The initial interpretation of these results based on a comparison with the corresponding silyllithium-silylmercury systems is that the line at δ −0.03 ppm with $J_{^{199}\mathrm{Hg}-^{1}\mathrm{H}} = 16$ Hz arises from an anion of the form $\mathrm{Hg(SiMe_3)_4}^{2-}$ and that centered at δ 0.13 with $J_{^{199}\mathrm{Hg}-^{1}\mathrm{H}} = 25.6$ Hz is associated with an anion of the form $\mathrm{Hg(SiMe_3)_3}^{-}$. These results are in good agreement with those found for $\mathrm{LiHg(SiMe_3)_3}$, $J_{\mathrm{Hg-H}} = 18$ Hz, and for $\mathrm{Li_2Hg(SiMe_3)_4}$, $J_{\mathrm{Hg-H}} = 26$ Hz. These suggested structures are unconfirmed as yet by other techniques, but the observed $^{199}\mathrm{Hg}$-$^{1}\mathrm{H}$ coupling clearly shows that the species present must contain Hg-Si bonds with relatively long lifetimes which permit the coupling to be observed.

Further work is now in progress to elucidate the structures of these species both in solution and in the solid state and to examine the possibility of formation of electron deficient silyl-bridged magnesium derivatives.

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Supplementary Material Available: Observed and calculated structure amplitudes (×10) (4 pages). Ordering information is given on any current masthead page.

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Highly Reduced Organometallic Anions. 1. Syntheses and Properties of Tetracarbonylmetalate(3−) Anions of Manganese and Rhenium

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Abstract: Reductions of $\mathrm{M(CO)_5}^-$ and $\mathrm{M_2(CO)_{10}}$ (M = Mn and Re) in hexamethylphosphoramide with sodium metal provide high yields of the "super-reduced" species $\mathrm{M(CO)_4}^{3-}$, which contain manganese and rhenium in their lowest known oxidation states. Infrared and chemical evidence is presented to corroborate proposed formulations for these salts. Their reactions with electrophilic species including $\mathrm{Ph_3ECl}$ (E = Ge, Sn, Pb), $\mathrm{Me_3ECl}$ (E = Ge, Sn), $\mathrm{Ph_3PAuCl}$, and benzyl chloride, provide a unique route to new organometallic derivatives of stoichiometry $\mathrm{(R_3E)_2M(CO)_4}^-$, $\mathrm{(Ph_3PAu)_3M(CO)_4}$, and $\mathrm{(C_6H_5CH_2CO)_2Mn(CO)_4}^-$. Physical properties of the anionic derivatives are discussed and compared to those of analogous neutral compounds of iron, ruthenium, and osmium.

One of the most exciting recent developments in organometallic chemistry is the recognition that many low-valent organotransition metal fragments mimic to a surprising degree the chemical properties of electronically equivalent groups containing only nonmetallic elements.[1,2] Undoubtedly, the most celebrated work on such mimicry has involved carbene complexes of the type $\mathrm{(OC)_5MC(OR)R'}$ (M = Cr, Mo, and W), which Fischer and co-workers have shown to have reactivity patterns very similar to those of organic esters.[3] In these cases the $\mathrm{M(CO)_5}$ unit is electronically equivalent to the doubly bonded oxygen in an ester. More recently, Lukehart prepared a series of metalloacetylacetonates in which a 15-electron transition metal fragment plays the role of a five-electron carbyne function.[4] Also, our research group has shown that metallodithiocarboxylate anions, which contain a 17-electron transition metal group, resemble organometallic analogues of dithiocarbamates, an extraordinarily versatile and important class of ligands.[5] Most certainly, other novel metalloanalogues of familiar organic and other nonmetallic compounds will be reported in the near future. However, undoubtedly the greatest impact of this new area of organometallic chemistry will be in the selective modification of chemical and physical properties of polymers, catalysts, and reagents by the replacement of familiar nonmetallic functional groups with their transition metal equivalents.

An extremely important, direct, and general method for introducing 17- and 16-electron organometal functionalities into inorganic and organic substrates is by the nucleophilic substitution of carbonyl mono- and dianions for halides, as shown by the following equations:

$$\mathrm{CH_3I + V(CO)_4DIARS^- \rightarrow CH_3V(CO)_4DIARS + I^-}$$ [6]

$$\mathrm{Me_2NCHCl_2 + Cr(CO)_5{}^{2-} \rightarrow Me_2NCHCr(CO)_5 + 2Cl^-}$$ [7]

The unavailability of corresponding carbonyl trianions,[1] which would serve as unique sources of 15-electron organometal units, has severely limited studies in this area. However, we now report on the syntheses and chemical properties of the tetracarbonylmetalates(3−) of manganese and rhenium which represent the first members of a new family of highly reduced metal carbonyls.[8] In terms of standard formal oxidation state assignments they are the most highly reduced anionic transition metal complexes presently known.[9-12]

Experimental Section[13]

Precautions against oxidation of products as outlined in an earlier paper[6] were rigorously applied to all syntheses, transfers, and workups of the highly reduced species described below. To ensure reliability of infrared solution spectra, 0.1-mm path length sodium chloride cells, factory sealed with mercury[14] and equipped with steel stopcocks, were employed. These cells contained metal spacers between the windows, making them imprervious to attack by HMPA. Cell integrity was adequate: blue solutions containing carbonyl trianions did not discolor over 30 min following introduction via syringe.

Hexamethylphosphoramide (Aldrich) as obtained was lightly yellow in color, having a strong oder of dimethylamine. The solvent was initially distilled from calcium hydride under vacuum, and redistilled from sodium prior to use. On addition of sodium after the first distillation, a homogeneous deep blue color pervaded the solution. This subsequently gave way to red during the second distillation. The colorless and malodorous distillate was stored in the dark under vacuum in the drybox until needed.

Ammonia (Hawkins Chemical) was condensed into a cylindrical graduated vessel under reduced pressure at liquid nitrogen temperature. A small chunk of sodium metal had previously been placed in the vessel, and this was allowed to dissolve and impart the characteristic blue color to the contents as they warmed and liquified. It was assumed that the ammonia was anhydrous and oxygen-free when the blue color persisted, and at this point distillation into the flask containing the reducible reactant was begun. Since many of the compounds described are oxygen and peroxide sensitive, special care was taken in deoxygenating solvents. Tetrahydrofuran (THF), diethyl ether, benzene, toluene, heptane, and isopentane were distilled from alkali metal benzophenone ketyls immediately before use. Dichloromethane and chloroform were dried over molecular sieves and purged of air with a dispersed stream of nitrogen. Acetone, after drying over molecular sieves, was subjected to three freeze-thaw cycles under vacuum (or until no effervescence was noted at the melting point).

The following reactants were purchased from commercial sources and degassed before use: manganese decacarbonyl, rhenium decacarbonyl, elemental sodium and potassium, chlorotriphenylstannane, chlorotriphenylplumbane, bromotriphenylgermane, chlorotrimethylstannane, tetraethylammonium bromide, bromotrimethylgermane, and tetraphenylarsonium chloride. Benzyl chloride was distilled under argon before use. Chlorotriphenylphosphinegold(I) was prepared according to a literature procedure.[15] Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. NMR samples, sealed into 5-mm Pyrex tubes, were run on either a Varian T60 or XL100 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries under vacuum on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out in the laboratories of Spang (Ann Arbor, Michigan), Chemalytics, Inc. (Tempe, Arizona), and Galbraith (Knoxville, Tenn.). Osmometric molecular weights were performed by Spang or on a Mechrolab osmometer in the Department of Chemistry.

