$c = 9.493$ (3) Å; $\beta = 100.50$ (2)°; $\rho_o = 1.79$ (2), $\rho_c = 1.802$ g cm^{-3} with $Z = 4$. A total of 6546 independent nonzero reflections were measured on a Philips PW1100 diffractometer and 4874 reflections with $I > 3\sigma(I)$ were used in subsequent structure solution and least-squares refinement. Final block-diagonal matrix least-squares refinements with anisotropic thermal parameters for all nonhydrogen atoms converged to $R_F = 0.062$ and $R_{wF} = 0.091$.

The structure of **1** consists of discrete complex cations $[Cu^{II}_2 \subset (L)]^{4+}$ (Figure 2), perchlorate anions, and water molecules.

The two copper(II) ions are located *inside*[8] the molecular cavity of the macrotricyclic ligand (L). Each cation is bound to two nitrogens, two sulfurs, and one oxygen atom. The data (distances, angles, and dihedral angles) show that the complex cation has a virtual center of symmetry, a feature which implies an *identical role* for the two copper(II) cations. Their coordination polyhedron is a somewhat distorted tetragonal pyramid in which the metal ion lies ~0.34 Å *out* of the basal N_2S_2 plane[9,10] toward the axial oxygen atom. The four Cu-N and four Cu-S bond distances range from 2.020 (5) to 2.058 (5) and 2.306 (1) to 2.332 (1) Å, respectively. The values of the Cu(1)-O(4) and Cu(2)-O(16) bond lengths are 2.291 (5) and 2.283 (4) Å. The Cu(1)···Cu(2) separation of 5.621 (1) and the O(4)···O(16) distance of 4.211 (6) Å indicate that (i) there is little if any direct interaction between the two copper centers, as shown also by the EPR spectral data[4] ($g_\perp = 2.045$ $g_\parallel = 2.132$ and $A_\parallel = 8$ mK); (ii) there is a *large cavity* between the two copper cations which should allow *insertion* of a diatomic substrate. There is no evidence that such a process occurs; however, when adding KO_2 to $[Cu^{II}_2 \subset (L)]^{4+}$ or dioxygen to $[Cu^{I}_2 \subset (L)]^{2+}$, similar electronic spectra are obtained.[4] Among the possible binding modes of O_2^{n-} ($n = 1, 2$) to two metal centers[11] (μ-dioxygen bridging), the transplanar C_{2h} and nonplanar C_2 modes fit particularly well for the complex cation present in **1** since these modes necessarily impose a Cu···Cu distance varying between 4.0 and 5.2 Å owing to the Cu-O-O and dihedral Cu-O-O-Cu angles. In $[Cu^{II}_2 \subset (L)]^{4+}$ the N_2S_2 planes are almost parallel, the angle between their normals being 1.34°; this feature should lead to a value near 180° for the Cu-O-O-Cu torsion angle. The planar cis C_{2v} bonding mode of O_2 as proposed for hemocyanin[11a] probably necessitates the synthesis of a dissymetric ligand with $R_1 \neq R_2$ (Figure 1b).

References and Notes

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Highly Reduced Organometallics. 3.[1] Tetrasodium Tetracarbonylmetalates(4−) of Chromium, Molybdenum, and Tungsten, $Na_4M(CO)_4$

Sir:

Highly reduced organometallics which have properties consistent with those expected for noncluster binary carbonyl trianions, i.e., $V(CO)_5^{3-}$,[2] $M(CO)_4^{3-}$ (M = Mn and Re),[3] and $M'(CO)_3^{3-}$ (M' = Co, Rh, and Ir),[1] have been recently prepared by reduction of carbonylmetalate monoanions, $M(CO)_x^{1-}$, in liquid ammonia and/or hexamethylphosphoramide (HMPA). We now report on the syntheses and properties of more highly reduced species, tetrasodium tetracarbonylmetalates(4−) of chromium, molybdenum, and tungsten. These are the first examples of noncluster binary metal carbonyl tetraanions[4] and the only compounds presently containing molybdenum and tungsten in a formal −4 oxidation state.[5] A new synthetic approach, which may be of general importance as a route to other families of "superreduced" organometallics, has been used in this synthesis of $Na_4M(CO)_4$: *the reduction of substituted organometallics.*

