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Stuttgart University. Data were not corrected for extinction or absorption, $\mu = 1.65$ cm^{-1}. Tables IV and V of atomic positional and thermal parameters are available as supplementary material. Bond lengths and angles are summarized in Table I, and dihedral angles between planes, in Table II.

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Supplementary Material Available: Listings of atomic coordinates and temperature factors for hydrogen and non-hydrogen atoms (Tables IV and V) (2 pages). Ordering information is given on any current masthead page.

Reactions of Trisodium Tetracarbonylmetalates(3−) of Manganese and Rhenium with Brønsted Acids and Other Electrophiles. Synthesis of $H_2M(CO)_4^-$ (M = Mn and Re), $(CH_3)_2Re(CO)_4^-$, the First Dialkyl Derivative of a Carbonylmetalate Trianion, and Related Anionic Species[1]

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Abstract: Treatment of hexamethylphosphoramide (HMPA) solutions of the trisodium tetracarbonylmetalates(3−) of manganese and rhenium with excess liquid ammonia causes precipitation of very thermally stable materials (dec ≥300 °C) that are isolated in high yields (85–95%) and represent the first available pure samples of unsolvated $Na_3[M(CO)_4]$. Infrared and ^1H NMR spectral studies of the protonation of $Na_3[M(CO)_4]$ in HMPA show initial formation of the new monohydrides, $HM(CO)_4^{2-}$, which are then converted quantitatively to the dihydrides, $H_2M(CO)_4^-$. The new manganese dihydride, which is isoelectronic with the first known carbonyl hydride, $H_2Fe(CO)_4$, and the previously established rhenium complex are isolated in high yields (75–80%) as the pure salts, $[Ph_4As][cis\text{-}H_2M(CO)_4]$. The monohydride dianions, $HM(CO)_4^{2-}$, also react with Ph_3SnCl to provide $cis\text{-}H(Ph_3Sn)M(CO)_4^-$, which can be isolated as the Et_4N^+ salt for rhenium. The initial successful alkylation reactions of carbonylmetalates(3−) are also reported. Treatment of $Na_3[Re(CO)_4]$ with methyl *p*-toluenesulfonate (MeOTs) in HMPA first provides $MeRe(CO)_4^{2-}$ (identified by IR), which can be protonated or further methylated to give $cis\text{-}H(Me)Re(CO)_4^-$ or $cis\text{-}(Me)_2Re(CO)_4^-$, both of which are isolated in good yields (70–80%) as Ph_4E^+ (E = P, As) salts. These represent the first isolated alkyl derivatives of metal carbonyl trianions. IR, ^1H, and ^{13}C NMR spectra also confirm that $Na_3[Re(CO)_4]$ reacts with 1,4-butaneditosylate to provide solutions of the somewhat thermally unstable rhenacyclopentane $\overline{CH_2CH_2CH_2CH_2Re}(CO)_4^-$, the initial example of an anionic 18-electron metallacycloalkane. Infrared, ^1H, and ^{13}C NMR spectral data have been obtained for many of these compounds and are compared with those of analogous previously known iron and osmium species.

Before 1975, numerous binary and substituted carbonylmetalate mono- and dianions were well established and shown to be quite useful reagents in chemical synthesis.[2] Such materials were known for all d-block transition elements except for the very early (Sc, Y, La, Ti, Zr, Hf) and very late (Cu, Ag, Au) triads.[3] Although carbonylmetalate trianions were unknown, several formal derivatives of these materials did exist as well as electronically equivalent (or isolobal) main group analogues such as P^{3-} and As^{3-}.[4] For these reasons, the reduction of $Mn(CO)_5^-$ was examined with the hope of preparing $Mn(CO)_4^{3-}$, the manganese analogue of $Fe(CO)_4^{2-}$, the first characterized carbonylmetalate.[2]

In the unusually effective reducing medium of sodium hexamethylphosphoramide (HMPA), $Mn(CO)_5^-$ underwent facile reduction to form a golden yellow to yellow brown solution. On the basis of derivative chemistry and infrared spectra, the major soluble component was formulated as "the superreduced species" $Na_3[Mn(CO)_4]$.[5] Related studies resulted in the syntheses of carbonyl trianions of V, Nb, Ta, Re, Co, Rh, and Ir.[6] While good evidence for the existence of the trianions of the group 5 metals has been obtained recently,[7] until now, the case for the mononuclear tetracarbonylmetalates(3−) of Mn and Re has been less satisfactory. Our inability to obtain pure samples of these trianion salts and the inherent uncertainty in distinguishing between anions

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and their conjugate Brønsted acids on the basis of derivative chemistry[8] prompted further examination of these materials.

In this study, we have developed a facile method for the isolation of the first relatively pure samples of unsolvated trisodium tetracarbonylmetalates(3−) of manganese and rhenium. Studies of the reactions of $Na_3[M(CO)_4]$ with proton sources conclusively demonstrate the nonhydridic nature of the trisodium salts and thereby provide further evidence for the existence in solution of $M(CO)_4^{3-}$ units, which undoubtedly interact strongly with sodium cations. Particularly significant developments of this study include the isolation in high yields of relatively stable salts containing $H_2Mn(CO)_4^-$, $H_2Re(CO)_4^-$, $H(CH_3)Re(CO)_4^-$, and $(CH_3)_2Re(CO)_4^-$. Dihydridotetracarbonylmanganate(1−) is a new substance and an anionic analogue of $H_2Fe(CO)_4$, the first known carbonyl hydride.[9] While the corresponding rhenium hydride was previously known,[10] our synthesis represents a dramatic improvement in both yield and facility. Finally, we are especially pleased to report on the first syntheses of alkylmetal compounds from carbonyl trianions. These include the previously known $H(CH_3)Re(CO)_4^-$,[11] and the new dialkylrhenate species, $(CH_3)_2Re(CO)_4^-$ and $\overline{CH_2CH_2CH_2CH_2Re}(CO)_4^-$, where the latter is the only presently known anionic metallocycloalkane. As we have gained experience on how best to synthesize, handle, and employ these highly reduced carbonyl anions, it is becoming quite clear that they have a bright future as useful and perhaps unique precursors to new classes of organometallic and inorganic materials.

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. A detailed description of the laboratory apparatus and general techniques used in this study has been published recently.[12] Ammonia was dried with sodium metal and transferred in vacuo directly into the reaction vessel or added via cannula. Hexamethylphosphoramide (HMPA) was twice distilled in vacuo, first from calcium hydride and subsequently from a small piece of sodium metal. (**Caution**: *HMPA should be handled with extreme care as it is a potential carcinogen.*) Sodium sand was obtained by a literature procedure.[13a] Sodium pentacarbonylmanganate(1−) was prepared in 95% yield as a colorless and thermally stable (dec ca. 122 °C) unsolvated solid, which provided satisfactory elemental analyses (C, H) by a 2-h reduction of $Mn_2(CO)_{10}$ with excess 0.8% Na-Hg in THF followed by filtration and removal of solvent in vacuo at room temperature. With exceptions noted below, all other reagents were used as received from commercial sources. Solutions of $Na_3[M(CO)_4]$ for infrared spectra in HMPA were very difficult to obtain free of oxidation products and were prepared in a Vacuum Atmosphere Corporation drybox and transferred into CaF_2 cells that had been previously purged with dilute blue solutions of Na in HMPA to remove absorbed moisture, oxygen, and other potential oxidants. Proton and ^{13}C NMR spectra were obtained on a NT-300 spectrometer. Melting and/or decomposition points are uncorrected and obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus.

Unsolvated $Na_3[Mn(CO)_4]$ (1). In a typical synthesis, 20 mL of HMPA was added to a mixture of $Na[Mn(CO)_5]$ (1.13 g, 5.2 mmol) and sodium sand (0.38 g, 17 mmol) in a flask equipped with a glass covered magnetic stir bar. A golden yellow solution formed after this mixture was stirred under a dynamic vacuum (ca. 0.1 Torr) for 12 h at room temperature. Infrared solution spectra of similar reactions established that $Na_3[Mn(CO)_4]$ was the sole or principal metal carbonyl species present at this stage. After readmitting nitrogen (or argon), the reaction mixture was cooled to −78 °C and 200 mL of cold (−78 °C) anhydrous, oxygen free liquid ammonia was added by cannula. A pale yellow solid formed after the resulting solution was stirred at −78 °C for 1 h. The product was isolated by a low-temperature filtration (cf. Figure 13 of ref 12), thoroughly washed with liquid ammonia (4 × 50 mL), and then dried in vacuo at room temperature. By this procedure 1.20 g (98% yield) of tan, powdery product was obtained, which provided satisfactory analyses for unsolvated $Na_3[Mn(CO)_4]$.

Anal. Calcd for $Na_3[Mn(CO)_4]$ (%): C, 20.36; H, 0.00; Na, 29.23. Found: C, 20.10; H, 0.05; Na, 29.15.

Compound **1** is of remarkable thermal stability for metal carbonyls (darkens irreversibly above 320 °C) and is insoluble in all inert solvents, including HMPA. Freshly prepared solutions of $Na_3[Mn(CO)_4]$ in HMPA show IR bands at 1792 (w), 1665 (vs, broad) cm^{-1} in the carbonyl stretching frequency region. Corresponding Nujol mull IR spectra of **1** exhibit a very weak sharp shoulder at about 1790 cm^{-1} and an extremely broad intense absorption centered at about 1600 cm^{-1}.

Unsolvated $Na_3[Re(CO)_4]$ (2). Essentially the same procedure for the preparation of compound **1** was employed in this synthesis except $Re_2(CO)_{10}$ (1.00 g, 1.53 mmol) and sodium sand (0.28 g, 12.2 mmol) were used. From the resulting dark brown-yellow solution, 0.99 g (88% yield) of pale yellow brown powder was obtained which provided satisfactory elemental analyses for unsolvated $Na_3[Re(CO)_4]$.

Anal. Calcd for $Na_3[Re(CO)_4]$ (%): C, 13.08; H, 0.00; Na, 18.78. Found: C, 12.91; H, 0.12; Na, 18.75 (washed only with NH_3); C, 12.87; H, 0.10; Na 18.65 (washed with NH_3 and THF).

Compound **2**, like **1**, is extremely stable thermally (darkens above 340 °C) and after isolation from HMPA does not tend to dissolve in this or other unreactive solvents. IR (HMPA), ν(CO): 1805 (w), 1690 (vs, br) cm^{-1}. (Nujol): 1790 (vw), 1600 (s, very br) cm^{-1}. A more facile alternative route to a less pure version of **2**, involving the $NaC_{10}H_8$ reduction of $Re_2(CO)_{10}$, is shown in connection with the synthesis of compound **12**, vide infra.

$[Ph_4As][H_2Mn(CO)_4]$ (3). The reaction of $Na[Mn(CO)_5]$ (0.50 g, 2.3 mmol) with sodium sand (0.16 g, 6.9 mmol) in HMPA resulted in a yellow solution of $Na_3[Mn(CO)_4]$ as described above. Ethanol (0.62 g, 13.5 mmol) was added slowly by syringe to produce an orange-brown solution. This solution was cooled to 5 °C and transferred by cannula into a stirred solution of $[Ph_4As]Cl$ (3.00 g, 6.87 mmol) in 100 mL of water at 0 °C. Immediately a creamy-white precipitate formed. After being stirred for 1 h the precipitate was collected on a cooled medium porosity frit (0 °C) and washed extensively with oxygen free ice-cold water (5 × 20 mL). The white precipitate was dried in vacuo for 12 h to yield 0.95 g of product (75% yield). The substance was found to darken between 95 and 100 °C and melt (with decomposition) at 104 °C. Compound **3** slowly decomposed in the solid state at 0 °C. While freshly prepared solutions of **3** are colorless to pale yellow, they quickly darken at room temperature under argon or nitrogen.