Tetracarbonylmanganate(3−) Ion (1). Typically, 0.50 g (1.3 mmol) of $\mathrm{Mn_2(CO)_{10}}$ was briefly degassed, dissolved in 20 mL of THF, and treated with a tenfold excess of 1% Na/Hg amalgam (4 mL) or a twofold excess of $\mathrm{NaK_{2.8}}$ alloy (0.32 mL).[14] The light yellow solution gradually turned green over 1 h of stirring. Following decantation from the amalgam, or filtration from excess alkali metal, the THF was removed under vacuum leaving a green tinged, white, crystalline mass of $\mathrm{M[Mn(CO)_5]}$ (M = Na or K).

Addition of 20 mL of HMPA and a slight excess (0.20 g, 8.7 mmol) of sodium sand produced a pale green solution. Agitation with a glass-clad stirring bar (Teflon is attacked under these conditions) under full pump vacuum (ca. 0.1 Torr) for 1 h caused the solution to become turbid and to evolve CO. When the deep blue color of sodium dissolved in HMPA persisted, the reaction was presumed to be complete. Infrared spectra confirmed the absence of $\mathrm{[Mn(CO)_5]^{1-}}$ and the presence of $\mathrm{[Mn(CO)_4]^{3-}}$. Overall conversion efficiency is greater than 80%, based on yields of $\mathrm{Et_4N[(Ph_3Sn)_2Mn(CO)_4]}$ (**3**) prepared from similar reductions (vide infra).

Solutions of $\mathrm{[Mn(CO)_4]^{3-}}$ were generally treated with an appropriate electrophile at this point, and subsequently worked up from aqueous solution. Alternatively, a precipitate of the solvated salt $\mathrm{[M(HMPA)_x]_3[Mn(CO)_4]}$ could be obtained by adding excess heptane (250 mL) to the blue HMPA solution of the trianion. The salt precipitated as a brown tar that solidified to a free-flowing, brown-to-green solid on further heptane addition and trituration. Attempts to obtain reproducible elemental analyses for the pyrophoric sodium salt, formulated as $\mathrm{[Na(HMPA)_x]_3Mn(CO)_4}$, (see Discussion) were not successful.

Syntheses of **1** may also be carried out by the direct reduction of $\mathrm{Mn_2(CO)_{10}}$ in HMPA or the reduction of $\mathrm{NaMn(CO)_5}$ in liquid ammonia. However, the yields of trianion are significantly lower in these preparations.

Tetracarbonylrhenate(3−) Ion (2). Whereas $\mathrm{Mn_2(CO)_{10}}$ was susceptible to disproportionation in HMPA, no evidence for this reaction was noted for $\mathrm{Re_2(CO)_{10}}$. Generation of $\mathrm{[Re(CO)_4]^{3-}}$ occurred with the same efficiency whether $\mathrm{Re_2(CO)_{10}}$ was directly reduced with 6 equiv of sodium, or the pentacarbonylrhenate(1−) anion[14] was first isolated and reduced independently. The direct route is described below.

A sample of 0.30 g (0.46 mmol) of $\mathrm{Re_2(CO)_{10}}$ was combined with a slight excess of sodium sand (0.07 g, 3.0 mmol) and treated with 15 mL of HMPA in the drybox. The decacarbonyl dissolved slowly as the solution gradually became dark orange. Following 1.5 h of stirring under vacuum, the usual deep blue color was obtained. Yields of 35-70% of $\mathrm{Et_4N[(Ph_3Sn)_2Re(CO)_4]}$ (**4**) were realized upon reaction of $\mathrm{Ph_3SnCl}$ with solutions thus prepared.

In liquid ammonia, no appreciable reduction of $\mathrm{[Re(CO)_5]^{1-}}$ to $\mathrm{[Re(CO)_4]^{3-}}$ occurred with sodium sand, in contrast to the manganese system.

$\mathrm{[Et_4N][(Ph_3Sn)_2Mn(CO)_4]}$ (3). Method 1. Manganese decacarbonyl (0.30 g, 0.77 mmol) was dissolved in 20 mL of THF and stirred for 1.5 h with a twofold excess of $\mathrm{NaK_{2.8}}$ alloy (0.19 mL). Following isolation of $\mathrm{K[Mn(CO)_5]}$, the second stage of reduction was carried out in 20 mL of HMPA with 0.11 g of sodium sand. The blue solution obtained after 1 h of stirring under high vacuum rapidly turned orange when 1.19 g (3.1 mmol) of solid $\mathrm{Ph_3SnCl}$ was added. Water (160 mL) containing a small excess of $\mathrm{Et_4NBr}$ (0.44 g, 2.1 mmol) caused precipitation of a white, curdy solid that was collected on a medium frit and extensively washed with $\mathrm{Et_2O}$ (eight 20-ml portions) to rid it of excess $\mathrm{Ph_3SnCl}$. A single recrystallization from 20 mL of acetone/excess diethyl ether produced 1.84 g of analytically pure **3**, corresponding to a yield of 83%. (Melts with decomposition at 208-209 °C). Anal. Calcd for $\mathrm{C_{48}H_{50}MnNO_4Sn_2}$: C, 57.81; H, 5.05; N, 1.40; Sn, 23.80. Found: C, 57.55; H, 5.07; N, 1.45; Sn, 23.87.

Method 2. The direct reduction of 0.50 g (1.3 mmol) of $\mathrm{Mn_2(CO)_{10}}$ with 0.30 g (13 mmol) of sodium sand in 20 mL of HMPA generated a deep blue solution after 2 h. Addition of 2.04 g (5.3 mmol) of $\mathrm{Ph_3SnCl}$ followed by 1.26 g (6 mmol) of $\mathrm{Et_4NBr}$ in 200 mL of water gave a tan precipitate that was worked up as in Method 1 to yield 1.68 g (65%) of product identical with **3**.

Method 3. Yellow $\mathrm{Mn_2(CO)_{10}}$ (1.00 g, 2.6 mmol) was reduced to almost colorless $\mathrm{Na[Mn(CO)_5]}$ by a threefold excess of 1% Na/Hg (3 mL) in 20 mL of THF (reaction time—30 min). Sodium sand (50% excess, 0.48 g) was added to the monoanion, and 100 mL of anhydrous ammonia was condensed into the reaction flask at −78 °C. The resulting slurry of brown precipitate in a deep blue liquid phase was stirred and refluxed until the blue coloration faded to yellow (2 h). (Rather large amounts of insoluble tan material were present at this stage. Other experiments in which the ammonia solution was filtered at −40 °C confirmed that this solid was mostly $\mathrm{Na_3Mn(CO)_4}$. Evaporation of the filtrate gave very little solid, which was shown to be mostly sodium amide.) Following overnight evaporation of $\mathrm{NH_3}$ through a mercury bubbler, the residue was treated with 3.94 g (10.2 mmol) of $\mathrm{Ph_3SnCl}$ in 40 mL of THF and stirred for 12 h. Filtration through infusorial earth left a light yellow solution that yielded an off-white solid on evaporation. Metathesis with Et_4NBr in 10 mL of acetone/200 mL of H_2O provided a finely divided white product that was washed with ten 20-mL portions of diethyl ether to remove unreacted Ph_3SnCl. A yield of 2.00 g (39%) of white crystals shown to be identical with **3** was obtained. It should be noted that the THF-insoluble residue collected during workup contains $Na_2[OC{\equiv}CO]$,[16] a shock-sensitive substance in the dry state. Detonations of this material have occurred spontaneously while contaminated glassware dried in the hood. Under no circumstances should any residues obtained in the reduction step be scratched with spatulae or mulled!

