetrical trimeric unit $[Cr_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$ is likely to be a component of the mixture.

Methoxy Complexes (4, 5, and 6). The reaction of sodium methoxide with $M(CO)_3PMTA$ (M = Cr, Mo, and W) provides substances which have strikingly different spectroscopic properties than those obtained above. In this case, it was possible to isolate pure samples of only the chromium and molybdenum derivatives, 4 and 5. The infrared mull and solution spectra of 4 and 5 show only two intense bands in the carbonyl stretching frequency region instead of the four bands observed for 1 and 2. Also, the ^{1}H NMR spectra of 4 and 5 show only one singlet due to the methoxy group down to −45 °C. These spectroscopic properties are more consistent with a much more symmetrical cube shaped tetranuclear structure, Figure 3, where all $M(CO)_3$ and XR units are equivalent, than the highly unsymmetrical trinuclear structure established for 1. On this basis, we favor the tetranuclear formulations $[Et_4N]_4[M(CO)_3(\mu_3\text{-}OCH_3)]_4$ (M = Cr, Mo) for 4 and 5, which do not formally contain metal–metal bonds.

However, the possibility that 4 and 5 are trinuclear species which have structures analogous to those of 1 and 2 *cannot* be ruled out presently. An intra- or intermolecular process which allows rapid exchange of the doubly and triply bridging methoxy groups on the NMR time scale could also be responsible for the observed single methoxy environment. Although the infrared solution spectra of 4 and 5 in the ν(CO) region are very simple and suggest the presence of a highly symmetrical molecule, one must be cautious in assigning structures based only on infrared spectra especially for carbonylmetalates since one absorption envelope may consist of two or more nearly superimposed carbonyl stretching frequencies. There also exists the possibility that the complex, sometimes inseparable, mixtures observed in some reactions reported herein (e.g., in the reaction leading to impure 6) may contain both trimers and tetramers and possibly other units; e.g., the dinuclear $M_2(CO)_6(XR)_3^{3-}$ structure observed in $W_2(CO)_6(OH)_3^{3-}$[18] and compound 10 (vide infra). Further work is required to resolve this issue.

Interestingly, the neutral manganese analogue of 4 has been unequivocally shown to be a trimer and has the unsymmetrical structure $Mn_3(CO)_9(\mu\text{-}OCH_3)(\mu_3\text{-}OCH_3)_2$ characteristic of 1.[5] Abel and co-workers report that the ^{1}H NMR spectrum of this manganese complex shows two singlets (of relative intensities 1:2) which are due to the two nonequivalent methoxy groups. This manganese complex, unlike 4, also has a very complex spectrum in the ν(CO) region. Treatment of the related ethoxy derivative, $Mn_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2$ with thiophenol gives a compound formulated as the tetrameric $[Mn(CO)_3(\mu_3\text{-}SPh)]_4$, for which only two infrared active bands are observed in the ν(CO) region. Abel and co-workers also find that the (benzyloxy)manganese derivative is the tetrameric $[Mn(CO)_3(\mu_3\text{-}OCH_2Ph)]_4$ on the basis of ^{1}H NMR, infrared, and mass spectral data.[5] Interestingly, in the synthesis of this latter compound, small amounts of the trimeric $[Mn_3(CO)_9(\mu\text{-}OCH_2Ph)(\mu_3\text{-}OCH_2Ph)_2]$ also form. It is puzzling why certain –XR groups appear to promote the formation of trimers in the manganese system, while others appear to favor the formation of tetramers. Also, we have no explanation as to why $[Mo_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$ is trimeric in the solid state and in solution while its methoxy analogue appears to be the tetrameric $[Mo(CO)_3(\mu_3\text{-}OCH_3)]_4^{4-}$.