Anal. Calcd for $C_{28}H_{22}AsMnO_4$ (%): C, 60.89; H, 4.01; As, 13.56. Found: C, 60.71; H, 4.08; As, 13.70.

IR (Nujol), ν(CO): 2004 (m), 1909 (s), 1887 (vs), 1873 (vs) cm^{-1}. See Tables I and II for other data.

$[Ph_4As][H_2Re(CO)_4]$ (4). Dirhenium decacarbonyl (1.55 g, 2.37 mmol) was reduced by sodium metal (0.44 g, 19.0 mmol) in HMPA (20 mL) as described above. Oxygen free water (0.25 mL, 14.2 mmol) was slowly added via syringe while the solution was stirred. The solution was cooled to 5 °C and transferred to a stirred solution of $[Ph_4As]Cl$ (4.14 g, 9.48 mmol) in 100 mL of water at 0 °C. Immediately a creamy-white precipitate was formed. After being stirred for 1 h the precipitate was collected on a cooled medium porosity frit (0 °C) and washed extensively with ice-cold water (5 × 20 mL). The precipitate was dried in vacuo to yield 2.59 g (80% yield). The substance was found to darken between 105 and 110 °C and to melt (with decomposition) at 111 °C. Unlike the manganese analogue, compound **4** appears to survive indefinitely under nitrogen at room temperature.

Anal. Calcd for $C_{28}H_{22}AsO_4Re$ (%): C, 49.20; H, 3.24; As, 10.96. Found: C, 49.01; H, 3.29; As, 10.70.

IR (Nujol), ν(CO): 2024 (m), 1930 (vs), 1905 (vs), 1881 (vs) cm^{-1}. See Tables I and II for other data.

$[Ph_4P][H_2Re(CO)_4]$ (5). To a dark brown yellow solution of $Na_3[Re(CO)_4]$ (1.22 mmol) in 15 mL of HMPA (prepared as usual) at 0 °C, oxygen-free water (0.10 mL, 5.6 mmol) was added dropwise by syringe. The solution rapidly changed to a clear red-brown color. It was stirred for 15 min at 0 °C and then added by cannula to a rapidly stirred ice cold solution of $[Ph_4P]Cl$ (0.919 g, 2.45 mmol) in 175 mL of water. A cream precipitate formed almost immediately and after 1 h was separated by filtration at 0 °C. After being washed with ice-cold water (5 × 20 mL), the solid was dried in vacuo to yield 0.667 g (85%) of ivory product which provided satisfactory analyses for compound **5** (mp 142 °C with dec).

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Table I. Infrared Data for New Carbonylmanganates and Carbonylrhenates and Selected Iron and Osmium Analogues[a]

compd	solvent	IR, ν(CO), cm^{-1}
$Na_3[Mn(CO)_4]$	hmpa	1792 (w), 1665 (vs, br)
$Na_3[Re(CO)_4]$	hmpa	1805 (w), 1690 (vs, br)
$Na_2[Fe(CO)_4]$[b]	hmpa	1771 (w), 1729 (vs)
$Na_2[Os(CO)_4]$[b]	hmpa	1780 (w), 1738 (vs)
$Na_2[HMn(CO)_4]$	hmpa	1865 (w), 1745 (sh), 1720 (s)
$Na_2[HRe(CO)_4]$	hmpa	1880 (w), 1762 (sh), 1735 (s)
$[PPN][HFe(CO)_4]$[c]	thf	1998 (w), 1905 (sh), 1876 (s)
$[PPN][HOs(CO)_4]$[d]	thf	2008 (w), 1945 (w-m), 1881 (s)
$[Ph_4As][cis\text{-}H_2Mn(CO)_4]$	thf	2005 (w), 1905 (s), 1879 (m)
$[Ph_4As][cis\text{-}H_2Re(CO)_4]$	thf	2024 (w), 1919 (s), 1892 (m)
$[H_2Fe(CO)_4]$[e]	hexane	2121 (w), 2053 (m), 2042 (s), 2010 (m)
$[H_2Os(CO)_4]$[f]	methylcyclohexane	2141 (w), 2066 (m), 2054 (s), 2047 (vs)
$Na_2[Ph_3SnMn(CO)_4]$	hmpa	1880 (m), 1756 (s)
$Na_2[Ph_3SnRe(CO)_4]$	hmpa	1900 (m), 1780 (sh), 1765 (s)
$[Et_4N][Ph_3SnFe(CO)_4]$[g]	thf	1992 (m), 1905 (m), 1883 (s), 1869 (sh)
$[Et_4N][cis\text{-}H(Ph_3Sn)Mn(CO)_4]$	hmpa	1995 (m), 1906 (vs), 1890 (s)
$[Et_4N][cis\text{-}H(Ph_3Sn)Re(CO)_4]$	Nujol	2025 (m), 1938 (sh), 1907 (vs), 1899 (s)
$[Et_4N][(Ph_3Sn)_2Re(CO)_4]$	thf	2032 (m), 1968 (m), 1945 (sh), 1920 (vs)
$(Ph_3Sn)_3Re(CO)_4$	heptane	2108 (w), 2004 (s)
$cis\text{-}H(Ph_3Ge)Fe(CO)_4$[h]	hexane	2097 (m), 2036 (m), 2027 (s), 2022 (s)
$cis\text{-}H(Ph_3Sn)Os(CO)_4$[i]	CH_2Cl_2	2120, 2055, 2030
$Na_2[CH_3Re(CO)_4]$	hmpa	1870 (w), 1770 (sh), 1740 (s)
$[TMGH][CH_3Os(CO)_4]$[j]	CH_3CN	1995 (w), 1908 (m), 1880 (s)
$[Ph_4P][cis\text{-}H(CH_3)Re(CO)_4]$	hmpa	2020 (w), 1913 (vs), 1870 (s)
$cis\text{-}H(CH_3)Os(CO)_4$[k]	thf	2135 (w), 2063 (m), 2042 (vs), 2028 (s)
$[Ph_4P][cis\text{-}(CH_3)_2Re(CO)_4]$	thf	2024 (w), 1923 (vs), 1906 (s), 1855 (s)
$cis\text{-}(CH_3)_2Os(CO)_4$[k]	methylcyclohexane	2130 (w), 2044 (vs), 2012 (s), 1979 (vw)
$[Ph_4P][c\text{-}(CH_2)_4Re(CO)_4]$	thf	2020 (w), 1913 (vs), 1903 (sh), 1853 (s)
$c\text{-}(CH_2)_4Ru(CO)_4$[l]	hexane	2119 (w), 2049 (s), 2040 (vs), 2023 (s)

[a] All values are for solution spectra at room temperature except the Nujol mull spectrum for $[Et_4N][cis\text{-}H(Ph_3Sn)Re(CO)_4]$. ν(M–H) values for the manganese and rhenium hydrides have not been identified and may overlap those shown above. [b] Reference 24. [c] $PPN^+ = (Ph_3P)_2N^+$, ref. 25, 26. [d] Reference 28. [e] Reference 30. [f] Reference 31. [g] Reference 39a. The Ph_4As^+ salt has also been reported, ref 39b. [h] Reference 40a. Attempts to prepare the Ph_3Sn analogue were reported to be unsuccessful. [i] Reference 40a. $Ph_3SnOs(CO)_4^-$ is apparently unknown. [j] $TMGH^+$ = tetramethylguanadinium cation, ref 44. [k] Reference 43. [l] Reference 55.

Table II. ^1H NMR Spectra of New Carbonylmanganates, Carbonylrhenates, and Related Species[a]

compd	solvent	^1H NMR, δ, ppm
$Na_2[HMn(CO)_4]$	hmpa	–7.8 (s)
$Na_2[HRe(CO)_4]$	hmpa	–9.4 (s)
$[PPN][HFe(CO)_4]$[b]	thf-d_8	–8.7 (s)
$[PPN][HOs(CO)_4]$[c]	acetone-d_6	–10.2 (s)
$[Ph_4As][H_2Mn(CO)_4]$	dmso-d_6	–8.7 (s)
$[Ph_4As][H_2Re(CO)_4]$	dmso-d_6	–7.1 (s)
$H_2Fe(CO)_4$[d]	neat	–10.8 (s)
$H_2Os(CO)_4$[e]	benzene-d_6	–8.6 (s)
$[Et_4N][cis\text{-}H(Ph_3Sn)Mn(CO)_4]$	hmpa	–8.5 (t, 1 H, $J(^{117,119}Sn\text{–}H) = 137$ Hz)
$[Et_4N][cis\text{-}H(Ph_3Sn)Re(CO)_4]$	acetone-d_6	–7.0 ("quint", 1 H, $J(^{117}Sn\text{–}H) = 103$ Hz, $J(^{119}Sn\text{–}H) = 107$ Hz)
$[Ph_4P][cis\text{-}H(CH_3)Re(CO)_4]$	dmso-d_6	–0.72 (d, 3 H, $J = 3$ Hz), –5.8 (q, 1 H, $J = 3$ Hz)
$cis\text{-}H(CH_3)Os(CO)_4$[f]	benzene-d_6	0.12 (d, $J = 2.4$ Hz), –7.8 (q, $J = 2.4$ Hz)
$[Ph_4P][cis\text{-}(CH_3)_2Re(CO)_4]$	dmso-d_6	–0.71 (s)
$cis\text{-}(CH_3)_2Os(CO)_4$[f]	benzene-d_6	0.15 (s)
$[Ph_4P][c\text{-}(CH_2)_4Re(CO)_4]$	dmso-d_6	1.52 (m, 4 H), 0.89 (m, 4 H)
$c\text{-}(CH_2)_4Re(CO)_2Cp$[g]	benzene-d_6	2.51 (m, 2 H), 2.38 (m, 2 H), 1.82 (m, 4 H)
$c\text{-}(CH_2)_4Ru(CO)_4$[h]	$CDCl_3$ (–40 °C)	1.58 (s)

[a] NMR spectra recorded at room temperature unless otherwise indicated. Chemical shifts in δ (ppm) are referenced to Me_4Si. Cation resonances and Ph_3Sn resonances are not shown, but integrations were acceptable. hmpa = hexamethylphosphoramide, dmso = dimethyl sulfoxide. [b] References 25 and 26. [c] Reference 27. [d] Reference 29. [e] Reference 31. [f] Reference 43. [g] Reference 56. [h] Reference 55.

Anal. Calcd for $C_{28}H_{22}O_4PRe$ (%): C, 52.58; H, 3.47. Found: C, 52.33; H, 3.47.

Selected spectral data: IR (Nujol), ν(CO): 2024 (m), 1934 (s), 1910 (vs), 1890 (vs) cm^{-1}; IR (THF), ν(CO): 2020 (vw), 1918 (s), 1890 (m) cm^{-1}; IR (DMSO), ν(CO): 1923 (s), 1893 (m) cm^{-1}. ^1H NMR ($(CD_3)_2SO$): δ 7.7–8.0 (m, Ph_4P^+, 20 H), –7.1 (s, 2 H) ppm.

$[(Ph_3P)_2N][H_2Re(CO)_4]$ (6). An HMPA solution of $Na[H_2Re(CO)_4]$ was prepared by exactly the same procedure as in the synthesis of compound **5**. The sodium salt was added to a rapidly stirred, ice-cold solution of slightly less than 1 equiv of $[(Ph_3P)_2N]Cl$ (0.528 g, 0.920 mmol) in 175 mL of ice-cold, oxygen-free water. The metathesis appeared to be complete within 1 h. The pale yellow precipitate was filtered at 0 °C through a jacketed, medium-porosity, low-temperature fritted filter, washed extensively with water (5 × 20 mL), and dried overnight under vacuum. A yield of 0.862 g (81%) was obtained. (mp 140–141 °C dec).