$[Et_4N][(Ph_3Sn)_2Re(CO)_4]$ (4). Pale orange $NaRe(CO)_5$[14] was prepared by 0.8% sodium amalgam (1.6 mL) reduction of 0.3 g (0.46 mmol) of $Re_2(CO)_{10}$ in 50 mL of THF and after removal of mercury and solvent was treated with 0.08 g (3.5 mmol) of Na sand and 20 mL of HMPA. Within 30 min the solution turned blue, whereupon a solution of Ph_3SnCl (0.71 g, 1.8 mmol) in 5 mL of THF was added at once by syringe. After 15 min of stirring, excess aqueous Et_4NBr (2.0 g in 200 mL of water) was slowly added, resulting in formation of a voluminous precipitate of impure **4**. This solid was washed with water (three 30-mL portions), dried, washed with ether (three 30-mL portions) and then recrystallized from acetone/ether. After a final washing with isopentane (two 10-mL portions) and drying, 0.69 g (66% yield based on $Re_2(CO)_{10}$) of colorless, crystalline **4** was obtained. Anal. Calcd for $C_{48}H_{50}NO_4ReSn_2$: C, 51.09; H, 4.47; N, 1.24. Found: C, 51.08; H, 4.59; N, 1.28 (mp 222-223 °C). Direct reduction of $Re_2(CO)_{10}$ in HMPA to **2**, followed by treatment with Ph_3SnCl and workup as before, provided a 32% yield of product identical with **4**.

$[Et_4N][(Ph_3Pb)_2Mn(CO)_4]$ (5). An HMPA solution of $[Mn(CO)_4]^{3-}$ was prepared by initially reducing 0.30 g (1.3 mmol) of $Mn_2(CO)_{10}$ to $K[Mn(CO)_5]$ in 20 mL of THF with a twofold excess (0.20 mL) of $NaK_{2.8}$ alloy, removing the THF under vacuum, dissolving the residue in 20 mL of HMPA, and stirring the solution with 0.11 g (4.7 mmol) of Na sand until the characteristic blue color was achieved (40 min under full vacuum). Oxygen-free Ph_3PbCl (1.50 g, 3.2 mmol) was introduced as a solid, which changed the blue color to a deep red and caused evolution of heat. After 30 min of stirring, Et_4NBr (0.5 g, 2.4 mmol) in 200 mL of H_2O was added, which produced a brown solid. Thorough washing with water (four 20-mL portions) and diethyl ether (four 20-mL portions) and one recrystallization from 30 mL of acetone/excess diethyl ether gave a crystalline product that was still quite brown. A second recrystallization from acetone/diethyl ether, including passage through 2 cm of dry silica gel, greatly improved the appearance of the complex. After a final isopentane rinsing (two 10-mL portions), 1.16 g (64% yield) of analytically pure ivory **5** was collected (mp 198-200 °C dec). Anal. Calcd for $C_{48}H_{50}MnNO_4Pb_2$: C, 49.10; H, 4.29. Found: C, 49.20; H, 4.43.

$[Et_4N][(Ph_3Pb)_2Re(CO)_4]$ (6). An HMPA solution (20 mL) containing 0.50 g (0.76 mmol) of $Re_2(CO)_{10}$ and 0.12 g (5.2 mmol) of Na sand turned deep orange on stirring for 10 min under vacuum. After 1 h the blue color indicative of complete reduction to $[Re(CO)_4]^{3-}$ appeared. Addition of 1.44 g (3.04 mmol) of Ph_3PbCl followed by aqueous Et_4NBr (0.32 g, 1.52 mmol in 220 mL) precipitated impure, deep yellow **6**. Two recrystallizations from acetone/diethyl ether with silica gel (2 cm) filtrations produced 1.36 g (68% yield) of analytically pure **6** (mp 188-189 °C with minor dec). Anal. Calcd for $C_{48}H_{50}NO_4Pb_2Re$: C, 44.16; H, 3.86; N, 1.07. Found: C, 44.19; H, 3.71; N, 1.13.

$[Et_4N][(Ph_3Ge)_2Mn(CO)_4]$ (7). By a procedure identical with that used for the preparation of **5**, 1.00 g (2.6 mmol) of $Mn_2(CO)_{10}$ was first reduced to $KMn(CO)_5$ with 0.62 mL of $NaK_{2.8}$ in 20 mL of THF and finally converted to $Mn(CO)_4{}^{3-}$ with 0.40 g (17.4 mmol) of Na sand. Solid Ph_3GeBr (3.94 g, 16.5 mmol) was added directly to the HMPA and the resulting deep red solution was stirred for 15 min. An infrared solution spectrum at this time showed bands tentatively assignable to $[Ph_3GeMn(CO)_4]^{2-}$ (see Discussion) as well as $(Ph_3Ge)_2Mn(CO)_4{}^-$. Similar anomalies were not observed in the syntheses of **3** or **5**. Aqueous Et_4NBr (2.00 g/180 mL) precipitated a fine greenish-white powder that was collected over filter-aid from the dark brown $HMPA/H_2O$ liquid phase. Three recrystallizations from acetone (20 mL)/excess diethyl ether, including filtration through 4 cm of silica gel, were required to generate colorless, analytically pure crystals of **7** (1.04 g, 22% yield; mp 236-238 °C with yellowing). Anal. Calcd for $C_{48}H_{50}Ge_2MnNO_4$: C, 63.70; H, 5.57; N, 1.55. Found: C, 63.85; H, 5.66; N, 1.68.

$[Et_4N][(Ph_3Ge)_2Re(CO)_4]$ (8). Reduction of 0.49 g (0.75 mmol) of $Re_2(CO)_{10}$ with 0.12 g (5.22 mmol) of Na sand in 20 mL of HMPA formed $[Re(CO)_4]^{3-}$ after 1 h of agitation. The infrared spectrum following introduction of Ph_3GeBr (1.15 g, 4.18 mmol) indicated that both $[Ph_3GeRe(CO)_4]^{2-}$ (see Discussion) and $[(Ph_3Ge)_2Re(CO)_4]^-$ were in solution. Yellow, impure **8** was obtained after addition of 0.32 g (1.52 mmol) of Et_4NBr in 220 mL of water. Following two recrystallizations through dry silica gel with 20 mL of acetone/excess diethyl ether, 0.76 g (49% yield) of analytically pure colorless needles of **8** was isolated (mp 257-259 °C). Anal. Calcd for $C_{48}H_{50}Ge_2NO_4Re$: C, 55.63; H, 4.86; N, 1.35. Found: C, 55.74; H, 4.85; N, 1.43.

$[Ph_4As][(Me_3Sn)_2Mn(CO)_4]$ (9). Direct reduction of $Mn_2(CO)_{10}$ (2.00 g, 5.2 mmol) to $Mn(CO)_4{}^{3-}$ with 1.00 g (43.5 mmol) of Na sand in 20 mL of HMPA required 4 h. A solution of malodorous Me_3SnCl (4.10 g, 20.6 mmol) in 5 mL of THF was added to the HMPA solution by syringe. After removing THF under vacuum from the resulting deep red solution, 4.30 g (9.47 mmol) of $Ph_4AsCl{\cdot}2H_2O$ in water (240 mL) was added, whch caused the formation of a deep yellow solid. This was filtered off, washed with water (six 20-mL portions), dried, taken up in 20 mL of acetone, and eluted through 10 cm of dry silica gel with an additional 40 mL of acetone/20 mL of heptane solvent mixture. On reduction of the volume of the eluate to ca. 20 mL, there remained a viscous golden oil which immediately crystallized on dropwise addition of 5 mL of heptane. The golden crystals were carefully washed with isopentane (four 20-mL portions) and dried; they provided without further purification 6.31 g (70% yield) of analytically pure **9** (mp 91-92 °C, following slight darkening above 86 °C). Anal. Calcd for $C_{34}H_{38}AsMnO_4Sn_2$: C, 46.52; H, 4.36. Found: C, 46.63; H, 4.37.

