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XI *. FORMAL DERIVATIVES OF THE TRICARBONYLMETALLATES (6 –) OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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Summary

Reduction of $W(CO)_3(PMTA)$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) by six equivalents of potassium metal in liquid ammonia provides an incompletely characterized highly reduced carbonyltungstate ion which reacts with several electrophiles to provide derivatives containing only tungsten tricarbonyl units. These include $W(CO)_3(NH_3)_3$, $[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$, $HW(CO)_3(SnPh_3)_3{}^{2-}$ and the unusual $[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^-$. The latter compound results from an unprecedented phenyl-tin cleavage in the reaction of triphenyltin chloride and the highly reduced carbonyltungstate ion. Triphenyltin derivatives of the unknown $M(CO)_3{}^{6-}$ (M = Cr, Mo and W) have also been prepared by reacting $M(CO)_3(SnPh_3)_3{}^{3-}$ with Brønsted acids and Ph_3SnCl. From these reactions the previously unknown $HM(CO)_3(SnPh_3)_3{}^{2-}$ (M = Cr, Mo and W) and $M(CO)_3(Ph_3Sn)_4{}^{2-}$ (M = Mo and W) have been isolated and characterized. The latter are the first compounds containing more than three triphenyltin units attached to one transition metal.

Introduction

During the past several years our research group has used the "reductive labilization method" to synthesize several new compounds, including the first examples of substances formally containing carbonylmetallate tetraanions, i.e., $Na_4M(CO)_4$, where M = Cr, Mo, W [2]. This method is based on the important generalization that reduction of a non-cluster metal compound containing both good and poor π-acceptor ligands often causes preferential loss of the weaker or non-π acceptor groups. Thus, in the Na-NH_3 reduction of $M(CO)_4(TMED)$, M = Cr, Mo,

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W; TMED = N,N,N',N'-tetramethylethylenediamine, the TMED was effectively replaced by four electrons to produce $Na_4M(CO)_4$ in high (> 90%) yields; i.e.,

$$M(CO)_4(TMED) + 4Na \rightarrow Na_4M(CO)_4 + TMED \quad (1)$$

It occurred to us that since two nitrogen ligands can be formally replaced by four electrons then it might be possible to replace three nitrogen ligands by six electrons to yield the rather improbable "carbonylmetallate hexaanions", $M(CO)_x^{6-}$, provided the displaced ligands were not susceptible to attack by alkali metals in liquid ammonia:

$$M(CO)_3(NR_3)_3 + 6A \overset{?}{\rightarrow} A_6M(CO)_3 + 3NR_3 \quad (2)$$

(A = Alkali metal)

For these reasons, we examined the alkali metal reductions of $M(CO)_3(NR_3)_3$ (M = Cr, Mo, W) in liquid ammonia. In this paper are presented some of our observations from this study. Of particular interest is the reaction of a highly reduced carbonyltungstate ion with Ph_3SnCl to give a product which contains diphenyltin units coordinated to the tungsten. This is apparently the first report of a C–Sn bond cleavage resulting from the reaction of a carbonyl anion with an organotin halide.

Experimental

General procedures and starting materials. All operations were performed under an atmosphere of nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred via stainless steel cannulae and syringes; otherwise reactions were generally performed by using standard Schlenk apparatus with a double manifold vacuum line. Ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade acetonitrile was dried with CaH_2, freed of oxygen by a nitrogen purge and distilled immediately before use. Reagent grade tetrahydrofuran and diethyl ether were distilled from alkali metal benzophenone ketyls before use. Reagent grade acetone, heptane, absolute ethanol, and isopentane were freed of oxygen by bubbling nitrogen through the solvents for one to two hours before use and were used without further purification. A published procedure was followed for the preparation of $M(CO)_3(PMTA)$ (M = Cr, Mo, W; PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) [3]. All other reactants and solvents were obtained from commercial sources. Triphenyltin chloride was carefully recrystallized from hot hexane.

Infrared spectra were recorded on a Perkin–Elmer 283 grating spectrometer in 0.1 mm sealed NaCl cells, equipped with Becton-Dickinson steel stopcocks to permit filling outside of the dry box. Nujol mulls of air sensitive compounds were prepared in a Vacuum Atmospheres Corporation dry box under continuously recirculating nitrogen. NMR samples sealed into 5 mm Pyrex tubes were run on a Varian FT-80 or XL-100 spectrometer. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by Galbraith Laboratories or H. Malissa and G. Reuter Analytische Laboratorien, Engelskirchen, Germany.