Thiophenoxy Complexes (7, 8, and 9). It was hoped that the reaction of sodium thiophenoxide with $M(CO)_3PMTA$ would result in the formation of more inert $[M(CO)_3(XR)]_n^{n-}$ complexes, since sulfur derivatives of low-valent transition-metal complexes are generally more robust and easier to handle than their oxygen analogues. However, in this system only pure molybdenum and tungsten complexes were isolated in rather low yields (see Table III). The simplicity of their solution infrared spectra (Table I) and close resemblance to the tetrameric $[Mn(CO)_3(SPh)]_4$[5] suggests that these materials also contain tetrameric $[M(CO)_3(\mu_3\text{-}SPh)]_4^{4-}$ units. But we presently have no evidence that unambiguously rules out the possibility that trimeric or possibly other oligomeric units may also be present in solution or in the solid state.

The molybdenum complex 7 crystallizes with one molecule of acetonitrile per trimeric or tetrameric unit. A very weak band at 2140 cm^{-1} in the Nujol mull spectrum is assigned to acetonitrile of crystallization. A singlet at 1.96 ppm in the ^{1}H NMR spectrum of 7 is also due to CH_3CN, but the integration of the signals in this spectrum and the elemental analyses (Table III) do not permit a choice between trimeric (n = 3) or tetrameric (n = 4) units in $[Me_4N]_n[Mo(CO)_3(SPh)]_n\cdot CH_3CN$. By comparison, the tungsten analogue 8 crystallizes as an unsolvated solid. Compound 8 also has very simple and similar infrared spectra in solution and in the solid state which suggests that the same oligomeric unit (probably n = 4) is present in both phases.

Attempts to isolate pure samples of an analogous chromium complex were unsuccessful. As shown in Table I, the acetonitrile solution infrared spectrum of an impure tetraphenylphosphonium salt (or mixture of salts) obtained after cation exchange from the reaction of $Cr(CO)_3PMTA$ with sodium thiophenoxide is complex and does not obviously correspond to any of the anions reported in this paper or other known species such as $M_2(CO)_6(\mu\text{-}XR)_3^{3-}$ (X = OH,[18] OPh (this work)).

Synthesis of $[Et_4N]_3[W_2(CO)_6(OPh)_3]$ (10). In contrast to most of the other reactions of $M(CO)_3PMTA$ or $M(CO)_3(CH_3CN)_3$ with XR$^-$, the reaction of $W(CO)_3(CH_3CN)_3$ with 1 equiv of sodium phenoxide did not result in the expected $[W(CO)_3(OPh)]_n^{n-}$ complex. Instead, the product isolated in 17% yield after cation exchange and several recrystallizations was found by infrared and ^{1}H NMR spectra and elemental analyses to be consistent with the formulation $[Et_4N]_3[W_2(CO)_6(\mu\text{-}OPh)_3]$, 10. The infrared spectrum of **10** shows two bands in the ν(CO) region in about the same positions as those for compound **5**. On this basis, it was initially thought that **10** should be formulated as $[W(CO)_3(OPh)]_n^{n-}$. However, its elemental analyses (see footnote *d* of Table III) and ^{1}H NMR spectrum (Table II)[21] provide strong support for the dinuclear formulation.

The infrared spectrum of **10** is similar to that reported for the previously mentioned $K_3[W_2(CO)_6(\mu\text{-}OH)_3]\cdot 2H_2O$ (ν(CO) 1840, 1700 cm^{-1}). The structure of $W_2(CO)_6(\mu\text{-}OH)_3{}^{3-}$ consists of three doubly bridging hydroxy groups bound to two essentially noninteracting tungsten atoms, each containing three terminal CO groups. It seems likely that compound **10** adopts the same basic structure as the hydroxy derivative. It was noted briefly in the Experimental Section that attempts to isolate species such as $[M(CO)_3OH]_n^{n-}$ or $[M_2(CO)_6(OH)_3]^{3-}$ (M = Cr, Mo, W) from the complex product mixtures obtained in the reactions of OH$_-$ with corresponding M(CO)$_3$PMTA or M(CO)$_3$(CH$_3$CN)$_3$ have been unsuccessful.