Reduction of a noncluster metal complex containing both good and poor π-acceptor ligands often causes preferential loss of weaker or non-π acceptors.[6] Trivial examples where this generalization holds include the reduction of metal carbonyl halides.[7] More interesting and less well-understood examples involve reduction of phosphine or cyclopentadienyl substituted metal carbonyls.[8] We find that reduction of diamine substituted group 6 carbonyls, i.e., $(TMEDA)M(CO)_4$,[9] by sodium in liquid ammonia[10] provides essentially quantitative yields of analytically pure $Na_4M(CO)_4$ (**1**)[11] according to the equation

$$(TMEDA)M(CO)_4 + 4Na \rightarrow Na_4M(CO)_4 + TMEDA$$

The presence of the readily displaceable TMEDA ligand, which is not attacked by sodium in liquid ammonia, and the preformed $M(CO)_4$ unit appear to be of crucial importance in this synthesis.[12,13]

Infrared spectra of **1** (Figure 1) show bands at exceedingly low energies for terminal carbonyl groups. These values are almost 200 cm^{-1} lower than those reported for $Na_3M'(CO)_4$ (M' = Mn and Re)[3] which suggests that these insoluble "tetraanions" are most reasonably formulated as $[M(CONa)_4]_x$ where extensive and strong sodium ion–carbonyl oxygen interactions may be responsible for the very low ν(CO) values.[14,15] Differences in the spectra of $Na_4W(CO)_4$ and other $Na_4M(CO)_4$ shown in Figure 1 are not understood; however, they do not appear to be due to carbonyl containing impurities which form on partial oxidation of $Na_4M(CO)_4$. Other preparations of $Na_4Mo(CO)_4$ have provided infrared spectra nearly identical with those of $Na_4W(CO)_4$.

Treatment of slurries of **1** in tetrahydrofuran (THF) with 2 equiv of Ph_3SnCl results in an immediate reaction and formation of new anions which, on the basis of infrared data,

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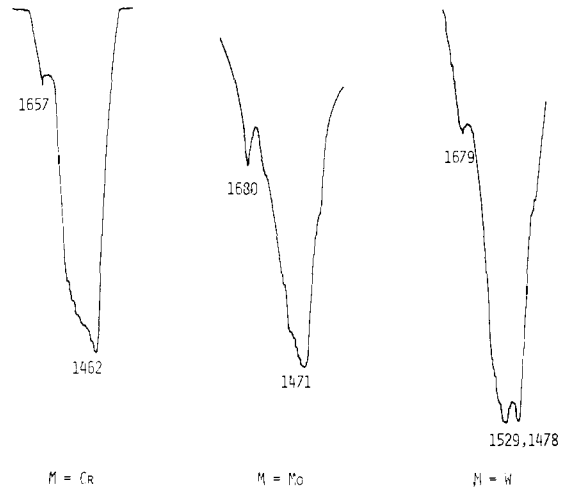

Figure 1. Silicone fluid mull spectra of $Na_4M(CO)_4$ (approximate positions of bands in cm^{-1}).

^1H NMR spectra (see Table I), and elemental analyses, are formulated as *cis*-$(Ph_3Sn)_2M(CO)_4^{2-}$. These may be isolated as moderately air-sensitive and white crystalline $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$ (**2**).[16] From the tungsten reaction a 17–20% yield of pale yellow, air-stable, and crystalline $[Et_4N][(Ph_3Sn)_3W(CO)_4]$ (**3c**), containing a seven-coordinate tungsten, is also obtained.[17] Conversion of **2** to **3** for Cr, Mo, and W is easily effected by treatment of **2** with 1 equiv of Ph_3SnCl in THF.[18] This reaction sequence is depicted by the following scheme:

$$Na_4M(CO)_4 \xrightarrow{Ph_3SnCl} Na_2[(Ph_3Sn)_2M(CO)_4]$$

$$\xrightarrow{Et_4NBr} [Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$$

$$[Et_4N]_2[(Ph_3Sn)_2M(CO)_4] + Ph_3SnCl \xrightleftharpoons{CH_3CN} [Et_4N][(Ph_3Sn)_3M(CO)_4] + Et_4N^+Cl^-$$

The pale yellow and crystalline chromium derivative (**3a**) is particularly unusual since it appears to be the first example of a thermally stable seven-coordinate chromium carbonyl species containing only monodentate ligands.[19] Owing to the unusual nature of **3a**, we have examined its chemistry in some detail and find that one triphenyltin group is easily lost under a variety of conditions, e.g., by reduction with triphenylstannyl lithium or heterolytic cleavage with hexamethylphosphoramide;[20] i.e., eq 1.

$$(Ph_3Sn)_2Cr(CO)_4^{2-} + Ph_6Sn_2 \quad (1)$$

$$(Ph_3Sn)_2Cr(CO)_4^{2-} \quad \begin{matrix} \xrightarrow{Ph_3SnLi\ (THF)} \\ \xrightarrow{HMPA} \end{matrix} \quad Ph_3Sn(HMPA)_n^+ + (Ph_3Sn)_2Cr(CO)_4^{2-}$$

Initial studies on the chemical reactivity patterns of $Na_4M(CO)_4$ show that these "superreduced" species are useful precursors to a variety of new organometallic compounds. Studies to further characterize the reactivity patterns of these new materials, especially in regard to their reactions with organic substrates, are in progress and will be reported in due course.