Potassium metal reduction of $W(CO)_3(PMTA)$

Approximately 80 ml of ammonia was condensed into a vessel containing six equivalents of potassium metal (0.75 g, 19.2 mmol) and $W(CO)_3(PMTA)$ (1.40 g, 3.2 mmol) at −78°C. After about 6 h at −33°C the blue color of the K-NH_3 solution was discharged leaving a finely divided green solid suspended in a colorless solution. The slurry was filtered at low temperature (< −40°C) onto a medium porosity fritted disc. After the insoluble product was washed with 50 ml of liquid ammonia in several small portions, it was dried for 12 h at room temperature to yield 1.34 g of powdery green solid. Elemental analysis of the solid gave the following percentage composition: C, 8.28; H, 0.83; N, 2.95; K, 33.08; W, 41.79 corresponding to an empirical formula of $C_{3.0}H_{3.6}N_{0.9}K_{3.7}W_{1.0}$. From the filtrate was isolated a tan solid identified as KNH_2 by comparison of its infrared spectrum (Nujol mull: $\nu(NH_2)$: 3260s, 3208s; $\delta(NH_2)$: 1542s, cm^{-1}) to that previously reported ($\nu(NH_2)$: 3258s, 3210s; $\delta(NH_2)$; 1546s, cm^{-1}) [4].

Cesium metal reduction of $W(CO)_3(PMTA)$

By using the same procedure described above, 0.87 g (2.0 mmol) of $W(CO)_3(PMTA)$ was treated with 1.57 g (11.8 mmol) of cesium metal in 100 ml of liquid ammonia at −33°C for 12 h. The product was then filtered at −78°C, washed with 100 ml of liquid ammonia in several portions and dried in vacuo. A pyrophoric greenish-tan product (0.93 g) was obtained. Elemental analysis gave the following percentage composition: C, 5.50; H, 0.37; Cs, 55.03; W, 21.67, which corresponds to an empirical formula of $C_{3.9}H_{3.1}Cs_{3.5}W_{1.0}$.

Preparation of $W(CO)_3(NH_3)_3$ (I) by the reaction of the potassium reduction product with NH_4Cl

A sample of the potassium reduction product was prepared as described above from $W(CO)_3(PMTA)$ (0.67 g, 1.5 mmol) and potassium (0.36 g, 9.2 mmol) in 80 ml of liquid ammonia. To the resulting green slurry was added at −78°C, 0.95 g (17.8 mmol) of NH_4Cl in small portions from a Schlenk tube bent to facilitate addition of a solid. On warming, vigorous gas evolution occurred while the green solid dissolved to form a yellow solution. Distilled water (20 ml) was added slowly to the liquid ammonia solution. After most of the ammonia evaporated, the product crystallized from solution. The yellow solid was filtered and dried in vacuo at room temperature overnight to provide 0.18 g (29% yield) of analytically pure $W(CO)_3(NH_3)_3$.

Anal. Found: C, 11.19; H, 2.98; N, 13.29. $C_3H_9N_3O_3W$ calcd.: C, 11.30; H, 2.85; N, 13.17%.

This compound has been previously reported and was characterized by gas analysis only [5].

Preparation of $[Me_4N]_3[W_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}OEt)_2]$ (II) from the potassium reduction product

A sample of the potassium reduction product was prepared in situ as described previously from $W(CO)_3(PMTA)$ (1.76 g, 4.0 mmol) and potassium (0.94 g, 24.0 mmol) in 60 ml of liquid ammonia. Tetramethylammonium chloride (2.63 g, 24.0 mmol) was added as a dry solid and the mixture was left to stir for 12 h as the ammonia evaporated. Infrared examination showed that the solid green reduction product had not reacted with $[Me_4N]Cl$. Acetonitrile (80 ml) was then added to the

solid, followed by 20 ml of absolute ethanol which caused the precipitation of a small amount of bright orange crystals. These were recrystallized from CH_3CN EtOH to provide 0.04 g (yield < 1%) of bright red-orange plate-like crystals of product which was identical to bonafide (II). This product has been previously prepared in 66% yield by the reaction of $W(CO)_3$(PMTA) with NaOEt and was characterized by a single crystal X-ray diffraction study [3].

Preparation of $[Ph_4P][(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]$ (III) from the potassium reduction product

In a typical preparation, 0.97 g (2.2 mmol) of $W(CO)_3$PMTA was reduced in liquid ammonia (60 ml) with 0.52 g (13.2 mmol) of potassium to provide the green reduction product. This was treated in situ with a solution of Ph_3SnCl (5.08 g, 13.2 mmol) in cold (−78°C) THF (100 ml) which was added by cannula. A dark yellow solution formed after stirring for 4 h at −78°C. The solution was then allowed to slowly warm to room temperature overnight. After all solvent was removed at or below room temperature, the residue was treated with excess Ph_4PBr in absolute ethanol (50 ml). The solid was filtered and recrystallized several times from CH_3CN/Et_2O and CH_2Cl_2/Et_2O to provide 0.52 g (12%) of nearly colorless and crystalline (III). The essentially air stable crystals lose all CH_2Cl_2 of crystallization when heated to 100°C in vacuo for 24 h to provide the unsolvated analytical sample.

Anal. Found: C, 56.51; H, 3.94; P, 1.93; W, 9.86. $C_{89}H_{75}O_4PSn_4W$ calcd.: C, 56.30; H, 3.99; P, 1.63; W, 9.68%. Compound III decomposes above 210°C.