Anal. Calcd for $C_{40}H_{32}O_4NP_2Re$ (%): C, 57.28; H, 3.85. Found: C, 56.95; H, 4.05.

Selected spectral data: IR (Nujol), ν(CO): 2024 (w), 1950 (m), 1918 (vs), 1892 (s) cm^{-1}. ^1H NMR ($(CD_3)_2SO$): δ 7.7–7.5 (m, $(Ph_3P)_2N^+$, 30 H), –7.1 (s, 2 H) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ 198.0, 196.6 (s, CO).

$[Ph_4As][(CH_3)_2Re(CO)_4]$ (7). Methyl tosylate (2.28 g, 12.2 mmol) in HMPA (10 mL at 5 °C) was added slowly via cannula to a solution of $Na_3[Re(CO)_4]$ (3.06 mmol) in 15 mL of chilled (5 °C) HMPA. After being stirred for 20 min at room temperature the solution was cooled to 0 °C. The cold solution was transferred via cannula into a stirred solution of $[Ph_4As]Cl$ (4.0 g, 9.2 mmol) in 100 mL of water at 0 °C. Immediate precipitation of a creamy-white solid was observed. After being stirred for 1 h, the solid was collected on a frit and washed extensively with water (5 × 20 mL). This creamy-white solid was dried under vacuum to furnish 1.9 g (91% yield) of powdery product that provided satisfactory elemental analyses for the proposed formulation. The ivory solid darkened irreversibly from 145–148 °C.

Anal. Calcd for $C_{30}H_{26}AsO_4Re$ (%): C, 50.63; H, 3.68; As, 10.53.

Table III. $^{13}C\{^1H\}$ NMR Spectral Data for Selected Rhenium and Group 8 Carbonyl Compounds[a]

compd	solvent	CO (ax)	CO (eq)	alkyl carbons
$[Ph_4P][cis\text{-}H_2Re(CO)_4]$	dmso-d_6	197.9	196.7	
cis-$H_2Os(CO)_4$[b]	toluene-d_8	173.5	171.6	
$[Ph_4P][cis\text{-}H(CH_3)Re(CO)_4]$	dmso-d_6	199.8	197.3, 194.4	−42.4
$CH_3Re(CO)_5$[c]	$CDCl_3$	185.2	181.3	−38.0
$[Ph_4P][cis\text{-}(CH_3)_2Re(CO)_4]$	dmso-d_6	201.1	195.5	−27.4
cis-$(CH_3)_2Os(CO)_4$[b]	toluene-d_8	177.7	170.6	−7.6
$[Ph_4P][c\text{-}(CH_2)_4Re(CO)_4]$	dmso-d_6	203.3	197.9	0.5 C(α), 38.4 C(β)
c-$(CH_2)_4Fe(CO)_4$[d]	$CDCl_3$ (<0 °C?)	212.2	205.1	22.1 C(α), 36.6 C(β)
c-$(CH_2)_4Ru(CO)_4$[e]	$CDCl_3$ (−40 °C)	197.3	189.7	11.6 C(α), 36.9 C(β)
c-$(CH_2)_4Re(CO)_2Cp$[f]	$CDCl_3$	209.3		6.7 C(α), 36.6 C(β)
$Na[Re(CO)_5]$[g]	dmso-d_6	217.7		
$Os(CO)_5$[h]	$CDCl_3$ (−40 °C)	182.6		

[a] NMR spectra recorded at room temperature unless otherwise indicated. Chemical shifts in δ (ppm) are referenced to Me_4Si. Ph_4P = tetraphenylphosphonium; resonances of cation not shown. All values for anions are from this work except $Re(CO)_5^-$ (vide infra). CO(eq) groups are in the equatorial plane which contains the metal and alkyl or hydride groups. For $CH_3Re(CO)_5$, the CO trans to the methyl group is defined as CO(eq). [b] Reference 57. [c] Reference 58. [d] Reference 59. [e] Reference 55. [f] Reference 56. [g] Reference 60. [h] Reference 61.

Found: C, 50.76; H, 3.76; As, 10.75.

Selected spectral data: IR (Nujol), ν(CO): 2026 (w), 1910 (vs br), 1842 (vs) cm^{-1}. IR (THF), ν(CO): 2022 (w), 1924 (vs), 1906 (s), 1852 (s) cm^{-1}. ^1H NMR ($(CD_3)_2SO$) δ 7.7–8.2 (m, Ph_4Ar^+, 20 H), −0.67 (s, 6 H).

$[Ph_4P][(CH_3)_2Re(CO)_4]$ (8). A freshly prepared solution of methyl tosylate (0.916 g, 4.92 mmol) in 10 mL of HMPA was cooled to 0 °C and added dropwise via cannula to a cold (0 °C) solution of $Na_3[Re(CO)_4]$ (prepared from $Re_2(CO)_{10}$ (0.400 g, 0.613 mmol) in 15 mL of HMPA as described previously.) After being stirred for 20 min at 0 °C, the reaction mixture was added to a rapidly stirred aqueous solution (175 mL) of $[Ph_4P]Cl$ (1.00 g, 2.67 mmol). After the mixture was stirred for an additional hour, the light peach precipitate was collected in a medium porosity filtration vessel (held at 0 °C), washed with cold, oxygen-free water (5 × 20 mL), and dried over vacuum overnight. By this procedure, 0.69 g (84%) of reasonably pure pale orange solid was obtained (mp 144 °C dec).

Anal. Calcd for $C_{30}H_{26}O_4PRe$ (%): C, 53.97; H, 3.92. Found: C, 53.72; H, 4.01.

Selected spectral data: IR (Nujol), ν(CO): 2026 (w), 1924 (s), 1903 (vs), 1853 (s) cm^{-1}. IR (HMPA), ν(CO): 2016 (m), 1918 (vs), 1908 (s), 1858 (s) cm^{-1}. ^1H NMR ($(CD_3)_2SO$) δ 7.7–8.0 (m, Ph_4P^+, 20 H), −0.71 (s, CH_3, 6 H).

$[Ph_4As][H(CH_3)Re(CO)_4]$ (9). To a cold solution at 5 °C of $Na_3[Re(CO)_4]$ (1.22 mmol) in 10 mL of HMPA was added by cannula a solution of ethanol (0.056 g, 1.22 mmol) in 5 mL of cold HMPA (5 °C) with efficient stirring. After 5 min of stirring, a cold solution (5 °C) of methyl tosylate (0.227 g, 1.22 mmol) in 5 mL of HMPA was added via cannula to the stirred solution of $Na_2[HRe(CO)_4]$ (vide infra) at 0 °C. After an additional 20 min of stirring at 0 °C the solution was added to a cold (0 °C) stirred aqueous solution (60 mL) of $[Ph_4As]Cl$ (1.60 g, 3.66 mmol). An immediate formation of a peach colored precipitate occurred. After the solution was stirred at 5 °C for 1 h, the solid was collected at 0 °C on a medium porosity frit, washed extensively with ice cold water (5 × 20 mL), and dried in vacuo. A 70% yield (0.60 g) of peach colored solid which provided satisfactory elemental analyses for compound **9** was thereby obtained. This material was not very thermally stable at room temperature. It darkened above 60 °C and melted with decomposition at 67 °C.

Anal. Calcd for $C_{29}H_{24}AsO_4Re$ (%): C, 49.93; H, 3.47; As, 10.74. Found: C, 49.72; H, 3.29; As, 10.65.

Selected spectral data: IR (Nujol), ν(CO): 2026 (m), 1932 (s), 1905 (vs), 1826 (vs) cm^{-1}. IR (HMPA), ν(CO): 2016 (w), 1917 (vs), 1866 (s) cm^{-1}. ^1H NMR ($(CD_3)_2SO$), δ 7.7–8.2 (m, Ph_4As^+, 20 H), −0.72 (d, 3 H, J = 3 Hz), −5.86 (unresolved quartet, 1 H).

$[Ph_4P][H(CH_3)Re(CO)_4]$ (10). By essentially the same procedure and quantities of reactants used for the synthesis of compound **9**, a light peach precipitate of $[Ph_4P][H(CH_3)Re(CO)_4]$ was obtained in 78% yield (0.625 g) which spectroscopically showed the presence of small amounts of $[Ph_4P][H_2Re(CO)_4]$. It appeared to be more thermally stable but less pure than compound **9** and had a mp of 114–115 °C with decomposition.

Anal. Calcd for $C_{29}H_{24}O_4PRe$ (%): C, 53.30; H, 3.70. Found: C, 52.53; H, 3.70.

Selected spectral data: IR (Nujol) ν(CO): 2024 (m), 1930 (s), 1908 (vs), 1866 (s) cm^{-1}. ^1H NMR ($(CD_3)_2SO$) δ 7.7–8.0 (m, Ph_4P^+, 20 H), −0.72 (d, 3 H, J = 3 Hz), −5.8 (q, 1 H, J = 3 Hz).

$[Ph_4As][H(Ph_3Sn)Re(CO)_4]$ (11). One equivalent of Ph_3SnCl (0.61 g, 1.58 mmol) in 10 mL of HMPA was cooled to 0 °C and added slowly by syringe to a stirred solution of $Na_3[Re(CO)_4]$ (1.58 mmol) in 20 mL of HMPA, also at 0 °C. (In a separate experiment the IR spectrum of this solution was taken and showed ν(CO) bands at 1900 (m), 1780 (sh), 1765 (s) cm^{-1}, which were attributed to $Na_2[(Ph_3Sn)Re(CO)_4]$. Attempts to isolate this salt and $[Et_4N]_2[(Ph_3Sn)Re(CO)_4]$ as pure substances were unsuccessful.) After being stirred for 20 min at room temperature, the solution was cooled to 0 °C and then added to a solution of $[Ph_4As]Cl$ (2.10 g, 4.8 mmol) in 100 mL of water. Immediate precipitation of a creamy-white solid occurred. After the solution was stirred for 1 h, the product was collected, washed extensively with water (5 × 20 mL), and dried in vacuo. By this procedure 1.34 g (82%) of rather thermally unstable product was obtained (mp ca. 50 °C dec), which nevertheless provided quite satisfactory elemental analyses. See Tables I and II for spectral data.

Anal. Calcd for $C_{46}H_{36}AsO_4ReSn$ (%): C, 53.37; H, 3.76; Sn, 11.47. Found: C, 53.34; H, 3.56; Sn, 11.35.

$[Ph_4P][\overline{CH_2CH_2CH_2CH_2Re}(CO)_4]$ (12). (a) Facile Synthesis of HMPA-Free $Na_3[Re(CO)_4]$. Naphthalene (1.18 g, 9.20 mmol) and Na (0.176 g, 7.66 mmol) were stirred for 3 h at room temperature in 15 mL of THF to prepare the $NaC_{10}H_8$. This solution was then added via cannula to $Re_2(CO)_{10}$ (0.50 g, 0.77 mmol) in 5 mL of THF with stirring. A finely divided brown precipitate of $Na_3[Re(CO)_4]$ formed almost immediately. After an hour of stirring at room temperature no carbonylrhenium species were present in solution and the reduction was judged to be complete and assumed to provide approximately 1.5 mmol of $Na_3[Re(CO)_4]$. (In other essentially identical syntheses of $Na_3[Re(CO)_4]$, IR spectra of THF suspensions of the product in the ν(CO) region showed the bands 1808 (w), 1673 (vs, br) cm^{-1}, along with a sharp spike at about 1600 cm^{-1} due to free naphthalene. This spectrum was quite similar to those of HMPA solutions or Nujol mulls of bonafide $Na_3[Re(CO)_4]$.)