Acknowledgments. We thank the National Science Foundation (CHE76-13341) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. J.E.E. is grateful to the E. I. du Pont de Nemours and Co. for a Young Faculty Award and to Professor Ken Klabunde for helpful suggestions in the preparation of this manuscript.

Table I. Infrared and ^1H NMR Data for $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$ (**2**) and $[Et_4N][(Ph_3Sn)_3M(CO)_4]$ (**3**)

Anion (M)	ν(C≡O), cm^{-1} [a]	NMR, δ [b,c]
2a (Cr)	1918 (m), 1822 (vs), 1782 (s)	6.91–7.05 (m, 9 H), meta and para 7.43–7.54 (m, 6 H), ortho
2b (Mo)	1948 (m), 1844 (vs), 1791 (s)	6.89–7.05 (m, 9 H), meta and para 7.42–7.58 (m, 6 H), ortho
2c (W)	1947 (m), 1838 (vs), 1790 (s)	6.90–7.07 (m, 9 H), meta and para 7.38–7.56 (m, 6 H), ortho
3a (Cr)	1956 (m), 1904 (s), 1864 (vs)	6.96–7.66 (m, 45 H)[d]
3b (Mo)	1999 (m), 1897 (vs), 1832 (w)	7.02–7.67 (m, 45 H)[d]
3c (W)	1997 (m), 1894 (vs), 1828 (w)	7.02–7.68 (m, 45 H)[d]

[a] In acetonitrile. [b] At 60 MHz recorded in acetonitrile-d_3. [c] Spectra of Et_4N^+ were nearly independent of anion: ~1.1 (t of t, 12 H, $-CH_3$), ~3.0 (q, 8 H, $-CH_2-$). [d] Unresolved multiplet of aromatic protons of Ph_3Sn groups.

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(7) Examples: $Br_2Fe(CO)_4 + (Na/Hg) \rightarrow Fe(CO)_4^{2-} + 2Br^-$ (W. Hieber and J. Muschi, *Chem. Ber.*, **98**, 3931 (1965)); $ClCr(CO)_5^- + (Na–HMPA) \rightarrow Cr(CO)_5^{2-} + Cl^-$ (J. E. Ellis and G. P. Hagen, *J. Am. Chem. Soc.*, **96**, 7825 (1974)). More examples appear in J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).
(8) Examples: $(Ph_3P)_2V(CO)_4 + (Na/Hg) \rightarrow V(CO)_5PPh_3^- + PPh_3 + ?$ (R. P. M. Werner, *Z. Naturforsch., B*, **16**, 477 (1961)); $Ph_3PCr(CO)_5 + (Na/Hg) \rightarrow Cr(CO)_5^{2-} + PPh_3$ (J. E. Ellis and G. L. Rochfort, unpublished results); $C_5H_5Co(CO)PPh_3 + (Na/Hg, CO) \rightarrow Co(CO)_4^- + C_5H_5^-$ + other products (N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1781 (1977)).
(9) TMEDA = *N,N,N',N'*-tetramethylethylenediamine.
(10) In a typical preparation, ammonia (40 mL), free of oxygen and moisture, was condensed into a vessel containing $(TMEDA)Cr(CO)_4$ (0.56 g, 2.0 mmol) and sodium metal (0.185 g, 8.0 mg-atoms) cooled to −50 °C. Within 30 min of stirring (glass-covered magnetic stir bar) a finely divided pale yellow solid began to precipitate from the blue solution. After 3 h at −50 °C, the blue color was completely discharged providing a pyrophoric solid which was isolated by evaporation of the liquid ammonia, followed by drying at room temperature under high vacuum. Without further purification a quantitative yield of homogeneous pale yellow powder was obtained. This material satisfactorily analyzed for $Na_4Cr(CO)_4$. Anal. Calcd for $C_4CrNa_4O_4$: C, 18.77; H, 0.0; Cr, 20.31; Na, 35.92. Found (A. Bernhardt): C, 18.53 H. 0.24; Cr, 20.42; Na, 35.56.
(11) Similar procedures provided high yields of analytically pure orange yellow $Na_4Mo(CO)_4$ (Anal. Calcd for $C_4MoNa_4O_4$: C, 16.02; H, 0.0; Mo, 31.99; Na, 30.66. Found: C, 15.75, H, 0.08; Mo, 32.23; Na, 31.03.) and orange $Na_4W(CO)_4$ (Anal. Calcd for $C_4Na_4O_4W$: C, 12.39; H, 0.0; Na, 23.71; W, 47.40. Found: C, 12.48; H, 0.12; Na, 23.47; W, 47.25.)
(12) Numerous other approaches to $Na_4M(CO)_4$ have been tried with little or no success. For example, reduction of norbornadiene-$Cr(CO)_4$ by sodium in liquid ammonia provided a deep brown solid which was shown to contain