Preparation of $[Me_4N]_2[HW(CO)_3(SnPh_3)_3]$ (IV) from the potassium reduction product

The green reduction product was prepared in situ in the usual fashion from 1.94 g (4.4 mmol) of $W(CO)_3$PMTA and 1.03 g (26.4 mmol) of potassium metal in 100 ml of liquid ammonia. After 8 h reflux at −33°C, the solution was cooled to −78°C and 5.09 g (13.2 mmol) of Ph_3SnCl in 100 ml of cold (−78°C) THF was added rapidly by cannula. On warming to −33°C the green solid changed to a turbid yellow solution after one hour. The ammonia was then allowed to evaporate for about 12 h giving a brown solution to which was added a solution of excess Me_4NCl (10 g) in 500 ml of water. The crude brown solid was filtered, washed with ethanol, and dried. Recrystallization from CH_3CN/EtOH gave 0.40 g (12% yield) of crystalline IV which was spectroscopically identical to bona fide IV prepared from $W(CO)_3$PMTA and Ph_3SnLi (vide infra). In all of these preparations of IV from the green reduction product, considerable amounts of the anion in compound III also form, but most of the latter is separated from IV in the recrystallization step.

$[Me_4N]_2[HW(CO)_3(SnPh_3)_3]$ (IV) and $[Et_4N]_2[HW(CO)_3(SnPh_3)_3]$ (V) from the protonation of $W(CO)_3(SnPh_3)_3^{3-}$ (VI)

A solution of Ph_3SnLi was prepared by stirring a solution of Ph_3SnCl (2.34 g, 6.1 mmol) in 50 ml of THF with excess lithium wire (0.35 g, 50.7 mmol) at room temperature. After 12 h, the deep green solution was added by cannula to 0.89 g (2.0 mmol) of crystalline $W(CO)_3$(PMTA). After approximately 4 h of refluxing, the resulting solution of (VI), $W(CO)_3(SnPh_3)_3^{3-}$, (see Discussion) was cooled to room temperature and was treated with 0.24 g (4.0 mmol) of glacial acetic acid in THF (20 ml). The solvent was removed in vacuo to give a deep green glass which was stirred

for 12 h at room temperature with 0.66 g (6.1 mmol) of Me_4NCl in 20 ml of absolute ethanol. Recrystallization of the crude material from $CH_3CN/EtOH$ gave 1.32 g (44%) of pale yellow crystalline IV which gave a satisfactory analysis.

Anal. Found: C, 53.03; H, 4.90. $C_{65}H_{70}N_2O_3Sn_3W$ calcd.: C, 53.20 H, 4.82% Compound IV decomposes above 230°C.

From an essentially identical reaction and purification procedure a 36% yield of V was obtained which also analyzed satisfactorily.

Anal. Found: C, 55.43; H, 5.55; N, 1.71. $C_{73}H_{86}N_2O_3Sn_3W$ calcd.: C, 55.51; H, 5.49; N, 1.77%. Compound V decomposes above 197°C.

Both IV and V are air sensitive in solution but may be handled briefly in air as crystalline solids.

$[Et_4N]_2[HMo(CO)_3(SnPh_3)_3]$ (VII) from the protonation of $Mo(CO)_3(SnPh_3)_3^{3-}$ (VIII)

A solution of Ph_3SnLi (4.7 mmol) prepared as described above was prepared in 20 ml of THF and was added to 0.55 g (1.6 mmol) of $Mo(CO)_3$(PMTA). After about 0.5 h of refluxing, $Mo(CO)_3(SnPh_3)_3^{3-}$ (VIII) was shown to be the major product in solution by infrared spectroscopy (see Discussion). The solvent was then removed in vacuo and the glassy residue was stirred for 12 h with 1.96 g (9.3 mmol) of Et_4NBr in absolute ethanol (20 ml). Recrystallization of the crude material from acetone/ether provided 0.91 g (39%) of pale yellow crystalline VII of satisfactory purity.

Anal. Found: C, 58.89; H, 5.63; N, 1.92. $C_{73}H_{86}N_2MoO_3Sn_3$ calcd.: C, 58.78; H, 5.82; N, 1.88%. Compound VII decomposes above 135°C.

$[Et_4N]_2[HCr(CO)_3(SnPh_3)_3]$ (IX) from the protonation of $Cr(CO)_3(SnPh_3)_3^{3-}$ (X)

As described above, a solution of X in 50 ml of THF was prepared by reacting approximately 10.8 mmol of Ph_3SnLi with 0.93 g (3.0 mmol) of $Cr(CO)_3$(PMTA) under reflux for 2 h. Solvent was removed and the residue was treated with excess Et_4NBr (3.8 g) in EtOH (50 ml). The crude (IX) was recrystallized several times from $CH_3CN/EtOH$ to yield 0.63 g (14%) of crystalline yellow product.

Anal. Found: C, 59.67; H, 6.15; N, 1.80. $C_{73}H_{86}N_2CrO_3Sn_3$ calcd.: C, 60.23; H, 5.95; N, 1.92%. Compound IX decomposes above 183°C.