(b) Conversion of $Na_3[Re(CO)_4]$ to 12. A solution of 1,4-butaneditosylate[13b] (1.22 g, 3.06 mmol) in 5 mL of THF was added dropwise to the above THF slurry of $Na_3[Re(CO)_4]$ at room temperature. The hetereogeneous reaction mixture was stirred for 12 h at room temperature and then filtered through a medium porosity glass filtration vessel. To the filtrate was added 1 equiv of $[(Ph_4P)]Cl$ (0.57 g, 1.5 mmol) and stirred was resumed for 12 h. After filtration and removal of solvent in vacuo a yellow-orange oil was obtained. Trituration of this material with ethyl ether and pentane provided a slightly sticky pale orange solid that in our hands could not be purified further. Satisfactory elemental analyses for the solid were not obtained, due to its thermal instability at room temperature, but the spectroscopic properties of the product were entirely consistent with its formulation as compound **12**. See Tables I, II, and III.

Attempts to prepare **12** by treatment of 1,4-butaneditosylate with HMPA solutions containing an equimolar amount of $Na_3[Re(CO)_4]$ followed by cation exchange and precipitation with water provided impure samples of **12**, which had the same spectroscopic properties as those obtained by the HMPA free route. Prior to treatment with $[Ph_4P]Cl$, HMPA solutions of $Na[\overline{CH_2CH_2CH_2CH_2Re}(CO)_4]$ had the following spectroscopic properties: IR, ν(CO): 2006 (m), 1913 (vs), 1903 (sh), 1853 (vs) cm^{-1}. ^1H NMR: δ 1.49 (s, br, 4 H), 0.88 (s, br, 4 H) ppm. $^{13}C\{^1H\}$ NMR: δ 204.2 (s, CO (ax)), 198.2 (s, CO(eq)), 39.2 (s, C(β)), 0.89 (s, C(α)) ppm, where C(α) refers to the ring carbons bound to rhenium.

Results and Discussion

Syntheses, Isolation, and Characterization of $Na_3[Mn(CO)_4]$ and $Na_3[Re(CO)_4]$. Prior to the present work, only impure samples of $Na_3[M(CO)_4]$ were available. Since these substances were the first examples of "superreduced" carbonyl anions reported, we felt that it was important to provide more substantive data in support of their formulations. This reexamination of the tetracarbonylmetalates(3–) also provided a good opportunity to further examine some of their basic chemical properties that still remain poorly explored.[5]

A variety of strong reducing agents including solutions of alkali metals in liquid ammonia, sodium solubilized by crown ethers or cryptands in THF, and alkali metal naphthalenides in THF reduce $M_2(CO)_{10}$ and/or $M(CO)_5^-$ (M = Mn and Re) to the respective $M(CO)_4^{3-}$; however, $Re(CO)_5^-$ has often been observed to be more resistant to reduction than the manganese analogue. For example, sodium benzophenone slowly converted $Na[Mn(CO)_5]$ to $Na_3[Mn(CO)_4]$ in refluxing dioxane, but under these conditions $Na[Re(CO)_5]$ appeared to be unreactive. This Na-Ph_2CO route is entirely analogous to that developed by the Collman group for the conversion of $Fe(CO)_5$ to $Na_2[Fe(CO)_4]\cdot(dioxane)_{1.5}$ (eq 1 and 2).[14] Although the $Na_3[Mn(CO)_4]$ obtained from this

$$Na[Mn(CO)_5] \xrightarrow[\text{dioxane}\atop\Delta]{\text{Na-Ph}_2\text{CO}} Na_3[Mn(CO)_4] + \ldots \qquad (1)$$

$$Fe(CO)_5 \xrightarrow[\text{dioxane}\atop\Delta]{\text{Na-Ph}_2\text{CO}} Na_2[Fe(CO)_4]\cdot(dioxane)_{1.5} \qquad (2)$$

method was generally dark brown and obviously impure, one reaction provided an attractive homogeneous light tan solid. Its Nujol mull infrared spectrum in the ν(CO) region was nearly superimposable on that of pure $Na_3[Mn(CO)_4]$ (vide infra), but attempts to obtain satisfactory analyses for any composition of the type $Na_3[Mn(CO)_4].(dioxane)_x$ were unsuccessful. Contrary to our previous report,[5] we have found both $Mn(CO)_5^-$ and $Re(CO)_5^-$ to be reduced by Na-NH_3, or more rapidly by K-NH_3, to provide insoluble and impure (especially for Re) tan to brown solids containing the trianions. Similar insoluble materials were obtained by the rapid reduction of $M_2(CO)_{10}$ by deep blue solutions of sodium dicyclohexyl-18-crown-6 in THF, which very likely contain Na^-,[15] an extremely potent reducing agent. Unfortunately, however, these materials generally react with various electrophiles to provide lower yields of products, which are usually less pure and consequently more difficult to crystallize than those obtained from corresponding reactions with solutions of $Na_3[M(CO)_4]$ in HMPA. Sodium naphthalenide in THF has also been shown to reduce $Na[M(CO)_5]$ (M = Mn, Re).[6c] Initially it was believed that *solutions* of $Na_3[M(CO)_4]$ were obtained, but a more careful examination established that only very fine suspensions of insoluble and impure brown trisodium salts had formed. For example, treatment of $Re_2(CO)_{10}$ with 10 equiv of $NaC_{10}H_8$[3c] in THF provided a complete conversion to finely divided brown insoluble $Na_3[Re(CO)_4]$ within an hour at room temperature.[16] However, our attempts to find practical routes to relatively pure salts of $M(CO)_4^{3-}$, which do not involve the use of the toxic and high-boiling HMPA, have not been entirely successful to date.

Indeed, the Na-HMPA route consistently provided the cleanest products and has been the only synthesis to provide *solutions* of $Na_3[M(CO)_4]$. We have learned that it is important to use solutions rather than slurries of trianion salts to minimize the formation of side products during the reactions of these materials with electrophiles. Until recently, product separation from the viscous and high-boiling HMPA has always been a problem (and remains so in some cases). For example, addition of excess THF to solutions of $Na_3[M(CO)_4]$ in HMPA invariably resulted in the formation of sticky solids which contained HMPA and did not analyze satisfactorily.[5] But recently, we were very pleased to discover that addition of these HMPA solutions to excess liquid ammonia resulted in practically quantitative precipitation of tan to pale yellow brown solids, which provided satisfactory elemental analyses for unsolvated $Na_3[M(CO)_4]$ (M = Mn, Re). All impurities remained in the HMPA-NH_3 filtrate (eq 3 and 4). Unlike

$$Na[Mn(CO)_5] + 3Na \xrightarrow{\text{i,ii}} \underset{95\text{–}100\%}{Na_3[Mn(CO)_4]\downarrow} + \ldots \qquad (3)$$

$$\tfrac{1}{2}Re_2(CO)_{10} + 4Na \xrightarrow{\text{i,ii}} \underset{85\text{–}90\%}{Na_3[Re(CO)_4]\downarrow} + \ldots \qquad (4)$$

(i) HMPA, 12 h, 20 °C, (ii) Excess liquid NH_3, –78 °C

the related $Na_3[M'(CO)_5]$, where M' = V, Nb, and Ta, which undergo thermolysis below 0 °C,[6] these materials possess remarkable thermal stabilities for metal carbonyls and briefly survive without melting at temperatures as high as 300 °C. By comparison, $K_2[Fe(CO)_4]$, another metal carbonyl salt of high thermal stability, has been reported to melt at 270–273 °C with decomposition.[17a] The related $K[Co(CO)_4]$ melts at about 203 °C with decomposition.[17c]

As mentioned previously,[5] $Mn_2(CO)_{10}$ should not be used directly in this reaction, as it undergoes slow disproportionation in this medium to form $[Mn(HMPA)_x][Mn(CO)_5]_2$, while $Re_2(CO)_{10}$ shows no tendency to react with HMPA at room temperature. The slightly lower yields of $Na_3[Re(CO)_4]$ compared to those of $Na_3[Mn(CO)_4]$ probably arise from the fact that $Re_2(CO)_{10}$ does not cleanly reduce to $Re(CO)_5^-$ in HMPA or other solvents.[17b] It should also be noted that more than 2 equiv of sodium are required for the complete reduction of $M(CO)_5^-$, undoubtedly because some of the liberated CO also undergoes reduction by Na-HMPA. While we have firm infrared spectral evidence for the formation of disodium acetylenediolate, $Na_2C_2O_2$,[6b,18] during the reduction of $Na[Mn(CO)_5]$ by sodium in liquid ammonia, the nature of possible CO reduction products in HMPA remains unknown.

This new procedure for the isolation of $Na_3[M(CO)_4]$ from HMPA is straightforward and promises to be of general importance for the purification and/or isolation of other highly reactive anions from HMPA, provided they form reasonably insoluble salts in and do not react with liquid ammonia.[19] Evidently ammonia interacts strongly enough with HMPA, perhaps by hydrogen bonding, to effectively cause full dissociation of $Na(HMPA)_x^+$ and subsequent precipitation of unsolvated or weakly ammoniated $Na_3[M(CO)_4]$. The only other solvents we have found to be effective in this regard include water, methanol, or ethanol, which are incompatible with the trianions and many of their derivatives. It is interesting to note that solutions of $Na_3[M(CO)_4]$ in HMPA are stable for at least a week at room temperature under strict anaerobic conditions and do not deposit any solid during this time. By comparison, after unsolvated $Na_3[Mn(CO)_4]$ or $Na_3[Re(CO)_4]$ precipitate from the HMPA-NH_3 mixture, they show no tendency to redissolve—either in HMPA (at room temperature) or in any other unreactive solvent.[20] On the basis of the similarity of HMPA solution and Nujol mull infrared spectra of $Na_3[M(CO)_4]$ (see Figure 1 for M = Mn), it seems likely that the nature of the anionic units in solution and in the solid state are not dramatically different.

When these studies were initiated about 15 years ago,[22] it was obvious that solutions of sodium in HMPA were qualitatively more effective for many organometallic reductions than, for example,

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[14] Finke, R. G.; Sorrell, T. N. *Org. Synth.* **1988**, *Collect. Vol. 6*, 807.

[15] (a) Lacoste, J.; Schue, F. *J. Organomet. Chem.* **1982**, *231*, 279. (b) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 329. (c) Pyper, N. C.; Edwards, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 78.

[16] Although $Na_3[Re(CO)_4]$ prepared with excess $Na[C_{10}H_8]$ is impure, we have found that these HMPA free suspensions can be useful in reactions where removal of HMPA is very difficult. See, for example, the preparation of compound **12** in the Experimental Section.

[17] (a) Gladysz, J. A.; Tam, W. *J. Org. Chem.* **1978**, *43*, 2279. (b) Boag, N. M.; Kaesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, pp 162–167 and references cited therein. (c) Warnock, G. F. P., unpublished research.

[18] Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 2111.

[19] For example, unsolvated and analytically pure $Na_3[Ir(CO)_3]$ has been prepared recently by this method. Warnock, G. F. P.; Ellis, J. E. To be submitted.