$[Ph_4As][(Me_3Sn)_2Re(CO)_4]$ (10). By the procedure outlined for **9**, 1.50 g (2.3 mmol) of $Re_2(CO)_{10}$ was reduced to $[Re(CO)_4]^{3-}$ in 20 mL of HMPA with 0.32 g (13.9 mmol) of Na sand and treated with Me_3SnCl (1.85 g, 9.3 mmol) in 5 mL of THF. Somewhat sticky, brown **10** was precipitated by addition of 1.95 g of Ph_4AsCl/280 mL of H_2O. It was necessary to pass CH_2Cl_2/heptane solutions of the crude product through two columns (10 cm each) of dry silica gel to generate the analytical sample. The final recrystallization and workup were the same as described for **9**, except CH_2Cl_2 rather than acetone was employed in the solvent mixture. A yield of 2.92 g (63%) of pale, orange crystalline **10** was obtained (mp 83-86 °C). Anal. Calcd for $C_{34}H_{38}AsO_4ReSn_2$: C, 40.47; H, 3.80. Found: C, 40.59; H, 3.81.

$[Ph_4As][(Me_3Ge)_2Mn(CO)_4]$ (11). After generating $[Mn(CO)_4]^{3-}$ in 20 mL of HMPA via the reduction of 0.50 g (1.3 mmol) of $Mn_2(CO)_{10}$ with 0.22 g of Na sand, Me_3GeBr (1.02 g, 5.2 mmol) was added directly to the blue solution. The infrared spectrum contained carbonyl bands assignable to $[(Me_3Ge)_2Mn(CO)_4]^-$ and none for $[Me_3GeMn(CO)_4]^{2-}$. Precipitated as the $[Ph_4As]^+$ salt by addition of 1.07 g of Ph_4AsCl/200 mL of H_2O, the drab yellow complex was passed through 10 cm of dry silica gel in 90 mL of CH_2Cl_2/30 mL of heptane. Crystallization occurred when the eluate was reduced to 5 mL and slowly mixed with 10 mL of additional heptane. The pure, slightly tan crystals were then washed with isopentane (three 20-mL portions) and dried, leaving 0.92 g (47% yield) of **11** (mp 97-99 °C). Anal. Calcd for $C_{34}H_{38}AsGe_2MnO_4$: C, 51.98; H, 4.87. Found: C, 51.94; H, 4.96.

$[Ph_4As][(Me_3Ge)_2Re(CO)_4]$ (12). Addition of 1.22 g (6.18 mmol) of Me_3GeBr by syringe to $Re(CO)_4{}^{3-}$ in 20 mL of HMPA, generated by reduction of 1.00 g (1.5 mmol) of $Re_2(CO)_{10}$ with 0.25 g (10.9 mmol) of Na sand, left a deep red solution containing $(Me_3Ge)_2Re(CO)_4{}^-$ as the only carbonyl species. Analytically pure product was obtained by the same work-up procedure as outlined for **11**, totaling 1.27 g (45% yield) of pale orange crystals (mp 88-91 °C with slight dec). Anal. Calcd for $C_{34}H_{38}AsGe_2O_4Re$: C, 44.54; H, 4.18. Found: C, 44.27; H, 4.01.

$(Ph_3PAu)_3Mn(CO)_4$ (13). A 0.20-g (0.51 mmol) quantity of $Mn_2(CO)_{10}$ was reduced to $K[Mn(CO)_5]$ in 20 mL of THF with 0.12 mL of $NaK_{2.8}$ alloy. The white, crystalline salt was dried under vacuum, dissolved in 20 mL of HMPA, and further reduced with 0.08 g of Na sand, requiring 45 min for completion. Solid Ph_3PAuCl (1.52 g, 3.08 mmol) was added directly, causing the viscous solution to turn deep red. Addition, with stirring, of 200 mL of water precipitated dark brown, crude $(Ph_3PAu)_3Mn(CO)_4$. To free the product of a highly colored dark impurity, it was necessary to pass the material, dissolved in acetone, through 12-cm columns of silica gel. After two such filtrations a brilliant yellow solution was obtained. Evaporating the acetone down to 10 mL, and adding diethyl ether dropwise until turbidity was observed (10 mL), initiated crystal formation. The procedure yielded 0.32 g (20%) of bright yellow crystalline **13** after 12 h of storage of 0 °C. A final washing with isopentane (two 10-mL portions) completed the workup (dec above 174 °C). Anal. Calcd for $C_{58}H_{45}Au_3MnO_4P_3$: C, 45.10; H, 2.94; Au, 38.25; P, 6.01. Found: C, 45.13; H, 3.03; Au, 37.94; P, 5.92. An osmometric molecular weight determination in benzene was limited by the low solubility of **13**. Two data points averaged 1850 g/mol compared to the calculated mol wt of 1545.

$(Ph_3PAu)_3Re(CO)_4$ (14). To determine whether cleaner $(Ph_3PAu)_3M(CO)_4$ preparations were attainable at low temperature, solid $[Na(HMPA)_x]_3[Re(CO)_4]$, prepared via reduction of 0.30 g (0.46 mmol) of $Re_2(CO)_{10}$ in 15 mL of HMPA with 0.07 g of Na sand and precipitated as a dark brown powder by addition of 130 mL of heptane, was employed in this synthesis. The solvated salt was combined dry with the equivalent amount of Ph_3PAuCl (1.37 g, 2.77 mmol), cooled to −78 °C, and treated with 20 mL of THF at −60 °C. Immediately a deep red color developed, reminiscent of the manganese syntheses. Filtration after warming to room temperature gave an almost black solution, yielding a solid of similar color on solvent removal. The rhenium complex was less stable toward silica gel, as three filtrations through 10-cm portions of the column material in CH_2Cl_2 left conIderably less product each time. A final recrystallization from 10 mL of acetone/2 mL of heptane left 0.10 g (6% yield) of dark golden needles (dec above 126 °C). Anal. Calcd for $C_{58}H_{45}Au_3O_4P_3Re$: C, 41.57; H, 2.71; P. 5.54. Found: C, 41.73; H, 3.05; P, 5.09.

Reaction of $Mn(CO)_4{}^{3-}$ with Methyl Chloride. The reduction of 1.00 g (2.6 mmol) of $Mn_2(CO)_{10}$ to $[Mn(CO)_4]^{3-}$ proceeded smoothly in 20 mL of HMPA with 0.48 g of Na sand. Excess isopentane (60 mL) precipitated tan $[Na(HMPA)_x]_3[Mn(CO)_4]$, which was transferred to another flask, slurried in 20 mL of THF, and cooled to −78 °C. A large excess (10 mL) of CH_3Cl was condensed upon the slurry, initiating a reaction that turned the flask contents deep red. On warming to room temperature, the infrared spectrum contained bands for $Mn(CO)_5{}^-$. Excess Ph_3SnCl readily converted the anion to $Ph_3SnMn(CO)_5$, also identified *via* infrared spectra. No evidence for the formation of a methyl complex of manganese carbonyl was obtained for this reaction.

Reaction of $Mn(CO)_4{}^{3-}$ with Benzyl Chloride: Formation of $Ph_4As[(PhCH_2CO)_2Mn(CO)_4]$ (15). Benzyl chloride (0.92 g, 7.27 mmol) was added via syringe to the blue solution resulting from a 2-h reduction of 0.70 g (1.8 mmol) of $Mn_2(CO)_{10}$ with 0.30 g of Na sand in 20 mL of HMPA. An exothermic reaction occurred and the contents of the flask became deep red. Tetraphenylarsonium chloride (1.50 g) in 200 mL of water precipitated an orange solid that was purified twice by passage through 10 cm of silica gel in acetone solution. The pure benzyl derivative was crystallized as light yellow platelets from acetone/diethyl ether, and washed with small amounts of isopentane (three 10-mL portions). The yield was 1.22 g, or 45% (mp 91-92 °C after the sample reddens at 80 °C). Anal. Calcd for $C_{44}H_{34}AsMnO_6$: C, 67.01; H, 4.35; As, 9.50. Found: C, 67.11; H, 4.34; As, 9.65.