$[Ph_4P]_2[W(CO)_3(SnPh_3)_4]$ (XI)

A solution of VI prepared as before from 0.87 g (2.0 mmol) of $W(CO)_3$(PMTA) with approximately 5.9 mmol of Ph_3SnLi in THF, was treated with a solution of Ph_3SnCl (1.52 g, 4.0 mmol) in 30 ml of THF. After the solvent was removed, the residue was stirred for 12 h with a solution of Ph_4PBr (1.68 g, 4.0 mmol) in CH_2Cl_2 (50 ml). Crystallization from $CH_2Cl_2/EtOH$ and CH_2Cl_2/Et_2O and drying at 70°C in vacuo for 24 h provided 1.35 g (29%) of pale yellow and crystalline XI.

Anal. Found: C, 62.59; H, 4.23; Sn, 20.17. $C_{123}H_{100}O_3P_2Sn_4W$ calcd.: C, 62.94; H, 4.30; Sn, 20.23%. Compound XI decomposes above 197°C.

$[Et_4N]_2[Mo(CO)_3(SnPh_3)_4]$ (XII)

As described above, a solution containing ca. 1.6 mmol of VIII in THF was treated with Ph_3SnCl (1.19 g, 3.1 mmol). After stirring for 12 h, the solvent was removed and the residue was metathesized with an alcoholic solution of excess

Et_4NBr. Crystallization from $CH_3CN/EtOH$ provided 1.82 g (64%) of pale yellow and crystalline XII of satisfactory purity.

Anal. Found: C, 59.05; H, 5.52; Mo, 5.27; Sn, 25.80. $C_{91}H_{100}MoN_2O_3Sn_4$ calcd.: C, 59.38; H, 5.49; Mo, 5.21; Sn, 25.80%. Compound XII decomposes above 200°C.

Infrared and ^1H NMR data for most of these products are summarized in Tables 1 and 2.

Results and discussion

Alkali metal reductions of $W(CO)_3$(PMTA)

When liquid ammonia is condensed into a vessel containing six equivalents of alkali metal and $W(CO)_3$(PMTA), almost immediately an intense blue solution is formed, which is characteristic of solutions of alkali metals in liquid ammonia. Reduction of the complex is extremely slow at −78°C, but at −33°C it is usually complete within 4–6 h when K or Cs metal is employed. The reduction products precipitate as olive green (M = K) or pale green, nearly tan (M = Cs) solids which are extremely oxygen and moisture sensitive. Corresponding lithium and sodium reductions of $W(CO)_3$(PMTA) have not been examined in any detail, but these appear to provide similar products which are heavily contaminated with insoluble MNH_2 (M = Li, Na). The potassium reduction product was generally used in further studies since it was readily separated from KNH_2 by virtue of the good solubility of the latter in liquid ammonia.

Elemental analyses of the potassium and cesium amide free reduction products show that the alkali metal to tungsten ratios are similar (K/W = 3.7/1 and Cs/W = 3.5/1). Silicone fluid mull spectra of these materials (Figs. 1a and 1b) also closely match one another suggesting that similar species are present. It is definite that we have not formed $M_6[W(CO)_3]$ (M = K, Cs) but rather partially reduced materials (probably a mixture) which precipitate out of liquid ammonia before further reduction is possible. The remaining alkali metal then slowly reacts with ammonia to form amide salts. The exact natures of these reduced materials are unknown. Presently, we have a working hypothesis that these materials are mononuclear hydrides, perhaps a mixture of $H_2W(CO)_3^{4-}$ and $H_3W(CO)_3^{3-}$, but the elemental analyses, which also indicate the presence of approximately one nitrogen per tungsten are not consistent with this simple picture. We are fairly confident, however, that only reduced $W(CO)_3$ species are present since all derivatives prepared from these reduction products contain only $W(CO)_3$ units.

A closer examination of the mull infrared spectra of the potassium and cesium reduction products (Fig. 1) reveals two intense bands at ca. 1800 and 1630 cm^{-1}. These are roughly in the region where carbonylmetallate trianion salts such as $Na_3Mn(CO)_4$ [6] and $Cs_3V(CO)_5$ [7] absorb. These bands rapidly disappear on exposure of the mulls to air. The bands at 1445 and 1411 cm^{-1} are due to the silicone fluid mulling agent. This material was used rather than the more conventional mineral oil or Nujol since its absorptions in the 1500–1300 cm^{-1} region are weaker than those for Nujol. Fluorolube could not be used in this regard as it rapidly reacts with the reduction products. Fluorolube has also been observed to decompose, sometimes explosively, with $Na_4M(CO)_4$ [2].