[20] The possibility that $Na_3[M(CO)_4]$ might dissolve in HMPA at higher temperatures has not been explored. Also nothing is presently known about the thermal stability of HMPA solutions of $Na_3[M(CO)_4]$ at elevated temperatures.

sodium amalgam, sodium sand in THF, sodium in liquid ammonia or sodium naphthalenide, but only recently has it been established that sodium dissolves in HMPA to provide appreciable amounts of Na^-.[21] The presence of this potent reducing agent in Na-HMPA may well explain the unusually effective reducing ability of this medium. In retrospect, these initial studies represented some of the first investigations of the reactions of the sodide (or natride) ion with organometallics![22]

Protonations of $M(CO)_4^{3-}$ in HMPA. Synthesis and Spectral Characterizations of $HMn(CO)_4^{2-}$ and $HRe(CO)_4^{2-}$. Our recent studies on the pentacarbonylmetalates(3−) of V, Nb, and Ta and their conjugate acids, $HM(CO)_5^{2-}$,[7] suggested that a similar examination of the trianions of manganese and rhenium could provide valuable information on the nature of these species. Proton NMR spectra of approximately 0.1 M HMPA solutions of the freshly prepared trianions at room temperature often showed *very weak* sharp singlets at δ −7.8 and −9.4 ppm for manganese and rhenium, respectively. These experiments suggested, but did not prove, that most of the manganese and rhenium species in solution were nonhydridic in nature. However, addition of 1 equiv of ethanol to these solutions caused IR absorptions in the ν(CO) region attributed to the trianions to entirely disappear and new bands at higher energies to appear (Table I). Also, the aforementioned very weak singlets in the ^1H NMR spectra of these solutions grew dramatically on addition of the ethanol. Although the monoprotonated products have not been isolated as pure substances, their ^1H NMR and IR spectra are consistent with the presence of mononuclear dianions of C_{3v} symmetry of the general formula $HM(CO)_4^{2-}$.[23] Spectral data for these materials and the isoelectronic species $HFe(CO)_4^-$ and $HOs(CO)_4^-$ are collected in Tables I and II and provide good confirmation for our formulations. Also, the downfield ^1H NMR chemical shifts exhibited by $HMn(CO)_4^{2-}$ compared to $HFe(CO)_4^-$ or $HRe(CO)_4^{2-}$ compared to $HOs(CO)_4^-$ (Table II) are qualitatively analogous to similar trends previously established for $HV(CO)_5^{2-}$ (δ −4.8 ppm)[7] vs $HCr(CO)_5^-$ (δ −6.7 ppm)[33] or $HTa(CO)_5^{2-}$ (δ −2.2 ppm)[7] vs $HW(CO)_5^-$ (δ −4.1 ppm).[33]

Prior to the deliberate addition of ethanol, water, or other Brønsted acids to freshly prepared solutions of $M(CO)_4^{3-}$ in HMPA, which were blue in color due to the presence of a slight excess of sodium metal, no IR bands due to the respective conjugate acids, $HM(CO)_4^{2-}$, were observed. We believe this observation is the best evidence that the "superreduced" species in solution are almost exclusively unprotonated $Na_3[M(CO)_4]$. In an earlier paper it was correctly predicted that the most intense ν(CO) band of the then unknown $HMn(CO)_4^{2-}$ would occur at about the same position as the corresponding absorption of $Fe(CO)_4^{2-}$ (i.e., 1729 cm^{-1} in HMPA).[5b,24] This extrapolation was based on the useful generalization that the very intense E mode vibration of $HM(CO)_4^z$ (M = Co or Fe) occurs at practically the same energy as the single infrared active ν(CO) band of $M(CO)_4^z$ (M = Ni or Co) for $Z = 0$ or -1, respectively.[32] It is important to point out, however, that this "rule" may be violated if the anionic carbonyls are involved in extensive ion pairing with cations.[24]

Synthesis, Isolation, and Properties of *cis*-$H_2Mn(CO)_4^-$ and *cis*-$H_2Re(CO)_4^-$. Perhaps the most persuasive chemical evidence for the existence of the monohydrides of manganese and rhenium is their high yield conversion to corresponding dihydrides, $H_2M(CO)_4^-$, which can be isolated as relatively stable crystalline solids. Treatment of solutions of the trianions in HMPA with 1.6 equiv of ethanol provided spectra which showed monohydrides as well as new singlets at δ −8.6 and −7.2 ppm due to the dihydrides of manganese and rhenium, respectively. Two equivalents of ethanol or water caused complete conversion of $M(CO)_4^{3-}$ to the corresponding $H_2M(CO)_4^-$. These processes are represented by eq 5 below.[34]

$$M(CO)_4^{3-} \xrightarrow[\text{HMPA}]{\text{EtOH}} HM(CO)_4^{2-} \xrightarrow[\text{HMPA}]{\text{EtOH}} H_2M(CO)_4^- \qquad (5)$$

$$(M = Mn, Re)$$

Addition of the resulting solutions to ice-cold aqueous tetraphenylarsonium chloride caused rapid and nearly quantitative precipitation of colorless to tan solids. These were collected on a frit at 0 °C, washed with cold water, and dried in vacuo at room temperature to provide 70–80% yield of products (eq 6). Satisfactory elemental analyses for the compositions $[Ph_4As][H_2M(CO)_4]$ (M = Mn, Re) were obtained without further purification.

$$M(CO)_4^{3-} + 2H_2O \xrightarrow[0\ ^\circ C]{\text{HMPA}} \xrightarrow[\substack{Ph_4AsCl \\ 0\ ^\circ C}]{\text{aqueous}} \underset{(70\text{–}80\%)}{[Ph_4As][H_2M(CO)_4]\downarrow} \qquad (6)$$

$$(M = Mn, Re)$$

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(21) Edwards, P. P.; Guy, S. H.; Holton, D. M.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1981**, 1185.

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

(23) Direct spectroscopic evidence for the composition of the dianions should be available from corresponding NMR spectral studies of the 99% ^{13}C-labeled species. This study will be reported on in the near future.

(24) (a) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. Unpublished research, 1975. These spectra were obtained for HMPA solutions of commercially available $Na_2[Fe(CO)_4](dioxane)_{1.5}$ or $Na_2[Os(CO)_4]$. The osmium salt was prepared either by the standard procedure involving the reduction of $Os_3(CO)_{12}$ in $Na-NH_3$ (see: Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955) or more readily (and cleanly) by the direct reduction of $Os_3(CO)_{12}$ in Na-HMPA. The weak bands at higher energies are due to the dianions (and not impurities) and probably arise via a small degree of ion pairing between Na^+ and $[M(CO)_4]^{2-}$ in HMPA. Interestingly, the very broad intense band at about 1780 cm^{-1} observed for solutions of $Na_2[Fe(CO)_4]$ in THF (first reported: Edgell, W. F.; Yang, M. T.; Bayer, R.; Koizumi *J. Am. Chem. Soc.* **1965**, *87*, 3080) qualitatively resembles that of $Na_3[Mn(CO)_4]$ in HMPA, suggesting that the latter is strongly ion paired in this very polar medium. (b) An excellent review of ion pairing effects on transition-metal carbonylates has been published recently: Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

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(33) (a) Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961. (b) Gaus, P. L.; Kao, S. C.; Darensbourg, M. Y.; Arndt, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4752 and references therein.

(34) No attempts have been made to determine the pK_a values of these hydrides or whether these protonation reactions are reversible. However, it is anticipated that the group 7 hydrides will prove to be substantially less acidic then their group 8 analogues (Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257 and references cited).

(35) (a) Ciani, G.; D'Alfonso; Romiti, R.; Sironi, A.; Freni, M.; *J. Organomet. Chem.* **1983**, *244*, C27. (b) Ciani, G.; D'Alfonso; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *157*, 199.

(36) Another rhenium hydride, $HRe_2(CO)_9^-$, has also been reported to have a hydride resonance at −7.1 ppm (ref 37). However, the $^{13}C\{^1H\}$ NMR spectra of the latter substance (δ 201.1, broad singlet at room temperature in THF-d_8 and a complex five-band pattern at −70 °C) and $H_2Re(CO)_4^-$ (δ 198.0 (s, CO) and 196.7 (s, CO) ppm at room temperature in DMSO-d_6) establish that these substances are entirely different.

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(41) (a) L'Eplattenier, F. *Inorg. Chem.* **1969**, *8*, 965. (b) L'Eplattenier, F. *Chimia* **1969**, *23*, 144.

(42) George, W. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972.

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While we presently have no quantitative data on the pK_b's of $Na_3[Mn(CO)_4]$ and $Na_3[Re(CO)_4]$ in HMPA, they are clearly quite basic substances. Relatively weakly acidic liquid ammonia and HMPA show no tendency to protonate the trianions, but many organic substances have been observed to function as effective Brønsted acids. For example, 4 equiv of dry methyl acetate (pK_a ca. 25) reacted with $Na_3[Re(CO)_4]$ in HMPA to provide high yields (quantitative by IR) of $H_2Re(CO)_4^-$, which was isolated in 85% yield as the Ph_4As^+ salt. Presumably, the dihydride formed by the reaction

$$2CH_3C(O)OCH_3 + Re(CO)_4^{3-} \xrightarrow{HMPA} H_2Re(CO)_4^- + 2CH_2{=}C(O^-)OCH_3 \quad (7)$$

This reaction was initially carried out to determine whether methyl acetate would methylate $Re(CO)_4^{3-}$, as methyl tosylate does quite effectively (vide infra), but ^1H NMR spectra of the Ph_4As^+ salt showed no evidence for the presence of $H(CH_3)Re(CO)_4^-$ or $(CH_3)_2Re(CO)_4^-$ (vide infra). Since $Re(CO)_4^{3-}$ is quantitatively converted to $H_2Re(CO)_4^-$ by methyl acetate, it follows that the dihydridorhenate must have a p$K_a \geq 25$ in HMPA. By comparison, $H_2Os(CO)_4$ has been reported to have a pK_1 of about 21 in acetonitrile.[44]

The manganese dihydride $H_2Mn(CO)_4^-$ is a new substance. While it is substantially more thermally stable than the long-known, isoelectronic, and neutral $H_2Fe(CO)_4$,[9] solid $[Ph_4As][H_2Mn(CO)_4]$ does suffer considerable darkening after about a week at room temperature or after several months at 0 °C. Its solutions are also fairly unstable under nitrogen or argon at room temperature, although no difficulties were encountered in obtaining clean IR and ^1H NMR spectra of freshly prepared solutions under ambient conditions. Attempts to isolate $H_2Mn(CO)_4^-$ with tetraethylammonium cation were unsuccessful, but the possible use of other cations in the stabilization of this interesting substance has not been examined.

Dihydridotetracarbonylrhenate(1−) has been obtained previously in low yields (ca. 10%) as a tetraethylammonium salt from the reaction of $Re_2(CO)_{10}$ with refluxing methanolic KOH, followed by metathesis.[10] Ciani and co-workers indicated that the isolation of pure samples of $[Et_4N][H_2Re(CO)_4]$ from this reaction was a difficult endeavor due to the presence of other carbonylrhenates of similar solubilities. For these reasons, our high yield (quantitative by IR or NMR) and relatively facile procedure should help to make this previously rather inaccessible but useful substance[10,35] available for further study. It should be noted that we have found Ciani's salt, $[Et_4N][H_2Re(CO)_4]$, to be substantially less stable in solution and in the solid state than the salts described in this paper (of which the PPN^+ salt is the most difficult to obtain pure). Indeed, our attempts to isolate relatively pure samples of the tetraethylammonium salt from $Na[H_2Re(CO)_4]$ in HMPA after metathesis and aqueous workup have not been successful. One problem may be the ease with which $H_2Re(CO)_4^-$ undergoes further protonation in water as the Et_4N^+ salt. In this context, the conversion of $H_2Re(CO)_4^-$ to a possible trihydride, $H_3Re(CO)_4$, is a very interesting problem and presently under study.