Reaction of $Mn(CO)_4{}^{3-}$ with Water: Formation of $H_3Mn_3(CO)_{12}$. An HMPA solution (15 mL) of $[Mn(CO)_4]^{3-}$ was generated by reduction of $K[Mn(CO)_5]$ with 0.30 g of sodium sand. The monoanion was synthesized by reducing 1.00 g (2.6 mmol) of $Mn_2(CO)_{10}$ with 0.62 mL of $NaK_{2.8}$ in 20 mL of THF. Water (ten 5-mL portions) was cautiously added to the blue HMPA solution, turning it deep violet. Another 50-mL addition of water containing 1.10 g of Et_4NBr precipitated a purple solid that was collected on a medium frit and washed with two 20-ml portions more water. Storage of the dry material at 0 °C under argon for several hours caused decomposition to uncharacterized yellow solid. The violet material had essentially the same infrared spectra as an uncharacterized intermediate reported by Johnson et al. in the reaction of $Mn_2(CO)_{10}$ with aqueous hydroxide on the route to $H_3Mn_3(CO)_{12}$.[17]

A second $HMPA/H_2O$ solution of the purple anion was prepared in the same manner, but not metathesized with Et_4NBr. Addition of 40 mL of 4 N HCl precipitated a dark red, malodorous solid (0.30 g) that had carbonyl absorptions at 2077, 2028, 2012, and 1982 cm^{-1} in cyclohexane. This material, prepared in 35% yield, was identical with $H_3Mn_3(CO)_{12}$, characterized previously.[17]

Results and Discussion

Our recent discovery that the pentacarbonylmetalate dianions of molybdenum and tungsten[1] are generated rapidly and in high yield from the sodium metal reduction of the corresponding neutral hexacarbonyls in HMPA[18] indicated that HMPA was a unique solvent for organometallic reductions and suggested that new highly reduced transition metal complexes could be prepared in this medium. Since cyclopentadienyltricarbonylvanadate(1−) was the only known cyclopentadienyl-substituted carbonyl dianion,[1] our initial aim was to determine whether the unknown $C_5H_5Mn(CO)_2{}^{2-}$ and $C_5H_5Co(CO)^{2-}$ could be prepared by reduction of $C_5H_5Mn(CO)_3$ and $C_5H_5Co(CO)_2$ in HMPA. Although the reduction of $C_5H_5V(CO)_4$ in HMPA provides high yields of $C_5H_5V(CO)_3{}^{2-}$, no evidence for the generation of corresponding monomeric manganese or cobalt dianions was obtained under identical conditions.[19] Reduction of $C_5H_5Mn(CO)_3$ was particularly interesting, however, in that $Mn(CO)_5{}^-$ initially formed as the principal carbonyl containing species. Addition of excess sodium to the solution also gave a new material, which had one intense absorption at 1670 cm^{-1}. Quenching the reaction mixture with chlorotriphenylstannane provided an air-stable derivative, $(Ph_3Sn)_2Mn(CO)_4{}^-$, in 64% yield.[19a] Subsequently, we showed that cleaner preparations of the highly reduced precursor were obtained by direct reductions of $Mn(CO)_5{}^-$ and $Mn_2(CO)_{10}$ in HMPA. Also, reductions of corresponding rhenium carbonyl species provided a similar highly reduced anion. We have strong evidence that these materials are the first noncluster binary carbonyl trianions[20] and will now describe their properties.

Synthesis and Properties of $M(CO)_4{}^{3-}$ (M = Mn and Re). Treatment of $M_2(CO)_{10}$ and $NaM(CO)_5$ (M = Mn and Re) in HMPA, with sufficient sodium metal (see Experimental section) to cause eventual (after about 1.5 h) formation of a blue color,[21] results in complete reduction of these species to salts containing "super-reduced" carbonyl anions. Somewhat lower yields of the manganese reduction product were obtained using $Mn_2(CO)_{10}$ as reactant, since the latter slowly undergoes disproportionation in HMPA at room temperature. For example, after 72 h at 50 °C all $Mn_2(CO)_{10}$ was converted to $[Mn(HMPA)_x][Mn(CO)_5]_2$.[22] No evidence for the presence of carbonyl cations was observed in this disproportionation.[23] In contrast, $Re_2(CO)_{10}$ exhibits no pronounced tendency to disproportionate in HMPA.[24] A solution of $Re_2(CO)_{10}$ in HMPA deteriorated slightly after 3 days at 70 °C, but no infrared bands due to $Re(CO)_5{}^-$ were observed during this time.

The reduced manganese and rhenium species are formulated as $[Na(HMPA)_x]_3M(CO)_4$ (**1** and **2**) on the basis of their spectral and chemical properties. Infrared spectra of $M(CO)_4{}^{3-}$ in HMPA are very similar and show one weak and one extremely intense and broad band in the carbonyl stretching frequency region. Figure 1 shows the spectrum of a rather concentrated solution (0.05 mmol/mL) of $Na_3Re(CO)_4$ in HMPA. Significantly, the weaker band at 1821 cm^{-1} nearly disappears and the strong band becomes sharper, but does not change its position on addition of more HMPA or 18-crown-6-ether. Similar changes occur in analogous bands of $Na_3Mn(CO)_4$ in HMPA. These observations strongly suggest that the higher energy band results from ion pair formation, which perturbs the tetrahedral symmetry of the $M(CO)_4{}^{3-}$ in concentrated solutions. Similar observations of ion pairing of $NaCo(CO)_4$ in THF/DMF,[25] $NaMn(CO)_5$ in THF/HMPA,[26] and $LiMn(CO)_5$ in THF/HMPA[27] have been reported recently.

Attempts to corroborate the formulations of **1** and **2** by elemental analyses and conductivity measurements have been thwarted by the extreme air sensitivity of these materials. However, the high yields (>80%) of several derivatives of $M(CO)_4{}^{3-}$ from **1** and **2**, the lack of hydridic signals of **1** and **2** in HMPA-d_{18} and HMPA-d_0 between 0 and 40, even at high

Table I. Infrared Solution Spectra of $M(CO)_4^z$ and $HM(CO)_4^z$ in the Carbonyl Stretching Frequency Region[a,b]

$Mn(CO)_4^{3-}$	(HMPA)	1805 w, 1670 vs			
$Fe(CO)_4^{2-}$	(HMPA)	1771 w, 1729 vs[29]	$[HMn(CO)_4^{2-}]$[c]	(−)	ca. *1730* s
$Co(CO)_4^-$	(THF)	1883 vs, 1861 m,sh[25]	$HFe(CO)_4^-$	(THF)	2000 w, 1915 m, *1880* s[31]
$Ni(CO)_4$	(THF)	2040 vs[30]	$HCo(CO)_4$	(gas)	2122 w, 2062 m, *2043* s[32]

[a] Values in cm^{-1}. [b] w = weak, m = medium, sh = shoulder, s = strong, vs = very strong. [c] Extrapolated value of *E* band for uncharacterized species.

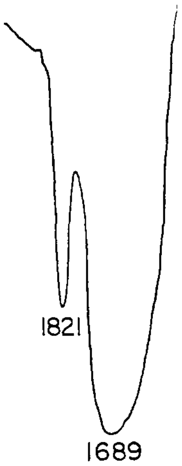

Figure 1. Solvent-compensated spectrum of $Na_3Re(CO)_4$ in the carbonyl stretching frequency region in HMPA. Position of bands are in cm^{-1}.