Alkali metal reductions of $Cr(CO)_3$(PMTA) and $Mo(CO)_3$(PMTA) in liquid ammonia were also examined briefly [8a]. Both products obtained from potassium

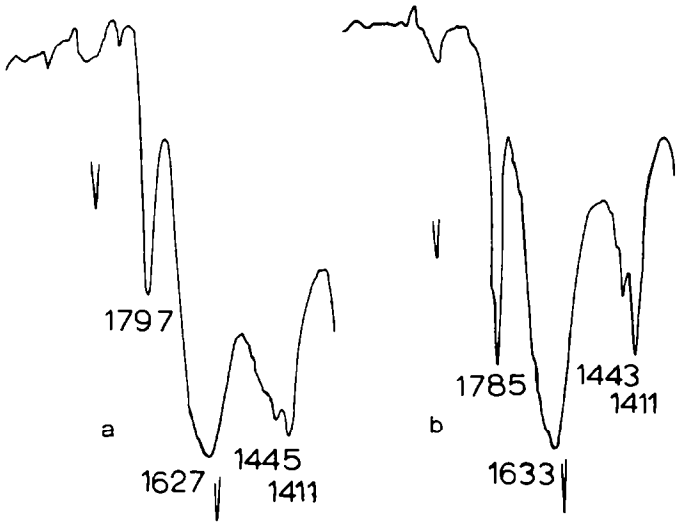


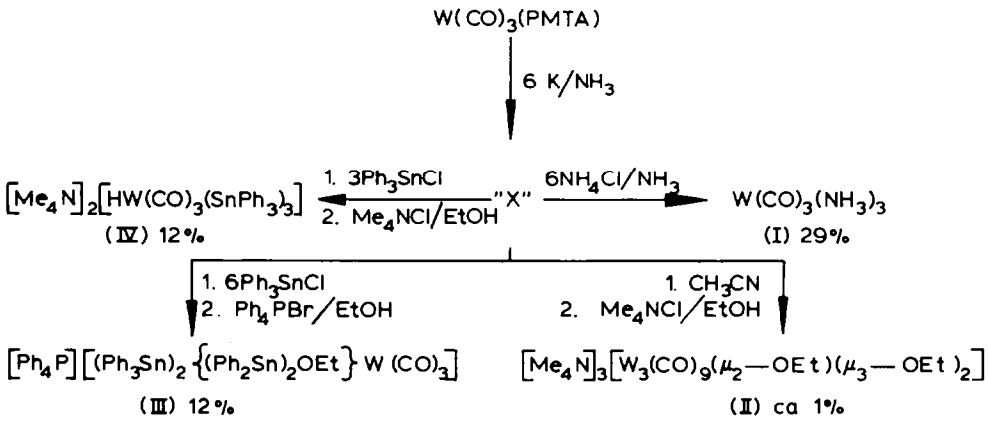
Fig. 1. Silicone oil infrared mull spectra of the product resulting from the reduction of $W(CO)_3(PMTA)$ with (a) six equivalents of potassium metal and (b) six equivalents of cesium metal. Positions of bands are in cm^{-1}, polystyrene calibration peaks are at 1944 and 1602 cm^{-1}. Bands due to silicone oil are at 1443 and 1411 cm^{-1}.

reductions had very similar mull infrared spectra to those reported for the corresponding tungsten species (for Cr species ν(CO): 1782m, 1600s, very broad cm^{-1}; for Mo species ν(CO): 1812m, 1635s broad cm^{-1}) but gave extremely low to no yields of derivatives. For the latter reason no further studies on these materials have been carried out.

Reactions of the $W(CO)_3(PMTA)$-potassium reduction product

As shown in Scheme 1, all products isolated from the reaction of the uncharacterized potassium reduction product (signified by "X") with various electrophiles contain only $W(CO)_3$ units.

SCHEME 1



The actual yields of the products I–IV are probably much higher than the yields shown for the analytically pure samples. For example, before recrystallization, I was obtained in 67% yield and found to have an infrared spectrum essentially superimposable with the analytical sample from 4000–625 cm^{-1}. The formation of I by the reaction of "X" with NH_4Cl is noteworthy since several other highly reduced carbonyl anions also undergo protonation in liquid ammonia to provide amine complexes. Two examples of such reactions are shown in eqs. 3 and 4.

$$Na_3V(CO)_5 + 2NH_4^+ \rightarrow NaV(CO)_5NH_3 + H_2 + NH_3 + 2Na^+ \quad (90\text{–}95\% \text{ yields}) \qquad (3)\ [7]$$

$$Na_4Mo(CO)_4 + 4NH_4^+ \rightarrow Mo(CO)_4(NH_3)_2 + 2H_2 + 2NH_3 + 4Na^+ \quad (70\text{–}75\% \text{ yields}) \qquad (4)\ [18]$$

Compound I was originally reported over 20 years ago [5] but very little spectroscopic data for this substance has appeared in the literature [8b]. Its infrared spectrum (Table 1) shows the two band pattern in the ν(CO) region expected for a $L_3M(CO)_3$ species of C_{3v} symmetry and is similar to that reported previously for $Mo(CO)_3$dien (ν(CO) 1898, 1758 cm^{-1} in CH_3NO_2) [9]. The ^1H NMR of I in dimethylsulfoxide-d_6 (Table 2) shows a broad signal at about 2.2 ppm attributable to the coordinated NH_3 group. The latter are also clearly observed in the infrared spectrum of I (see Table 1).