Nujol mull and tetrahydrofuran solution infrared spectra of the tetraphenylarsonium salts of $H_2Mn(CO)_4^-$ and $H_2Re(CO)_4^-$ are shown in Figures 2 and 3 are indicate that both anions possess the same basic cis-octahedral geometry. X-ray analysis previously established *cis*-$H_2Re(CO)_4^-$ units to be present in $[Et_4N][H_2Re(CO)_4]$.[10] Spectroscopic properties for the anion in Ciani's salt and our materials are in excellent agreement with each other and leave no doubt that the same anionic units are present. In Tables I and II the IR and ^1H NMR spectral properties of $H_2Mn(CO)_4^-$, $H_2Re(CO)_4^-$, and group 8 analogues are compared and show the same basic trends.[36,37] Curiously, while the proton resonance position of $H_2Re(CO)_4^-$ is downfield of that for $H_2Mn(CO)_4^-$, the corresponding resonance for $HRe(CO)_4^{2-}$ is substantially upfield of that for the dianion, $HMn(CO)_4^{2-}$. These differences seem surprising, but the same qualitative trends have also been observed for the analogous pairs of iron and osmium hydrides (see Table II). In Table III, the $^{13}C\{^1H\}$ spectra of *cis*-$H_2Re(CO)_4^-$ and *cis*-$H_2Os(CO)_4$ are summarized and show no surprising features.

Figure 1. Mineral oil mull infrared spectrum of unsolvated $Na_3[Mn(CO)_4]$ in the $\nu(CO)$ region. Position of bands: 1790 (w), 1600 (vs, br) cm^{-1}. The daggers show bands due to mineral oil. A polystyrene reference band at 1602 cm^{-1} is indicated below the most intense carbonyl absorption.

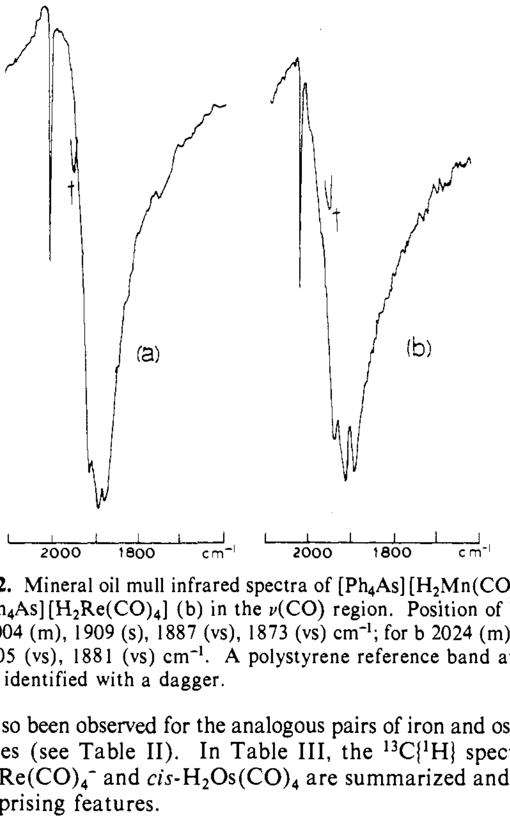

Figure 2. Mineral oil mull infrared spectra of $[Ph_4As][H_2Mn(CO)_4]$ (a) and $[Ph_4As][H_2Re(CO)_4]$ (b) in the $\nu(CO)$ region. Position of bands: for a 2004 (m), 1909 (s), 1887 (vs), 1873 (vs) cm^{-1}; for b 2024 (m), 1930 (s), 1905 (vs), 1881 (vs) cm^{-1}. A polystyrene reference band at 1944 cm^{-1} is identified with a dagger.

Characterization of $H(R)M(CO)_4^-$ (M = Mn, Re; R = $SnPh_3$, CH_3) and Related Substances. Many other electrophiles also react with the monohydrides $HM(CO)_4^{2-}$. Two that we report on now are chlorotriphenylstannane and methyl *p*-toluenesulfonate, CH_3OTs (for Re only), which proceed according to eq 8 and 9.

$$HM(CO)_4^{2-} + Ph_3SnCl \rightarrow H(Ph_3Sn)M(CO)_4^- + Cl^- \quad (8)$$

$$HRe(CO)_4^{2-} + CH_3OTs \rightarrow H(CH_3)Re(CO)_4^- + OTs^- \quad (9)$$

In the case of the triphenylstannyl derivatives, identical products are also available from $Ph_3SnM(CO)_4^{2-}$ (M = Mn, Re), which, like the corresponding monohydrides $HM(CO)_4^{2-}$, have not been isolated as pure substances but are reasonably well characterized in terms of their infrared spectra and reaction chemistry (eq 10).

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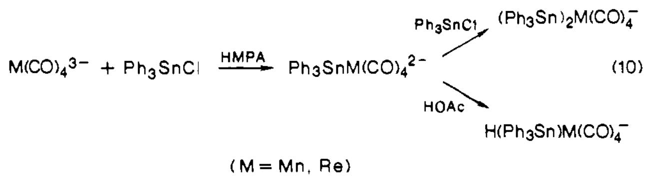
[44] Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.



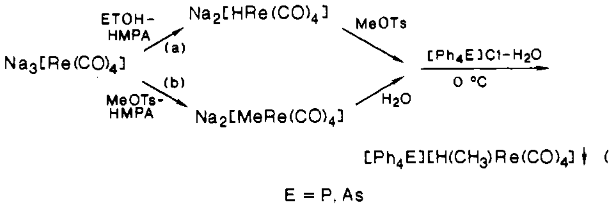
(10)

Addition of 1 equiv of Ph_3SnCl to solutions of $Na_3[M(CO)_4]$ in HMPA resulted in light yellow solutions whose IR spectra were consistent with the presence of the disodium salts, $Na_2[(Ph_3Sn)M(CO)_4]$ (Table I). Weak bands due to the previously described $(Ph_3Sn)_2M(CO)_4^-$ (M = Mn, Re) were also present.[5] In the case of the manganese dianion, an impure tetraethylammonium salt, $[Et_4N]_2[(Ph_3Sn)Mn(CO)_4]$, was isolated, [IR ($\nu$(CO)) (Nujol) 1880 (m), 1740 (vs, br) cm^{-1}], but it did not analyze satisfactorily, probably due to the presence of tetraethylammonium halide. Both dianions have IR active ν(CO) bands at somewhat higher energies than those observed for the corresponding monohydrides, $HM(CO)_4^{2-}$. While only two of the expected three bands (for C_{3v} geometry) were resolved for $Ph_3SnMn(CO)_4^{2-}$, otherwise the HMPA solution spectra of the triphenylstannyl and hydrido manganese and rhenium dianions qualitatively resemble one another. On this basis, they are probably isostructural with the related $(Ph_3P)Mn(CO)_4^-$ and $(Ph_3P)Fe(CO)_4$, whose solid-state structures have been determined and show the phosphine groups to occupy axial positions of a trigonal bipyramid.[38] A four-band pattern in the ν(CO) region of the related $Na_2[(Ph_2P)Mn(CO)_4]$ in DME has been reported by Lindner and co-workers.[39c] The greater complexity of the spectrum of the phosphide complex compared to that of $Na_2[(Ph_3Sn)Mn(CO)_4]$ in HMPA (Table I) may indicate that the former has a different symmetry (e.g., C_{2v}) but could also arise via strong ion pairing between Na^+ and $(Ph_2P)Mn(CO)_4^{2-}$ in DME.[24b] HMPA interacts strongly with alkali metal cations and has a high dielectric constant; both effects help to minimize tight ion pairing between cation and carbonyl anion and thereby simplify the spectra of most carbonyl anions in this solvent.[39d]

The dianions reacted quantitatively with a second equivalent of Ph_3SnCl to provide *cis*-$(Ph_3Sn)_2M(CO)_4^-$,[5] but could also be protonated with acetic acid to give the new monohydrides, *cis*-$H(Ph_3Sn)M(CO)_4^-$. Only the rhenium complex was isolated as a pure product, $[Et_4N]$[*cis*-$H(Ph_3Sn)Re(CO)_4$], but IR and ^1H NMR spectra of the corresponding manganese compound, $[Et_4N]$[*cis*-$H(Ph_3Sn)Mn(CO)_4$], are consistent with the same cis-disubstituted octahedral structure. Tables I and II present spectral data for both materials. Further support of our formulations was provided by the observation of $^{117,119}Sn$-^1H couplings in the ^1H NMR spectra of these compounds. These are rather broad and unresolved for the manganese anion but are clearly separated for the rhenium complex (Figure 4). Corresponding spectra for known group 8 analogues are included in Tables I and II for comparison. While the iron anion, $(Ph_3Sn)Fe(CO)_4^-$, is known, its conjugate acid is not.[39a] For this reason, the IR spectrum of the germanium analogue, *cis*-$H(Ph_3Ge)Fe(CO)_4$, has been included in Table I.[39a] In the case of the osmium species, the hydride is known, but $(Ph_3Sn)Os(CO)_4^-$ apparently has not been described.[40a]

Although attempts to react *cis*-$H(Ph_3Sn)Re(CO)_4^-$ with additional Ph_3SnCl to provide the recently reported seven-coordinate complex $H(Ph_3Sn)_2Re(CO)_4$[40b] have not been made, there is no doubt that this alternative route should work, since the corresponding reaction of the sodium salt of the previously reported conjugate base of this new hydride, *cis*-$(Ph_3Sn)_2Re(CO)_4^-$,[5] has been shown to react with an equivalent of Ph_3SnCl in ethyl ether to provide the colorless seven-coordinate neutral compound, $(Ph_3Sn)_3Re(CO)_4$ (ν(CO) in heptane: 2108 (w), 2004 (s) cm^{-1}). The latter is isoelectronic with the known $(Ph_3Sn)_3W(CO)_4^-$,[40c] and it undergoes substantial heterolysis in tetrahydrofuran to generate $Ph_3Sn(THF)_x^+$ and $(Ph_3Sn)_2Re(CO)_4^-$.[17c]

Interactions of $HMn(CO)_4^{2-}$ with a variety of methylating agents such as MeI or methyl tosylate in HMPA gave only small amounts of $Mn(CO)_5^-$ and uncharacterized products, but corresponding reactions with $HRe(CO)_4^{2-}$ provided isolable salts containing *cis*-$H(CH_3)Re(CO)_4^-$, which is analogous to the known $H(CH_3)Os(CO)_4$.[41–43] As indicated in the Experimental Section, the rhenium anion was prepared by two independent routes (eq 11). The tetraphenylarsonium derivative was obtained in about



(11)

70% yield by route a, while the tetraphenylphosphonium salt was prepared in about 80% yield by route b. Route b involved the intermediate formation of $CH_3Re(CO)_4^{2-}$, which has not been isolated but was observed by IR solution spectra as the disodium salt in HMPA (Table I). These bands are of the same relative intensities as those reported previously for the osmium analogue, $CH_3Os(CO)_4^-$,[44] but, the bands of the dianion are all shifted to

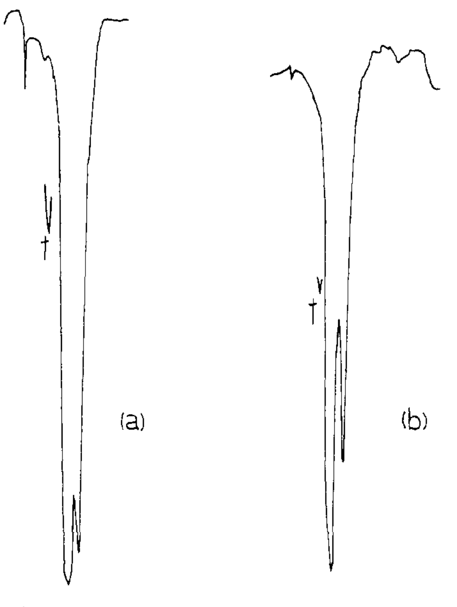


Figure 3. Solution infrared spectra of $[Ph_4As][H_2Mn(CO)_4]$ (a) and $[Ph_4As][H_2Re(CO)_4]$ (b) in tetrahydrofuran in the ν(CO) region. Position of bands: for a 2005 (w), 1905 (s), 1879 (m) cm^{-1}; for b 2024 (w), 1919 (s), 1892 (m) cm^{-1}. A polystyrene reference band at 1944 cm^{-1} is identified with a dagger.