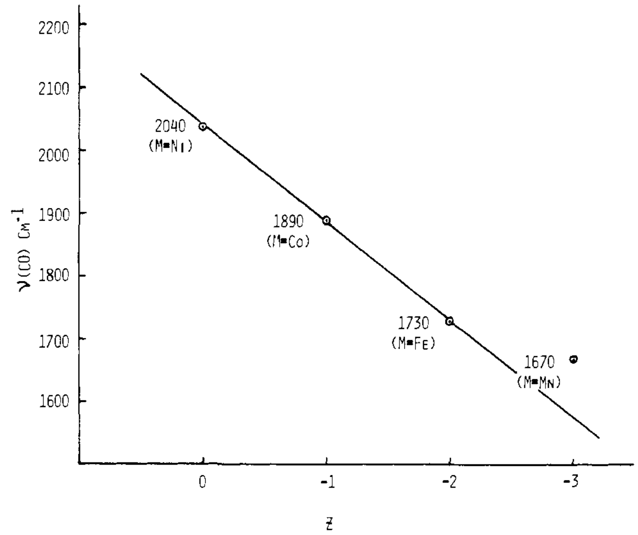

Figure 2. Infrared active carbonyl stretching frequency of $M(CO)_4^z$ as a function of *z*.

spectrum amplitude (Varian XL-100 spectrometer), and the single intense bands in the carbonyl stretching region observed for **1** and **2** (vide infra) are consistent with these formulations. Infrared spectra of these salts also provide indirect evidence that they do not contain $HM(CO)_4^{2-}$, which should have reactivity patterns similar to those of $M(CO)_4^{3-}$. It has been known for several years that the carbonyl stretching frequency for the very intense *E* mode vibration of $HM(CO)_4^z$ (M = Co or Fe) occurs at practically the same position as the corresponding single infrared active vibration of $M(CO)_4^z$ (M = Ni or Co) for $z = 0$ or -1, respectively. In fact, this interesting correspondence was originally cited as evidence that $HM(CO)_4^z$ possessed a tetrahedral structure rather than the correct trigonal bipyramidal geometry.[28] These values are shown in Table I. Extrapolation of this isoelectronic sequence to $z = -2$ indicates that $HMn(CO)_4^{2-}$ should have an intense absorption at ca. 1730 cm^{-1}, rather than the observed value of 1670 cm^{-1} for the manganese reduction product.

Attempts to determine the degree of solvation of the sodium ions in **1** and **2** by proton NMR with internal standards such as benzene or tetramethylsilane have not been successful thus far. An upper limit of $x = 5$ in the tan solids obtained by treatment of HMPA solutions with excess heptane (see Experimental Section) has been established from yields of $(Ph_3Sn)_2M(CO)_4^-$ obtained from these solids. The presence of HMPA in **1** and **2** has been proven by proton NMR and infrared spectroscopy. Interestingly, the HMPA solution and Nujol mull infrared spectra of **1** or **2** are nearly superimposable, except in regions where Nujol absorbs, which suggests that the anions are in similar environments whether in solution or in the solid state.

We have shown that **1** and **2** are unique precursors to new classes of organometallic compounds (vide infra); however, they are also of considerable intrinsic interest because of the very low formal oxidation state of the constituent metals. Indeed, $Re(CO)_4^{3-}$ is the only compound known to contain rhenium in the −3 oxidation state. Now that carbonyl trianions have been synthesized, the question arises as to whether more highly reduced carbonyl species will be stable. That is, can a binary carbonyl anion with a charge of −4 or lower be prepared? This question cannot be answered, presently. However, two obvious factors will be crucial in determining whether such species are characterizable: (1) the susceptibility of coordinated carbon monoxide to reduction and loss from the metal complex, an important but poorly understood area of metal carbonyl chemistry; (2) the ability of coordinated carbon monoxide groups to delocalize negative charge from the metal center and thereby stabilize the complex. A measure of this ability may be obtained by considering a plot of the infrared active carbonyl stretching frequency of $M(CO)_4^z$ as a function of *z* for the first row metal tetracarbonyls (Figure 2). Except for the ν(CO) value for $Co(CO)_4^-$ (1890 cm^{-1} in HMPA) determined in this laboratory, the sources of the band positions are given in Table I. From $Ni(CO)_4$ to $Fe(CO)_4^{2-}$ the ν(CO) values are found to be very nearly a linear function of *z*, which indicates that in this region the carbonyl groups remain relatively unimpaired in their ability to remove charge from the metal center as the value of *z* decreases. However, the observed ν(CO) value for $Mn(CO)_4^{3-}$ (1670 cm^{-1}) lies considerably above the extrapolated value (ca. 1570 cm^{-1}), which suggests that the carbonyl groups in the trianion are unable to remove charge from the metal center as effectively as they do in the less highly reduced tetracarbonyls.[33] Virtually the same curve is also obtained for third row $M(CO)_4^z$, except the carbonyl stretching frequencies are shifted 10-20 cm^{-1} to higher energy.[34-36] Interestingly, similar plots for $M(CO)_5^z$ (for either E′ or A_2'' modes, respectively) provide linear plots (for $z = 0$, -1, -2) of nearly the same slope,[37] which is apparently a measure of the ability of carbonyl groups to remove negative charge from the metal center.[37b] This qualitative treatment indicates that if $Cr(CO)_4^{4-}$ can be made, it should be an extraordinarily potent reducing agent. However, ion pair or covalent effects may be extremely important in the stabilization of highly reduced organometallic anions, as both of these in-

Table II. Infrared Active Carbonyl Stretching Frequencies for $[Et_4N][(Ph_3E)_2M(CO)_4]$ and $(Ph_3PAu)_3M(CO)_4$ Complexes[a]

Compd	ν(CO) (Nujol mull), cm^{-1}	ν(CO) (THF solution), cm^{-1}
$[Et_4N][(Ph_3Ge)_2Mn(CO)_4]$	1898 s	1906 s
$[Et_4N][(Ph_3Ge)_2Re(CO)_4]$	1915 s	1922 s
$[Et_4N][(Ph_3Sn)_2Mn(CO)_4]$	1997 s, 1920 s, 1900 vs	2000 s, 1922 sh, 1913 vs
$[Et_4N][(Ph_3Sn)_2Re(CO)_4]$	2033 m, 1963 m, 1936 s, 1911 vs	2032 m, 1968 m, 1945 sh, 1920 vs
$[Et_4N][(Ph_3Pb)_2Mn(CO)_4]$	2000 s, 1936 s, 1926 vs, 1907 s	2009 s, 1934 vs, 1920 s
$[Et_4N][(Ph_3Pb)_2Re(CO)_4]$	2033 s, 1950 sh, 1941 vs, 1920 vs	2041 m, 1959 vs, 1921 s
$(Ph_3PAu)_3Mn(CO)_4$	1948 s, 1878 sh, 1871 vs, 1860 vs	1954 s, 1882 s, 1867 sh
$(Ph_3PAu)_3Re(CO)_4$	1989 m, 1908 sh, 1901 vs, 1878 s	1999 m, 1922 sh, 1912 vs. 1892 s

[a] m = medium, s = strong, vs = very strong, sh = shoulder.

teractions would effectively remove negative charge from the metal center.

Reactions of $M(CO)_4^{3-}$. I. Triphenyl Group 4A Derivatives, $Et_4N[(Ph_3E)_2M(CO)_4]$. Triphenylgermanium, -tin, or -lead halides (2 equiv) readily react with $M(CO)_4^{3-}$ at room temperature in HMPA to provide species of the general formula $(Ph_3E)_2M(CO)_4^-$. These are isolatable as crystalline, colorless, and air-stable tetraethylammonium salts. No evidence for the formation of neutral trisubstituted complexes was observed when these anions were prepared in the presence of excess Ph_3EX in HMPA or THF. These salts are moderately soluble in acetone, DME, THF, methylene chloride, and HMPA, but insoluble in diethyl ether, benzene, alkanes, and water. In solution, they remain unaffected by air or moisture for several hours.