Very low yields of II were isolated from the reaction of "X" with acetonitrile followed by Me_4NCl metathesis in ethanol. From the initial reaction with acetonitrile

TABLE 1

INFRARED SPECTRA OF COMPOUNDS IN THE CARBONYL STRETCHING FREQUENCY REGION [a]

Compound		Medium	ν(CO) (cm^{-1})
$W(CO)_3(NH_3)_3$	(I)	Nujol mull	1872m, 1702s, br [b]
$[Ph_4P][(Ph_3Sn)_2((Ph_2Sn)_2OEt)W(CO)_3]$	(III)	Nujol mull	1947w, 1870sh, 1844s
		CH_3CN	1945w, 1861m, 1842s
$[Me_4N]_2[HW(CO)_3(SnPh_3)_3]$	(IV)	CH_3CN	1928w, 1835sh, 1814s
$[Et_4N]_2[HW(CO)_3(SnPh_3)_3]$	(V)	Nujol mull	1928w, 1826s, br, 1812s, br
		CH_3CN	1925w, 1831sh, 1813s
$Li_3[W(CO)_3(SnPh_3)_3]$ [c]	(VI)	THF	1837s, 1717s, 1659s
$[Et_4N]_2[HMo(CO)_3(SnPh_3)_3]$	(VII)	Nujol mull	1930m, 1834sh, 1815s
		CH_3CN	1931w, 1824s
$Li_3[Mo(CO)_3(SnPh_3)_3]$ [c]	(VIII)	THF	1842s, 1715s, 1660s
$[Et_4N]_2[HCr(CO)_3(SnPh_3)_3]$	(IX)	Nujol mull	1881m, 1801sh, 1784s
		CH_3CN	1911w, 1802s
$Li_3[Cr(CO)_3(SnPh_3)_3]$ [c]	(X)	THF	1825s, 1801sh, 1706s, 1658vs
$[Ph_4P]_2[W(CO)_3(SnPh_3)_4]$	(XI)	Nujol mull	1897w, 1832s, br, 1815s, br
		CH_3CN	1900w, 1834s
$[Et_4N]_2[Mo(CO)_3(SnPh_3)_4]$	(XII)	Nujol mull	1897m, 1832s, br, 1816s, br
		CH_3CN	1902w, 1840s

[a] The infrared spectrum of compound II is reported in ref. 3. [b] ν(NH) 3344m, 3276m; $\delta(NH_2)$ 1587m, br, cm^{-1}. [c] Not isolated as a pure substance.

TABLE 2

PROTON NMR SPECTRA OF COMPOUNDS [a]

Compound	δ(ppm)
I [b]	2.2, broad signal
III [c]	7.0, 7.2 (m, C_6H_5), 3.4 (q, OCH_2, J(HH) 6.7 Hz), 1.1 (t, CH_3, J(HH) 6.7 Hz)
IV [c]	7.5, 7.0 (m, $Sn(C_6H_5)_3$), 2.9 (s, $N(CH_3)_4^+$), −4.5 (s, W−H)
V [d,e]	7.6, 6.9 (m, $Sn(C_6H_5)_3$), −4.3 (s, W−H)
VII [d,e]	7.5, 7.0 (m, $Sn(C_6H_5)_3$), −4.2 (s, Mo−H)
IX [d,e]	7.6, 7.0 (m, $Sn(C_6H_5)_3$), −6.4 (t, Cr−H, J(Sn−H) = 48.1 Hz) [f]
XI	7.8, 7.1, 6.8 (m, $Sn(C_6H_5)_3$ and $P(C_6H_5)_4^+$)
XII [e]	7.6, 7.2, 6.8 (m, $Sn(C_6H_5)_3$)

[a] For identification of compounds see Table 1. The ^{1}H NMR spectrum of II is reported in ref. 3. The NMR spectra of VI, VIII and X were not recorded. Relative intensities of signals are not reported but integrations were satisfactory. [b] Recorded in $(CD_3)_2SO$. [c] Recorded in CD_3CN. [d] Recorded in $(CD_3)_2CO$. [e] Tetraethylammonium cations in compounds V, VII, IX and XII have very similar resonance positions: δ 3.0–3.1 (q, N−CH_2), 1.1 (t of t, N−CH_2CH_3). [f] ^{117}Sn−H and ^{119}Sn−H couplings are not observed for compounds V and VII probably due to the low solubilities of these species. Also a ^{183}W−H coupling is not observed for compound V for the same reason. Previously, unresolved ^{117}Sn−H/^{119}Sn−H couplings of 14–40 Hz have been observed for several (but not all) compounds of the type $H_2Pt(SnR_3)_2(PR'_3)_2$ [17].

an uncharacterized substance which has ν(CO) bands at 1890, 1850, 1716 and 1600 cm^{-1} forms. This material is decomposed during the Me_4NCl/EtOH treatment to form low yields of II. Compound II was later prepared in much higher yield (66%) by the direct reaction of OEt^- with $W(CO)_3PMTA$ [3]. It has been shown by a X-ray crystal structure study to contain a highly unsymmetrical metal triangle which is held together by one W–W bond, and three bridging ethoxy groups, two of which are triply bridging [3]. Each tungsten atom in II is also coordinated to three terminal CO groups.