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Registry No. 1, 81097-65-6; 2, 81097-67-8; 3, 81097-69-0; 4, 81097-71-4; 5, 81097-73-6; 6, 81097-75-8; 7, 81097-77-0; 8, 81097-79-2; 9, 81097-81-6; 10, 81097-83-8; Cr(CO)$_3$PMTA, 15225-94-2; Mo(CO)$_3$PMTA, 81120-72-1; W(CO)$_3$PMTA, 81097-61-2; Cr(CO)$_6$, 13007-92-6; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0.

Supplementary Material Available: Tables of weighted least-squares planes and the distances of the atoms from their respective planes, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors for the structure of $[Me_4N]_3[W(CO)_3(OEt)]_3$ (19 pages). Ordering information is given on any current masthead page.

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[21] The ratio of the integrated phenyl group hydrogens to the tetraethylammonium cation hydrogens is very close to that expected for a 1:1 ratio of C$_6$H$_5$ to Et$_4$N$^+$.

Structure and Properties of Tricarbonyl(2–5:9,10-η-9-methylenebicyclo[4.2.1]nona-2,4,7-triene)chromium(0). New Chromium–Olefin Stereochemistry

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Tricarbonyl(2–5:9,10-η-9-methylenebicyclo[4.2.1]nona-2,4,7-triene)chromium(0), prepared by the reaction of Cr(CO)$_3$(CH$_3$CN)$_3$ with the tetraolefinic ligand I, crystallizes in space group *C*2/*c* in a unit cell with dimensions a = 25.682 (5) Å, b = 6.850 (2) Å, c = 14.263 (3) Å, β = 115.90 (1)°, and Z = 8. Structural parameters for the molecule, including hydrogen atoms, were refined on F (2370 data in the range $0.043 < \lambda^{-1} \sin\theta < 0.7261$ Å^{-1} having $F_o^2 > 3\sigma(F_o^2)$) to final values for R and R_w of 0.040 and 0.048. Coordination is approximately octahedral with three mutually cis carbonyl ligands and with the butadiene and the semicyclic moieties coordinated: Cr–C$_{CO}$(av) = 1.847 (14, 3) Å; Cr–C$_{but}$(av) 2.367 (11, 3) (outer) and 2.200 (1, 3) Å; Cr–C$_{methylene}$ = 2.339 (2) and 2.386 (3) Å. When given, the first number in parentheses is the estimated standard deviation derived from the scatter of parameters about their mean and the second is the estimated standard deviation of an individual parameter. The C=C vector for the semicyclic olefin is approximately perpendicular to those for the butadiene group—this stereochemistry is unusual, since endo coordination to the bishomobenzene system is also feasible. Stereochemical arguments are presented in favor of the preferential exo approach toward the butadiene group. The unusual ^{13}C NMR high-field coordination shift of the quaternary carbon resonance of the semicyclic olefin (106 ppm compared to that for the free olefin) is attributed to shielding effects.

Introduction

It is often true that the products of chemical reactions fail to conform to the experimenters' predictions—witness the exponentially increasing numbers of crystal structures of compounds which have proved relatively intractable to conventional spectroscopic analysis. This is particularly true for organometallic reactions, where the variable coordination numbers, stereochemistries, and oxidation states of a metal center conspire to give greater scope for predictive disasters and hence to hinder attempts to systematize and understand mechanisms of organometallic reactions.

For example, given a multiolefin molecule, where the number of double bonds which could coordinate exceeds the number of coordination sites available, what stereochemistry may be expected? For the case of coordination of olefins to platinum species, which has long been of interest, considerable insight into the stereochemistry and reactivity of such complexes now exists.[1,2] The same cannot be said for olefin coordination to many other transition-metal species. Here we wish to consider the coordination of the tetraolefin 9-methylenebicyclo[4.2.1]nona-2,4,7-triene I to the well-known trienophilic M(CO)$_3$ (M = Cr, Mo) species.

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