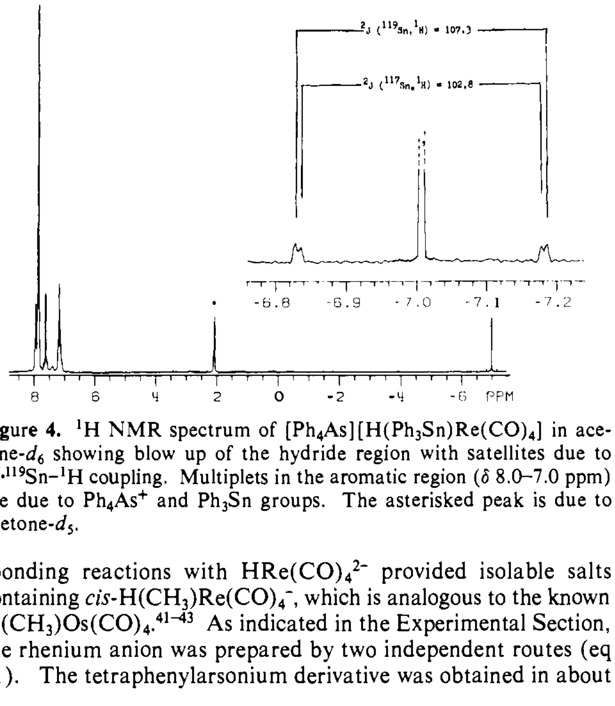


Figure 4. ^1H NMR spectrum of $[Ph_4As][H(Ph_3Sn)Re(CO)_4]$ in acetone-d_6 showing blow up of the hydride region with satellites due to $^{117,119}Sn$-^1H coupling. Multiplets in the aromatic region (δ 8.0–7.0 ppm) are due to Ph_4As^+ and Ph_3Sn groups. The asterisked peak is due to acetone-d_5.

substantially lower energies, as expected, on the the basis of the more electron rich nature of the rhenium complex.[45] Route a usually provided cleaner samples of *cis*-$H(CH_3)Re(CO)_4^-$,[46] but either route generally gave products that were contaminated by varying amounts of $H_2Re(CO)_4^-$. Salts obtained by path b also tended to contain some $(CH_3)_2Re(CO)_4^-$ (vide infra), which was easily detected by ^{13}C NMR spectroscopy (cf. Table III). Since the compositions of salts containing $H(CH_3)Re(CO)_4^-$ were very similar to the corresponding dimethyl- and dihydridorhenates, elemental analyses were not particularly useful indicators of product purity in these cases. Attempts to free $H(CH_3)Re(CO)_4^-$ from $H_2Re(CO)_4^-$ and/or $(CH_3)_2Re(CO)_4^-$ have not been fruitful owing to the quite similar solubilities of these three salts. Norton and co-workers had substantially more difficulty in obtaining relatively pure samples of the corresponding osmium species, $H(CH_3)Os(CO)_4$, with methyl tosylate.[43] Approximately 1:2:1 mixtures of $(CH_3)_2Os(CO)_4$, $H(CH_3)Os(CO)_4$, and $H_2Os(CO)_4$ were formed in these reactions due to the facility with which $H(CH_3)Os(CO)_4$ underwent deprotonation by $HOs(CO)_4^-$ to provide $H_2Os(CO)_4$ and the very reactive $CH_3Os(CO)_4^-$. The latter ion then was rapidly methylated to form $(CH_3)_2Os(CO)_4$.[47,48] Undoubtedly $H(CH_3)Re(CO)_4^-$ is significantly less acidic than $H(CH_3)Os(CO)_4$ and, on this basis as well as for electrostatic reasons, should not undergo deprotonation by $HRe(CO)_4^{2-}$ or $CH_3Re(CO)_4^{2-}$ as readily as $H(CH_3)Os(CO)_4$ does in corresponding reactions.[49] Also, since $HRe(CO)_4^{2-}$ is expected to be more nucleophilic than $HOs(CO)_4^-$, it may well be that methyl tosylate reacts with the rhenium dianion before any significant amount of proton transfer can occur.

Bergman and co-workers[11] previously reported that $H(CH_3)Re(CO)_4^-$ was the likely product formed in the reaction of $[PPN][CpV(CO)_3H]$ with $CH_3Re(CO)_5$ (eq 12). Although they

$$[PPN][CpV(CO)_3H] + CH_3Re(CO)_5 \xrightarrow[THF]{50\ ^\circ C} [PPN][H(CH_3)Re(CO)_4] + CpV(CO)_4 \quad (12)$$

were unable to isolate it from the reaction mixture and no infrared spectrum was reported, its ^1H NMR spectrum in THF (δ −0.65 (d, J = 3 Hz, 3 H), −5.56 br, 1 H)) is essentially identical with ours in DMSO (Table II). On this basis there is no doubt that Bergman's complex and our anion are identical. Bergman also reported in this paper that *cis*-$H(CH_3)Re(CO)_4^-$ was quite unstable in THF and at 50 °C under a CO atmosphere quickly decomposed to CH_4 and $Re(CO)_5^-$. The isoelectronic osmium compound $H(CH_3)Os(CO)_4$ has been observed to be far less thermally stable than either $H_2Os(CO)_4$ or $(CH_3)_2Os(CO)_4$.[50] Similarly, $H(CH_3)Re(CO)_4^-$ is of substantially lower thermal stability than either $H_2Re(CO)_4^-$ or $(CH_3)_2Re(CO)_4^-$ (vide infra). Norton has proposed a general explanation for the instability of alkyl hydrides.[50]

Synthesis and Spectroscopic Properties of $(CH_3)_2Re(CO)_4^-$ and $\overline{CH_2CH_2CH_2CH_2Re}(CO)_4^-$. In view of our discovery of a facile route to hydrides and other derivatives of $Na_3[Mn(CO)_4]$ and $Na_3[Re(CO)_4]$, it was felt that monoalkyl and dialkyl derivatives should be isolable materials despite earlier apparent failures.[5,51] Since only one (unisolated) monoalkyl complex of this type had been reported previously, i.e., $H(CH_3)Re(CO)_4^-$,[11] and no dialkylcarbonylmetalates(1−) were known, this investigation also represented an opportunity to explore the organometallic chemistry of these "superreduced" carbonyls for the first time. Several years ago corresponding carbonylmetalate dianions of iron and osmium had been shown to provide alkyl derivatives of the general formula $RFe(CO)_4^-$,[52] $ROs(CO)_4^-$,[44] and $RR'Os(CO)_4$,[41-43] where R = alkyl and R′ = H or alkyl. Certain of these also functioned as useful intermediates in organic and organometallic syntheses.[53] Collman and others have emphasized that alkyl tosylates are often more satisfactory alkylating agents of nucleophilic metal species than alkyl halides because of their greater reactivity (vs RCl) or lesser susceptibility toward reduction (vs RBr or RI).[54] Since the trianions, $M(CO)_4^{3-}$, are likely to be significantly better reducing agents than the corresponding group 8 dianions, it was felt that the use of alkyl tosylates could also be of importance in carbonyl trianion chemistry.

Although the reactions of alkyl tosylates with $Na_3[Mn(CO)_4]$ are not yet understood in detail and will be reported on in due course, treatment of a solution of $Na_3[Re(CO)_4]$ in HMPA with 2 equiv of methyl tosylate provided the first dialkyl derivative of a carbonyl trianion, as a thermally stable sodium salt. Addition of this solution to aqueous $[Ph_4E]Cl$ (E = P or As) caused nearly quantitative precipitation of product as shown in eq 13. High yields (80–90%) of almost colorless solids were obtained which provided satisfactory analyses and have spectroscopic properties

$$Re(CO)_4^{3-} + 2CH_3OTs \xrightarrow[25\ ^\circ C]{HMPA} \xrightarrow[Ph_4ECl]{H_2O} [Ph_4E][(CH_3)_2Re(CO)_4]\downarrow \quad (13)$$

$$(E = P, As)$$

consistent with the presence of discrete *cis*-$(CH_3)_2Re(CO)_4^-$ units. Both the Ph_4As^+ and Ph_4P^+ salts are of substantial and comparable thermal stability (dec ≥140 °C) and are indefinitely stable under nitrogen at room temperature. Spectral properties for these materials and corresponding osmium compounds are collected in Tables I–III. Infrared spectra (Table I) in the $\nu(CO)$ region show essentially the same features as those observed for *cis*-$(CH_3)_2Os(CO)_4$, with the expected shifts in band positions to lower energy due to the anionic nature of the rhenium complex. NMR spectra of the dimethyl rhenium and osmium carbonyls are collected in Tables II and III and exhibit anticipated differences. For example, the anionic rhenium complex shows an upfield ^1H NMR shift in the methyl hydrogen resonances position owing to its more electron rich nature compared to the osmium species.

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(45) More recently, related dianions of the type $RM(CO)_5^{2-}$ (R = acyl, alkyl; M = V, Nb, and Ta) have been prepared and have interesting chemistry; Ellis, J. E. Research in progress.

(46) In this context, it will be useful to determine how fast and complete is the reaction of $Re(CO)_4^{3-}$ with $H_2Re(CO)_4^-$ and whether species such as $H(D)Re(CO)_4^-$ are stable in solution with respect to H/D exchange. Essentially all that can be said with certainty at this time is that the slow addition of almost exactly 1 equiv of ethanol to an HMPA solution of $Na_3[Re(CO)_4]$ rapidly provided solutions of $HRe(CO)_4^{2-}$, which usually contain varying amounts of $H_2Re(CO)_4^{2-}$.

(47) Bergman has invoked an analogous sequence of reactions to account for the formation of $CpRe(CO)_2(CH_3)_2$ from $CpRe(CO)_2H^-$ and CH_3I (ref 8).

(48) Norton and co-workers obtained quite pure $H(CH_3)Os(CO)_4$ by the reaction of $HOs(CO)_4^-$ with methylfluorosulfate, which evidently methylates $HOs(CO)_4^-$ almost completely before any proton transfer reaction can occur (see citation in ref 44).

(49) Jordan and Norton (citation in ref 44) have determined that as the pK_a of a metal hydride increases, its rate of proton transfer to the conjugate base or an organic amine decreases in acetonitrile. Presumably the same trends would apply to metal hydrides in HMPA, which is also a very polar aprotic solvent.

(50) Norton, J. R.; Carter, W. J.; Kelland, J. W.; Okrasinski, S. J. *Adv. Chem. Ser.* **1978**, *167*, 170.

(51) Faltynek, R. A. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1976.