Further evidence for the presence of an anionic $W(CO)_3$ unit in "X" is obtained from its reaction with three equivalents of Ph_3SnCl in THF or liquid ammonia. This reaction provides, after metathesis with Me_4NCl in ethanol, 10–12% isolated yields of $[Me_4N]_2[HW(CO)_3(SnPh_3)_3]$ (IV). The formulation of IV as containing a di-anionic seven coordinate tungsten unit is consistent with its elemental analysis, infrared and ^{1}H NMR spectra. The latter indicates that the proportions of Me_4N to Ph_3Sn to hydride are 2/3/1. This compound, as well as the analogous tetraethylammonium salt (V), were not sufficiently soluble to permit observation of satellites due to ^{183}W–H coupling, but the presence of the weak singlet at ca. −4.4 ppm in IV and V establishes the presence of one hydrogen directly bound to the metal. The unusual compound III will be discussed later.

Syntheses of $M(CO)_3(SnPh_3)_3^{3-}$, $HM(CO)_3(SnPh_3)_3^{2-}$ and $M(CO)_3(SnPh_3)_4^{2-}$

Improved yields (40–50%) of IV and V were obtained by the reaction of $W(CO)_3(PMTA)$ with three equivalents of Ph_3SnLi in THF, followed by cation exchange in alcohol. It is very likely that the initial species formed in this two step

process is $Li_3W(CO)_3(SnPh_3)_3$ (VI), which is subsequently protonated; i.e.,

$$3Ph_3SnLi + W(CO)_3(PMTA) \rightarrow Li_3W(CO)_3(SnPh_3)_3 + PMTA \quad (5)$$

$$Li_3W(CO)_3(SnPh_3)_3 + EtOH + 2Me_4NCl \rightarrow [Me_4N]_2[HW(CO)_3(SnPh_3)_3] + LiOEt + 2LiCl \quad (6)$$

Completely analogous compounds have also been prepared from $Mo(CO)_3(PMTA)$ and $Cr(CO)_3(PMTA)$ and Ph_3SnLi. Although we have not yet succeeded in isolating analytically pure salts containing the $M(CO)_3(SnPh_3)_3^{3-}$ ions of W, (VI), Mo, (VIII), and Cr, (X), these materials have spectroscopic and chemical properties which are entirely consistent with this formulation. For example, their infrared spectra in THF solution (Table 1) show virtually the same three band pattern at quite low energies in the ν(CO) region indicative of highly charged anions. Also, we have established that VI, VIII and X undergo protonation to provide analogous $HM(CO)_3(SnPh_3)_3^{2-}$ species, where the pure Mo and Cr species are isolated in 39 and 14% yields, respectively.

Interestingly, the chromium complex X is apparently only the fourth compound reported to contain seven unidentate ligands attached to a central chromium atom. The first was $(Ph_3Sn)_3Cr(CO)_4^-$ [2] which was subsequently proven by X-ray crystallography to contain seven coordinate chromium [10]. More recently, $H_2Cr(P(OMe)_3)_5$ [11] and $Cr(CN\text{-}t\text{-}Bu)_7^{2+}$ [12] have also been reported. The ^1H NMR and infrared spectra and elemental compositions suggest that the three $HM(CO)_3(SnPh)_3^{2-}$ species have very similar properties. As expected, the chemical shift of the chromium species, (IX), is at a more negative value (−6.5 ppm), than those of the corresponding molybdenum, (−4.2 ppm) and tungsten (−4.3 ppm) compounds. This chemical shift trend is entirely analogous to that observed for other homologous series of Cr, Mo and W hydrides, where the Cr analogues invariably have more shielded hydrides. For example, the δ(M − H) for $[PNP][HCr(CO)_5]$ (−6.9 ppm) is at a more negative value than corresponding chemical shifts of $[PNP][HMo(CO)_5]$ (−4.0 ppm) and $[PNP][HW(CO)_5]$ (−4.3 ppm) [13].