Their composition and infrared spectra in the carbonyl stretching frequency region are shown in Table II. Although $(Ph_3E)_2M(CO)_4^-$ have infrared spectra which are consistent with those of cis-octahedral complexes, Graham and coworkers have stressed that infrared spectroscopy will not reliably detect a cis-trans mixture because the single carbonyl band of the trans isomer is often coincident with one of the four bands due to the cis isomer.[38] This latter condition is found for several of the isoelectronic and neutral $(R_3E)_2M'(CO)_4$ (M′ = Fe, Ru, and Os) discussed in Graham's work. Interestingly, these substances have been shown to exist in solution as pure cis, pure trans, or a mixture of cis and trans isomers.[38] Several of these neutral species are also known to be stereochemically nonrigid at room temperature[38] and may have pseudo bicapped tetrahedral structures.[39]

Surprisingly, $(Ph_3Ge)_2M(CO)_4^-$ (M = Mn and Re) are pure trans isomers, on the basis of infrared spectra, while the corresponding previously unreported and very Lewis base sensitive $(Ph_3Ge)_2Fe(CO)_4$[40] has an infrared spectrum (ν(CO) in heptane: 2097 s, 2035 vs, 2024 sh, 2020 vs cm^{-1}) almost superimposable with that of $(Ph_3Sn)_2Fe(CO)_4$, which is thought to be entirely the cis isomer.[41] Evidently, steric effects are unimportant in influencing the trans geometry adopted by $(Ph_3Ge)_2Mn(CO)_4^-$, since in *cis*- (or predominantly *cis*-) $(Ph_3Ge)_2Fe(CO)_4$, the iron atom is likely to be smaller than the isoelectronic manganese atom. The relative unimportance of steric effects in influencing the geometries of these species is also emphasized by comparing the structures of $(Ph_3Sn)_2M(CO)_4^-$, which are either pure or predominantly cis isomers,[42] and $(Ph_3Sn)_2M'(CO)_4$ (M′ = Ru and Os) which, unlike the iron analogue, are entirely trans isomers.[41] Clearly, more work is required to determine what factors influence the isomer distribution in these systems, but the recently published theoretical study on the stereochemistry of $L_2M(CO)_4$ complexes represents an important contribution in this regard.[39]

The reaction of Ph_3GeBr with $[M(CO)_4]^{3-}$ is anomalous in two respects: it generates the trans isomers $[(Ph_3Ge)_2M(CO)_4]^-$, and the yield is only 20-45%. Infrared spectra following addition of Ph_3GeBr to $M(CO)_4^{3-}$ in HMPA show that appreciable amounts of an uncharacterized highly reduced species, possibly $Ph_3GeM(CO)_4^{2-}$ (for M = Re, ν(CO): 1896 s, 1790 m, 1769 vs cm^{-1}), form along with $(Ph_3Ge)_2M(CO)_4^-$ (M = Re, ν(CO): 1914 vs cm^{-1}). Similar low-energy bands are not observed in the reactions of any of the other R_3EX species with $M(CO)_4^{3-}$. Addition of water during the isolation of *trans*-$(Ph_3Ge)_2M(CO)_4^-$ destroys the highly reduced species to provide a yellow-green species which could not be obtained free of *trans*-$(Ph_3Ge)_2M(CO)_4^-$ after several fractional recrystallizations. The nature of the hydrolysis product, possibly *cis*-$(Ph_3Ge)HMn(CO)_4^-$ (ν(CO) in CH_2Cl_2: 2007 m, 1961 sh, 1906 vs cm^{-1}), is still under investigation.

II. Trimethyl Group 4A Derivatives, $Ph_4As[(Me_3E)_2M(CO)_4]$. The unexpected trans geometry observed for $(Ph_3Ge)_2M(CO)_4^-$ prompted us to prepare the analogous bistrimethylgermyl- and bistrimethylstannyl-substituted anions to help shed more light on this interesting isomer problem. Syntheses of these anions were carried out in the same manner as for the $(Ph_3Sn)_2M(CO)_4^-$ species, except precipitation with aqueous Ph_4AsCl rather than Et_4NBr was employed to avoid cation interference in the methyl proton resonance region. Generally, the salts were more difficult to crystallize than corresponding triphenylmetallo species. They exhibited moderate affinity for HMPA. It was necessary to elute their solutions through rather long (10-12-cm) columns of silica gel to remove the last traces of the polar solvent. The crystalline compounds slowly decomposed after several days exposure to air, and exhibited melting points around 100 °C lower than the analogous $[(Ph_3E)_2M(CO)_4]^-$ salts. Readily dissolving in acetone, CH_2Cl_2, THF, and diethyl ether, the trimethylmetallo complexes were also moderately soluble in aromatics, but completely insoluble in alkanes and water.

Spectral data for $(Me_3E)_2M(CO)_4^-$ are shown in Table III. All have carbonyl stretching frequencies lower than those of corresponding bands for $(Ph_3E)_2M(CO)_4^-$, in accord with the expected greater electron donor ability of the Me_3E groups vs. that of the Ph_3E groups. The band patterns are consistent with those expected for pure cis-disubstituted tetracarbonyls. Additionally, proton NMR spectra of $(Me_3E)_2M(CO)_4^-$ show only one sharp singlet in $CDCl_3$ at 9.95 τ. For E = Sn, M = Mn, the spectrum remains essentially unchanged except for slight viscosity broadening down to −80 °C, which implies either pure cis geometry, extremely facile cis-trans isomerization even at this temperature, or accidental degeneracy of the proton resonances for the *cis*-methyl and *trans*-methyl groups. The latter seems unlikely to occur in all four complexes; however, extremely facile cis-trans isomerization even at low temperature remains a possibility, since Graham and coworkers have shown for $(Me_3E)_2Fe(CO)_4$ (E = Si, Ge, and Sn) rapid interconversion of isomers at room temperature with coalescence occurring at −20 °C for E = Ge, −55 °C for E = Si, and −75 °C for E = Sn.[38] By contrast, however, the corresponding ruthenium and osmium analogues which are cis-trans mixtures exhibited two methyl proton NMR resonances that coalesced in the range of 80-100 °C.[38,43] To obtain unambiguous information on the isomer distribution in (Me3-

Table III. Spectral Data for $Ph_4As[(Me_3E)_2M(CO)_4]$ Complexes[a]

Compd	ν(CO) (Nujol mull), cm^{-1}	ν(CO) (CH_2CL_2), cm^{-1}	NMR ($CDCl_3$), τ
$Ph_4As[(Me_3Ge)_2Mn(CO)_4]$	1981 s, 1900 s, 1887 vs, 1868 s	1983 s, 1891 sh, 1880 vs,br	9.95 (methyl)
$Ph_4As[(Me_3Ge)_2Re(CO)_4]$	2013 m, 1923 s, 1904 vs, 1874 vs	2013 m, 1912 vs,br, 1883 s	9.95 (methyl)
$Ph_4As[(Me_3Sn)_2Mn(CO)_4]$	1977 s, 1896 vs, 1886 vs, 1867 s	1976 s, 1890 sh, 1886 sh, 1877 vs	9.95 (methyl) J_{Sn-H} = 40 Hz
$Ph_4As[(Me_3Sn)_2Re(CO)_4]$	2008 s, 1921 s, 1906 vs, 1877 s	2008 m, 1909 vs,br, 1893 sh	9.95 (methyl) J_{Sn-H} = 40 Hz

[a] m = medium, s = strong, vs = very strong, sh= shoulder, br = broad.

$E)_2M(CO)_4^-$, we have begun to investigate the carbon-13 NMR spectra of these systems. The results of this study will be reported at a later date.