only small amounts of $Na_4Cr(CO)_4$ by its low conversion (2–3% yield) to **2a** (see Table I). The reduction of coordinated or uncoordinated norbornadiene by sodium in liquid ammonia may be responsible for this unfavorable results.[13a] Also, $Na_2M(CO)_5$[13b] (M = Cr or W) is not converted to $Na_4M(CO)_4$ either because it is stable to reduction (for M = Cr or W in HMPA or for M = Cr in NH_3) or decomposes (for M = W in NH_3) to an uncharacterized brown powder which contains no $Na_4W(CO)_4$ but rapidly converts Ph_3SnCl to hexaphenylditin. Reduction of (TMEDA)$M(CO)_4$ by sodium metal in HMPA at room temperature provides $Na_2M(CO)_5$ as the only carbonyl containing products. Reductions using other electropositive metals will be described in a subsequent paper.

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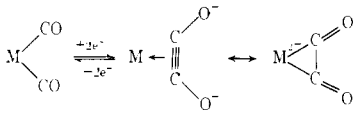
(14) Reductive coupling of coordinated carbon monoxide[15] to yield a π-acetylenediolate dianion complex (see below) could also explain the abnormally low ν(CO) values observed in these species. An analogous π-bisaminoacetylene complex has recently been prepared from the reductive coupling of coordinated isocyanides (C. T. Lam, P. Corfield, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 617 (1977)). We have no chemical evidence for reductive coupling in our compounds; i.e., all of the reactions of the "tetraanions" give rise to derivatives containing terminal carbonyls. However, as depicted, it is possible that reductive coupling of CO can be reversed on addition of an electrophile to yield the observed derivatives.



(15) Free carbon monoxide reacts with sodium in liquid ammonia to form disodium acetylenediolate and other products (V. M. Sinclair, R. A. Davies and J. L. Drummond, *Chem. Soc. Spec. Publ.*, **No. 22**, 260 (1967)).

(16) Yields are moderate to low (~30%, **2a**; ~1%, **2b**; ~50%, **2c**). Hexaphenylditin also forms in these reactions. Substantially better yields (~60–70%) of **2** are obtained from the reaction of (TMEDA)$M(CO)_4$ (M = Cr, Mo, and W) with 2 equiv of Ph_3SnLi in THF followed by metathesis with Et_4NBr in ethanol.

(17) Anal. Calcd for $C_{56}H_{70}CrN_2O_4Sn_2$ (**2a**): C, 59.81; H, 6.27; N, 2.49; Sn, 21.11. Found: C, 59.78; H, 6.17; N, 2.43; Sn, 21.17. Anal. Calcd for $C_{56}H_{70}MoN_2O_4Sn_2$ (**2b**): C, 57.56; H, 6.04; N, 2.40. Found: C, 57.47; H, 6.13; N, 2.28. Anal. Calcd for $C_{56}H_{70}N_2O_4Sn_2W$ (**2c**): C, 53.54; H, 5.62; N, 2.23. Found: C, 53.20; H, 5.58; N, 2.68. The total yield of derivatives (**2c** and **3c**) from $Na_4W(CO)_4$ is ~70%.

(18) Yields of analytically pure samples in these reactions are only moderate (~35% for **3a–c**) owing in part to incomplete conversion of **2** to **3**. However, **3** is easily separated from **2** by virtue of its moderate solubility in THF, in which **2** is insoluble. Anal. Calcd for $C_{66}H_{65}CrNO_4Sn_3$ (**3a**): C, 58.97; H, 4.87; N, 1.04; Sn, 26.49. Found: C, 59.25; H, 5.05; N, 0.85; Sn, 26.32. Anal. Calcd for $C_{66}H_{65}MoNO_4Sn_3$ (**3b**): C, 57.10; H, 4.72; N, 1.01; Sn, 25.65. Found: C, 56.89; H, 4.36; N, 1.77; Sn, 25.34. Anal. Calcd for $C_{66}H_{65}NO_4SN_3W$ (**3c**): C, 53.70; H, 4.44; N, 0.95; Sn, 24.12. Found: C, 53.37; H, 4.18; N, 1.25; Sn, 24.39.