Further support for our formulation of (VI), (VIII) and (X) as $Li_3M(CO)_3(SnPh_3)_3$ has been provided by examining the reactions of these materials with two equivalents of Ph_3SnCl. From the trilithium complexes of Mo and W, the new complexes $Mo(CO)_3(SnPh_3)_4^{2-}$ (XII) and $W(CO)_3(SnPh_3)_4^{2-}$ (XI) have been isolated in 64 and 29% yields, respectively; i.e.,

$$M(CO)_3(SnPh_3)_3^{3-} + Ph_3SnCl \rightarrow M(CO)_3(SnPh_3)_4^{2-} + Cl^- \quad (7)$$

(M = Mo, W)

We were rather surprised that a fourth triphenyltin group would bind to the seemingly very crowded tris(triphenyltin) precursors. However, elemental analyses for XI and XII are entirely consistent with these formulations. In the case of the molybdenum complex, the Sn/Mo ratio is almost exactly 4/1. A confirming tin analysis for the tungsten complex also establishes its composition. If indeed $M(CO)_3(SnPh_3)_3^{3-}$ (M = Mo, W) reacted with Ph_3SnCl to provide molecules containing four tin–tungsten bonds, one would expect the ν(CO) bands of the products to be shifted to substantially higher energies than those of the reactants. Examination of the ν(CO) values in Table 1 for the compounds in question indicates that this

is the case. Finally, the ^{1}H NMR spectrum of XII is consistent with a Et_4N^+/Ph_3Sn ratio of approximately 1/2. Although these complexes contain the largest number of triphenyltin groups attached to one transition metal, there do exist species, such as $[Cr(SnCl_3)_6]^{6-}$ or $[Cr(SnCl_2Br)_6]^{6-}$, which apparently contain six tin–chromium bonds [14]!

Attempts to prepare $Cr(CO)_3(SnPh_3)_4^{2-}$ by adding excess Ph_3SnCl to a solution of $Li_3[Cr(CO)_3(SnPh_3)_3]$ were unsuccessful. On mixing these reactants an opaque violet solution immediately formed. This solution had a complex infrared spectrum in the ν(CO) region (1955w, 1906m, 1868m, 1827s, 1775m, 1762m, 1725vs cm^{-1}) which was inconsistent with a mixture of reactants and the desired product. Treatment of this solution with ethanolic Me_4NCl resulted in the formation of an unstable violet solid which decomposed on attempted purification.

Reaction of the $W(CO)_3$(PMTA)-potassium reduction product with excess Ph_3SnCl. Formation of the novel anion $[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^-$

Treatment of the insoluble green $W(CO)_3$(PMTA)-potassium reduction product in liquid ammonia with three equivalents of Ph_3SnCl rapidly gave a yellow solution at −33°C. Acidification of the solution and metathesis with Me_4NCl in ethanol gave two products. One was identified as compound IV and was isolated in 10–12%. The other product obtained is formulated as $[Me_4N][(Ph_3Sn)_2\{(Ph_3Sn)_2OEt\}W(CO)_3]$ on the basis of its infrared and ^{1}H NMR spectra and other data [15]. It was not possible to free this product completely from IV. Comparison of the relative intensities of the ν(CO) bands in the crude mixture suggests that these products are formed in roughly equal amounts. The unusual anion may be obtained free of $HW(CO)_3(SnPh_3)_3^{2-}$ by treating the $W(CO)_3$(PMTA)-potassium reduction product with six equivalents of Ph_3SnCl. It is then isolated as nearly colorless and crystalline salts in 12–27% yields with Me_4N^+, Et_4N^+ or Ph_4P^+ counterions. The synthesis of the tetraphenylphosphonium salt, compound III, is described in the Experimental section. Satisfactory elemental analyses, in addition to consistent ^{1}H NMR and infrared data were obtained for this product. However, before we were able to rationalize the analytical data for this bizarre species, a crystal structure determination was performed on a closely related compound. This structure will be described in detail in the subsequent paper in this issue [15].

This compound is unlike any previously isolated from the reaction of metal carbonyl anions with organotin halides since there has been apparent cleavage of two Sn–C bonds and incorporation of an alkoxide group into the coordination sphere of the tin atoms. The fate of the cleaved phenyl rings is unknown. We noted in the experimental section that carefully recrystallized Ph_3SnCl was used in these syntheses since we were very concerned that this product could have formed from the reaction of "X" with impurities such as Ph_2SnCl_2. Careful monitoring of the infrared solution spectra in THF of the crude product before and after the Me_4NCl/ROH treatment showed that very little change in the position or intensity of the ν(CO) bands accompanies metathesis. On this basis it is concluded that the phenyl–tin cleavage occurs prior to the alcohol treatment; i.e., during the reaction of "X" with Ph_3SnCl. It should be noted that the best yields of compound III and related salts were obtained from the reaction of freshly prepared "X" with Ph_3SnCl at low temperature in liquid ammonia. *We cannot presently rule out the possibility that "X" may be thermally unstable; i.e., the infrared spectra and elemental analyses*

may in fact represent those of thermal decomposition products. Previously, we and others have observed that other highly reduced species such as $Na_3V(CO)_5$ [7] and $Na_2W(CO)_5$ [16] are unstable solids at room temperature.

We had hoped that the characterization of compound III would shed additional light on the nature of "X". Obviously, this objective was not realized beyond strengthening our belief that "X" is a highly reduced species containing one or more $W(CO)_3$ units. However, an important fact emerged from this study that we had not appreciated previously; namely, that the reactions of electron rich transition metal species with triorganotin halides need not always provide straightforward derivatives.

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