III. Triphenylphosphine Gold Derivatives, $(Ph_3PAu)_3M(CO)_4$. Interaction of $M(CO)_4^{3-}$ with 3 equiv of Ph_3PAuCl led to the formation of materials which have elemental analyses, molecular weights, and infrared spectra consistent with the formulation $(Ph_3PAu)_3M(CO)_4$, the first neutral seven-coordinate derivatives of manganese and rhenium carbonyl. Triphenylphosphinegold is unusual in its ability to stabilize organometallic complexes in high coordination number. The syntheses of these complexes as well as the eight-coordinate $(Ph_3PAu)_3V(CO)_5$[44] represent the most dramatic examples of this stabilizing ability. In contrast, none of the $(R_3E)_2M(CO)_4^-$ derivatives discussed earlier showed any tendency to add a third R_3E^+ group. Spectra of $(Ph_3PAu)_3M(CO)_4$ in HMPA show that these substances are completely ionized according to the equation:

$$(Ph_3PAu)_3M(CO)_4 + n\text{HMPA} \rightarrow Ph_3PAu(\text{HMPA})_n^+ + (Ph_3PAu)_2M(CO)_4^-$$

For example, the manganese complexes had bands in HMPA at 1900 s and 1812 vs cm^{-1} (broad). Addition of water to such solutions causes precipitation of the neutral seven-coordinate species which absorb at considerably higher energy than the anions (see Table II).

The bright yellow manganese complex and the golden rhenium analogue were moderately soluble in acetone, THF, and CH_2Cl_2, slightly soluble in benzene and diethyl ether, and insoluble in water and alkanes. They were completely air stable when pure, but somewhat temperature sensitive. Samples stored in the dark under argon at room temperature darkened appreciably in a month.

IV. Reactions of $Mn(CO)_4^{3-}$ with Benzyl Chloride and Water. Although many products from the reactions of $M(CO)_4^{3-}$ with alkyl halides are presently uncharacterized and will be the subject of a future paper in this series, benzyl chloride has been shown to provide the bisphenylacetyl complex $(PhCH_2CO)_2Mn(CO)_4^-$, isolated as a light yellow tetraphenylarsonium salt in 45% yield. Undoubtedly, the low yield results from the decomposition of less highly carbonylated precursors, but the nature of these materials is presently unknown.

Elemental analyses are unable to differentiate between $[(PhCH_2CO)_2Mn(CO)_4]^-$ and $[(PhCH_2)(PhCH_2CO)Mn(CO)_4]^-$. However, the proton NMR of the product in $CDCl_3$ shows only one benzyl proton resonance (8.30 τ), which is consistent with the proposed formulation. Infrared spectra also fully support the acyl formulation and together with the NMR data are consistent with an anion of cis geometry (ν(CO) as mull: 2006 m, 1908 vs, 1889 s, 1876 vs, 1593 m cm^{-1}; in CH_2Cl_2: 2014 m, 1924 vs, 1918 sh, 1868 s, 1591 m cm^{-1}).

Similar complexes have been prepared from the reaction of acylmanganesepentacarbonyls with alkyllithium reagents.[45] As indicated in the introduction, these materials function as metalloacetylacetonates, an important new class of metal containing ligands.[4] Curiously, only fluorinated diacyl neutral complexes of iron, such as $(CF_2HCF_2CO)_2Fe(CO)_4$,[46] are known presently.

Protonation of $Mn(CO)_4^{3-}$ causes immediate formation of a purple color, which after metathesis with aqueous Et_4NBr provided a thermally unstable purple salt, identical with that obtained previously by treatment of $Mn_2(CO)_{10}$ with KOH and Et_4NBr.[17] Acidification of this salt gave moderate (~35%) yields of substance identical with genuine $[HM(CO)_4]_3$. Effectively, in this reaction, the very potent reducing agent $Mn(CO)_4^{3-}$ is oxidized by water. We also have evidence that a variety of other easily reducible electrophilic species, such as thiophosgene, are preferentially reduced rather than added to the trianions. Details on these reactions will be the subject of a future paper in this series.

Concluding Remarks

Our initial studies with $M(CO)_4^{3-}$, the first members of a new class of highly reduced organometallics, have shown them to be valuable and often unique precursors to new organometallic compounds. For example, attempts to prepare $(R_3E)_2M(CO)_4^-$ from R_3ELi and $R_3EM(CO)_5$ invariably result in the formation of $(R_3E)_2$ and $M(CO)_5^-$ rather than the desired products. Further studies to elucidate the basic reactivity patterns of these trianions as well as those of other recently discovered "super-reduced" species which behave as $Na_3V(CO)_5$[44] and $Na_3Co(CO)_3$[47] are underway in our laboratory and will be reported in due course.

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(34) The value for $Pt(CO)_4$ (2054 cm^{-1}) was obtained in a frozen argon matrix by Ozin and co-workers;[35] $Ir(CO)_4^-$ is apparently an unknown species, but should absorb in approximately the same position as $Rh(CO)_4^-$ (1900 cm^{-1} in THF).[36] Solution spectra of $Na_2Os(CO)_4$ (1738 cm^{-1})[29] and $Re(CO)_4^{3-}$ (1690 cm^{-1}) were obtained in this laboratory in HMPA.
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A Comparative Study of the Chemistry of the Diastereomers of η^5-$C_5H_5FeCO[P(OPh)_3]CHPhSiMe_3$

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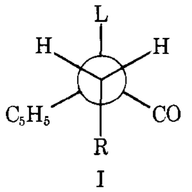
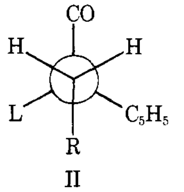
Abstract: Reaction of racemic or resolved η^5-$C_5H_5FeCO[P(OPh)_3]I$ with racemic $Me_3SiPhCHMgBr$ gives a mixture of the two diastereomers of η^5-$C_5H_5FeCO[P(OPh)_3]CHPhSiMe_3$ at low temperatures. Selective decomposition of the *RR,SS* diastereomer, predicted to be the more highly hindered, occurs above room temperature, however, leading to the isolation of the pure *RS,SR* isomer. Sulfonylation reactions of both diastereomers are reversible and provide a novel route, via the diastereomeric sulfinate complexes, to epimerization of the alkyl complexes. Kinetic and thermodynamic studies in SO_2-$CDCl_3$ mixtures show that although (*RS,SR*)-η^5-$C_5H_5FeCO[P(OPh)_3]CHPhSiMe_3$ (**1**) is the thermodynamically more stable diastereomer, (*RR,SS*)-η^5-$C_5H_5FeCO[P(OPh)_3]CHPhSiMe_3$ (**2**) can be formed in disproportionate amounts by the interaction of **1** with SO_2.

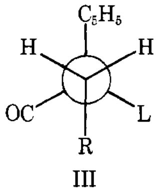
We have recently shown that primary alkyl-iron complexes of the type η^5-$C_5H_5FeCOLCH_2R$ (L = phosphorus donor; R = Ph, $SiMe_3$, 1-naphthyl) exist in solution as three staggered rotamers, I, II, and III.[1] On the apparently valid assumption that vicinal coupling constants, $^3J_{PH}$, between the phosphorus and the protons on the α-carbon atom of the alkyl group decrease in the order trans ≫ gauche, it was concluded that interconversion between rotamers is rapid on the NMR time scale and that ligand steric requirements determine rotamer populations. Since the order of ligand steric requirements is η^5-C_5H_5 > L > CO, III was found to be the most stable rotamer.



I



II



III

In this paper we extend our investigations to secondary alkyl complexes of the types η^5-$C_5H_5FeCOLCHRR'$. These should exist as mixtures of diastereomers, the relative stabilities of which should be affected by the sizes of the ligands on the iron