(19) Numerous examples of seven-coordinate molybdenum and tungsten carbonyl complexes exist (e.g., $M(CO)_4I_3^-$) for which there are no chromium analogues (see M. W. Anker, R. Colton, and I. B. Tomkins, *Rev. Pure Appl. Chem.*, **18**, 23 (1968)). However, seven-coordinate chromium carbonyl complexes with polydentate ligands are known (e.g., $[Cr(CO)_2(Diars)_2Br]Br$, J. Lewis, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 3009 (1964)).

(20) Triphenylstannyllithium reacts with $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (**3a**) to provide essentially quantitative yields of $(Ph_3Sn)_2Cr(CO)_4^{2-}$ and hexaphenylditin. Infrared studies show that HMPA causes complete heterolytic cleavage of one Sn–Cr bobd in **3a** to yield $(Ph_3Sn)_2Cr(CO)_4^{2-}$. Analogous heterolytic cleavages of tin–metal bonds by polar solvents have been known for several years (e.g., see A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **36**, 113 (1972)); however, generally the degree of solvation of the tin cation is unknown.

(21) NSF Undergraduate Research Participant, summer 1977.

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MNDO Parameters for Third Period Elements

Sir:

The MINDO/3 method[1] suffers from well-known problems[1] and, in the case of compounds containing heteroatoms and its use for third period elements (Si. P, S, Cl), is further restricted by the availability of parameters for them only for limited combinations of them with other elements[2,3] and without inclusion of 3d AOs. Furthermore, recent work[4] has uncovered a discrepancy between the published[2] results for compounds of phosphorus and those calculated using the published[1] parameters which are also included in our MINDO/3 computer program, and similar, though smaller discrepancies have now been found for silicon and sulfur.[5] Apparently an earlier set of parameters was inadvertently inserted in our final computer program and hence in the published list.[1] The results for chlorine[3] are, however, correct.[5]

Table I. MNDO Parameters for Third Row Elements

Optimized	Si	P	S	Cl
U_{ss}, eV	−40.568292	−56.143360	−75.239152	−100.227166
U_{pp}, eV	−28.089187	−42.851080	−57.832013	−77.378667
ζ_s, au	1.435306	2.108720	2.613591	3.784645
ζ_p, au	1.435306	1.785810	2.034393	2.036263
β_s, β_p, ev	−4.256218	−6.791600	−11.142231	−14.262320
α, Å^{-1}	2.1961078	2.4152800	2.4916445	2.542201

Table II. MNDO Parameters for Third Row Elements

Derived	Si	P	S	Cl
H_f^A, kcal mol^{-1}	108.39	75.57	66.40	28.99
E_{el}^A, eV	−90.53496	−152.95996	−235.45636	−353.137667
D_1, Å	0.744999	0.536030	0.435589	0.263889
D_2, Å	0.616918	0.495834	0.435248	0.434848
ρ_0, Å	0.733128	0.622778	0.558953	0.478996
ρ_1, Å	0.768732	0.541911	0.449254	0.328218
ρ_2, Å	0.664346	0.531356	0.468321	0.435983

In the meantime we have parameterized the MNDO method[6] for these elements (Si, P, S, Cl) and the results are, as expected, better than the published[2] MINDO/3 ones. MNDO has the further advantage of using only atomic parameters; so calculations can be carried out for any combinations of these elements with those already parameterized (H,[7] Be[8], B,[9] C,[7] N,[7] O,[7] F[10]). As yet, 3d AOs have not been included in MNDO; so the parameters refer only to compounds of these elements in their characteristic valence states (Si^{IV}, P^{III}, S^{II}, Cl^{I}). The calculated heats of formation for compounds of, e.g., P^V and S^{VI} are too positive by very large amounts.

This work will be repeated in full in due course but unexpected circumstances have delayed its publication. In view of the unexpected problems with MINDO/3 and the very wide demand for some procedure applicable in particular to compounds of P, we are therefore reporting the parameters for Si, P, S, and Cl here (Tables I and II). Computer programs for MNDO are available from Q.C.P.E., both ours and one written in a more general version of FORTRAN by Dr. W. Thiel.

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