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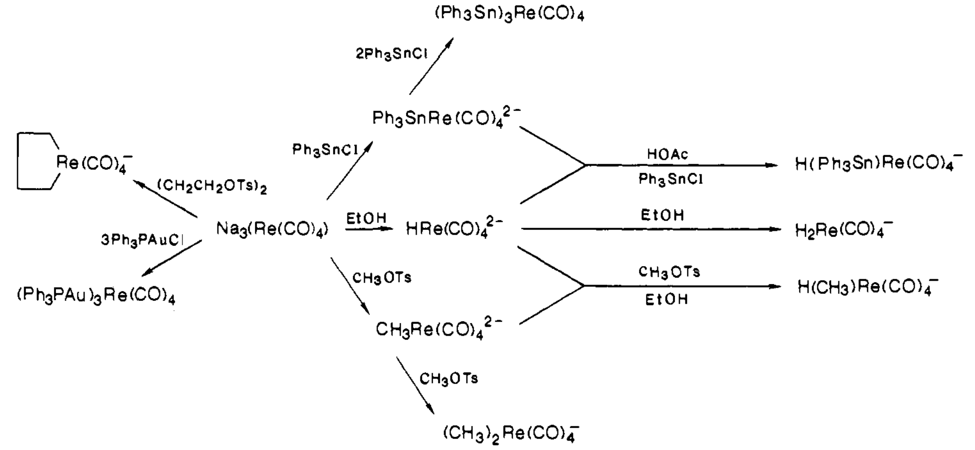
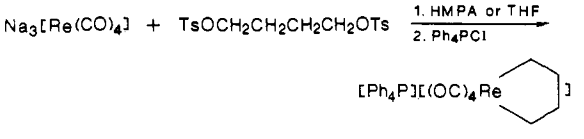
Scheme I. Several Reactions of $Na_3[Re(CO)_4]$



Corresponding downfield ^{13}C shifts for the axial and equatorial carbonyl carbons of the rhenium anion versus those of the neutral osmium complex are also reasonable since anionic carbonyls invariably have ^{13}C chemical shifts at more positive values than isoelectronic neutral species.[62–64] Axial carbonyl carbons, i.e., those cis to the methyl groups, were assigned the most downfield resonances on the basis of corresponding $^{13}C\{^1H\}$ NMR spectra of *cis*-$H(CH_3)Re(CO)_4^-$ in which the single resonance (of relative area 2) of the identical axial carbonyl carbons was downfield of the two resonances (each of relative area 1) of the equatorial carbonyl carbons. Vancea and Graham have observed for group 8 complexes of the type *cis*-$X_2M(CO)_4$, where X = hydrogen or a group 14 ligand, that the resonance position of the axial carbonyl carbons (i.e., those cis to X) is less shielded or downfield of those of the equatorial carbonyl carbons.[57] It would appear that the same situation pertains to corresponding anionic group 7 compounds. The substantial upfield ^{13}C shifts for the methyl carbons of *cis*-$(CH_3)_2Re(CO)_4^-$ (δ −27.4) and *cis*-$H(CH_3)Re(CO)_4^-$ (δ −42.4) are characteristic of methyl carbonyl complexes.[65] For example, methyl carbon shifts of δ −31.8 and −38.0 ppm have been reported for $CH_3W(CO)_5^-$[66] and $CH_3Re(CO)_5$,[58] respectively.

While attempts to prepare the corresponding *cis*-$(C_2H_5)_2Re(CO)_4^-$ by the reaction of $Na_3[Re(CO)_4]$ and ethyl tosylate in HMPA gave only thermally unstable and uncharacterized rhenium compounds, similar reactions with 1,4-butaneditosylate provided a fairly stable substance which proved to be the first example of an *anionic* metallacyclopentane species (eq 14). Although this substance appeared to be moderately stable in solution at room temperature, in contrast to the recently reported group 8 analogues c-$(CH_2)_4M(CO)_4$ (M = Fe,[59] Ru)[55] repeated attempts to isolate this material as a pure solid for elemental analyses were unsuccessful owing to its poor thermal stability at room temperature. However, essentially pure solutions (by IR, NMR) of $[Ph_4P][c\text{-}(CH_2)_4Re(CO)_4]$ were obtained. Its IR spectrum, shown in Figure 5, in the ν(CO) region closely matched that of *cis*-$(CH_3)_2Re(CO)_4^-$ and is qualitatively similar in terms of relative band intensities to that reported for the neutral ruthenium analogue.[55] NMR spectral data are shown in Table II (^1H) and Table III (^{13}C) and also provide good evidence for the existence of the anionic rhenacyclopentane. Two broad resonances of equal intensity at δ 0.89 and 1.52 ppm in the ^1H NMR spectrum of this material were assigned to the α and β hydrogens, respectively, on the ring. Although the position of the α-hydrogen resonance is somewhat downfield of the −0.71 ppm value for *cis*-$(CH_3)_2Re(CO)_4^-$, similar differences are observed in the corresponding ^1H chemical shifts of Bergman's rhenacyclopentane, c-$(CH_2)_4Re(CO)_2(C_5H_5)$, δ 1.82 ppm (for the α-hydrogens), and the dimethyl derivative, $(CH_3)_2Re(CO)_2(C_5H_5)$, δ 0.77 ppm.[67] Satisfactory relative integrated intensities of the multiplet at 7.7–8.0 ppm due to the cation Ph_4P^+ and the anion were also obtained. Surprisingly, Lindner reported that the ^1H NMR spectrum of the analogous ruthenacyclopentane, c-$(CH_2)_4Ru(CO)_4$, consisted of one singlet, despite the fact that its ^{13}C NMR showed distinctly different chemical environments for the α and β carbons.[55] The $^{13}C\{^1H\}$ NMR spectrum of c-$(CH_2)_4Re(CO)_4^-$



(14)

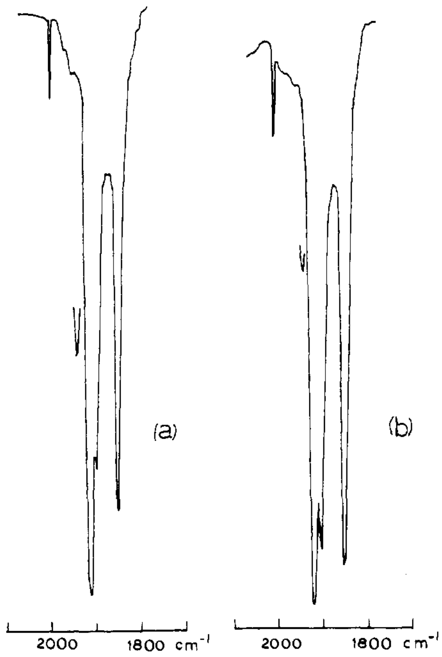


Figure 5. Solution infrared spectra of $[Ph_4P][\overline{CH_2CH_2CH_2CH_2Re}(CO)_4]$ (a) and $[Ph_4As][(CH_3)_2Re(CO)_4]$ (b) in tetrahydrofuran in the ν(CO) region. Position of bands: for a 2022 (w), 1924 (vs), 1906 (s, sh), 1852 (s) cm^{-1}; for b 2020 (w), 1913 (vs), 1903 (s, sh), 1853 (s) cm^{-1}. A polystyrene reference band at 1944 cm^{-1} is identified with a dagger.

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[62] For example, the observed ^{13}C resonance positions for $Os(CO)_5$, $Na[Re(CO)_5]$, $[Na(2.2.1)]_2[W(CO)_5]$, and $Na_3[Ta(CO)_5]$ are δ 182.6 ($CDCl_3$ at −40 °C),[61] 217.7 (dmso-d_6),[60] 257.3 (thf),[63] and 293.0 (NH_3(l) at −50 °C).[64] It is interesting to note that these values are nearly a linear function of atomic number or the charge on the complex.

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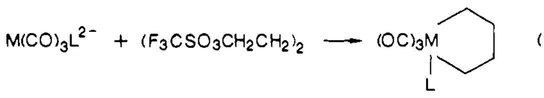
is shown in Table III. Two carbonyl carbon resonances of equal intensity were observed and have been assigned to the axial and equatorial carbonyls. The values are slightly downfield of the corresponding carbonyl resonance positions of *cis*-$(CH_3)_2Re(CO)_4^-$ but are reasonable for these assignments. Carbon-13 positions of the α and β carbons of c-$(CH_2)_4Re(CO)_4^-$ were substantially downfield of the methyl carbon resonance for the dimethylrhenate but are compatible with corresponding carbon resonances of other known 18-electron carbonylmetallacyclopentanes (cf. Table III).

Although metallacyclopentane species are now quite well established materials, the vast majority of these are coordinatively unsaturated and undoubtedly have significantly different reactivity patterns than those of formally saturated analogues.[68] Prior to this work, only four electronically saturated (i.e., 18 electron) metallacyclopentane species had been well characterized, i.e., the three shown in Table III and Lindner's very robust c-$(CH_2)_4Fe(CO)_3PPh_3$,[59] which, like Bergman's rhenacyclopentane, c-$(CH_2)_4Re(CO)_2(\eta^5\text{-}C_5H_5)$, has been further characterized by a single-crystal X-ray diffraction study. Of these, only the reaction chemistry of Bergman's compound has been reported in detail.[56] His species appears to be the only known metallacyclopentane that undergoes thermolysis to provide methylcyclopropane. Lindner's routes (shown in eq 15) to ferra- and ruthenacyclopentanes are quite analogous to the one employed in our study and involve the use of the tetracarbonylmetalates(2−) of iron and ruthenium. His interesting results suggest that under the correct conditions, it may be possible to synthesize an analogous manganacyclopentane, c-$(CH_2)_4Mn(CO)_4^-$, from $Na_3[Mn(CO)_4]$. The anionic nature of the rhenacyclopentane species implies that it should be significantly more susceptible to electrophilic attack than previously known substances of this type and therefore warrants further study.



(15)

M = Fe, L = CO, PPh_3 (ref 59); Ru, L = CO (ref 55)

Concluding Remarks

In this study, we have demonstrated that the carbonyl trianions of manganese and rhenium are valuable precursors to a variety of new substituted tetracarbonylmetalate mono- and dianions. Most of the reactions of $Na_3[Re(CO)_4]$ discussed in this article are summarized in Scheme I. Several of these also proceed as shown for $Na_3[Mn(CO)_4]$, but the products are often of lower thermal stability than their rhenium analogues. Especially poorly explored at present are the interactions of the manganese trianion with alkyl- and acylating agents.

Future studies of these and other carbonyl trianions will be carried out to determine whether their reactivity patterns closely parallel those of formally analogous carbonylmetalate mono- and dianions. For example, in principle, anionic manganese and rhenium analogues of the many useful neutral organometallics derived from $Fe(CO)_4^{2-}$ and $Os(CO)_4^{2-}$, such as (η-cyclobutadiene)tricarbonyliron, should be accessible from $Mn(CO)_4^{3-}$ and $Re(CO)_4^{3-}$. But perhaps more interesting is the possibility that in many cases the trianions and their derivatives will exhibit a unique chemistry of their own!

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemistry Society, and the National Science Foundation (CHE85-06710 and CHE88-13314) for continued funding of this research on highly reduced organometallics. Dr. Robert A. Faltynek, who began this project several years ago and is the coauthor of part 1 of this series (ref 5b), is acknowledged for his important early contributions which led to the present study. Special thanks go to Ruth K. Granheim and Kelly V. Beamer for expert assistance with the manuscript.

Registry No. **1**, 59123-04-5; **2**, 59069-02-2; **3**, 118831-26-8; **4**, 118831-27-9; **5**, 118831-28-0; **6**, 118831-29-1; **7**, 118831-31-5; **8**, 118831-32-6; **9**, 118831-33-7; **10**, 118831-34-8; **11**, 118831-36-0; **12**, 118831-38-2; $Na_2[HMn(CO)_4]$, 118831-39-3; $Na_2[HRe(CO)_4]$, 118831-40-6; $Na_2[Ph_3SnMn(CO)_4]$, 118831-41-7; $Na_2[Ph_3SnRe(CO)_4]$, 118831-42-8; $[Et_4N]$[*cis*-$H(Ph_3Sn)Mn(CO)_4$], 118867-59-7; $[Et_4N]$[*cis*-$H(Ph_3Sn)Re(CO)_4$], 118831-43-9; $[Et_4N][(Ph_3Sn)_2Re(CO)_4]$, 59030-46-5; $(Ph_3Sn)_3Re(CO)_4$, 118831-44-0; $Na_2[CH_3Re(CO)_4]$, 118831-45-1; $Na[Mn(CO)_5]$, 13859-41-1; $Re_2(CO)_{10}$, 14285-68-8; methyl tosylate, 80-48-8; 1,4-butaneditosylate, 94265-67-5.

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[68] (a) Chapter 9 of ref 53 is an excellent review on metallacycles. (b) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.