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Highly Reduced Organometallics. 14.[1] Six- and Seven-Coordinate Organotin Derivatives of the Tetrasodium Tetracarbonylmetalates(4−) of Chromium, Molybdenum, and Tungsten

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Treatment of $Na_4[M(CO)_4]$ with 2 equiv of Ph_3SnCl provides approximately 50% yields of $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$ for M = Cr and W and very low yields for M = Mo. The reaction of $L_2M(CO)_4$, where L_2 = norbornadiene, cyclooctadiene, tetramethylethylenediamine, or ethylenediamine (M = Cr, Mo, W), with 2 equiv of Ph_3SnLi is a more facile and often higher yield route (60–70% for M = Cr, Mo; 35% for M = W) to the same dianions. These materials react with Ph_3SnCl to provide 30–40% yields of $[Et_4N][(Ph_3Sn)_3M(CO)_4]$, in which Cr, Mo, and W are seven-coordinate. Reactions of $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$ (M = Cr, Mo) with acetic acid, $[Me_2NCCl_2]Cl$, and methyl iodide in acetonitrile provide 30–40% yields of $[Et_4N][H(Ph_3Sn)_2M(CO)_4]$, containing seven-coordinate metals, *trans*-$Ph_3Sn(CO)_4M{\equiv}CNMe_2$, and $[Et_4N][(Ph_3Sn)M(CO)_4(CH_3CN)]$, respectively. The coordinated acetonitrile in the latter compounds is slowly displaced by PPh_3 in acetonitrile at 25 °C to give 35–50% yields of $[Et_4N][Ph_3SnM(CO)_4(PPh_3)]$. All of these new materials are characterized by elemental analyses and IR and ^1H NMR spectra.

Introduction

Reactions of organotin halides and highly reduced metal carbonyl anions generally provide products which are much more easily handled and purified than the exceedingly oxygen and moisture-sensitive transition-metal precursors. By the synthesis and characterization of suitable organotin derivatives of metal carbonyl anions, important additional evidence has been obtained for the existence of $M(CO)_5^{3-}$ (M = V, Nb, Ta),[2,3] $M(CO)_4^{3-}$ (M = Mn, Re),[4] and $M(CO)_3^{3-}$ (M = Co, Rh, Ir).[5] More recently, this same procedure has been used in the preliminary characterization of materials which formally contain $M(CO)_4^{4-}$ (M = Cr, Mo, W).[6] Full details of this work are now presented in this paper.

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. 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 1–2 h before use. Published procedures were followed for the preparation of $(TMED)M(CO)_4$ (M = Cr, Mo, W; TMED = *N,N,N′,N′*-tetramethylethylenediamine),[7] $(COD)W(CO)_4$ (COD = 1,5-cyclooctadiene),[7] and $(NBD)M(CO)_4$ (M = Cr, Mo; NBD = norbornadiene).[8] Except where mentioned below, the compounds $Na_4M(CO)_4$ were prepared by using published procedures.[9] All other reactants and solvents were obtained from commercial sources, freed from oxygen, and used without further purification.

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 drybox. Nujol mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox 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.

$[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$ (1). Method A. From $Na_4Cr(CO)_4$ Generated in Situ. As described previously,[9] a slurry of yellow $Na_4[Cr(CO)_4]$ was prepared from $(TMED)Cr(CO)_4$ (1.96 mmol) in 40 mL of liquid ammonia. To the vigorously stirred slurry at −78 °C was added a cold (−78 °C) solution of Ph_3SnCl (1.51 g, 3.92 mmol) in 25 mL of THF dropwise. After all the Ph_3SnCl solution had been added over a period of 1 h, the insoluble $Na_4[Cr(CO)_4]$ was entirely consumed. Removal of solvent left a deep yellow solid which was treated with a solution of Et_4NBr (1.24 g, 5.90 mmol) in 15 mL of EtOH. After the mixture was allowed to stir for 12 h, a copius cream solid formed. This was filtered, dried, and recrystallized from CH_3CN–EtOH to provide 1.18 g (54%) of colorless crystalline 1 of satisfactory purity.

Anal. Calcd for $C_{56}H_{70}CrN_2O_4Sn_2$: C, 59.81; H, 6.27; N, 2.49; Sn, 21.11. Found: C, 59.78; H, 6.17; N, 2.43; Sn, 21.17.

Method B. From $(TMED)Cr(CO_4)$ and Ph_3SnLi. A deep green solution of Ph_3SnLi was prepared by stirring Ph_3SnCl (1.51 g, 39.2 mmol) and excess lithium wire clippings (1.36 g, 196 mmol) in 200 mL of THF for 12 h. To this was added by cannula a solution of $(TMED)Cr(CO)_4$ (5.50 g, 1.96 mmol) in 50 mL of THF. Following removal of solvent, the product was treated with Et_4NBr (12.5 g, 59.5 mmol) as described above. An identical workup provided 15.0 g (68%) of white crystalline product which had spectroscopic properties identical with those of bona fide 1 prepared by method A.

$[Et_4N]_2[(Ph_3Sn)_2Mo(CO)_4]$ (2). (Triphenylstannyl)lithium (3.90 mmol) was prepared as indicated above in 20 mL of THF. To this solution was added one containing $(NBD)Mo(CO)_4$ (0.585 g, 1.95 mmol) in 20 mL of THF. After the solution was stirred

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for 1 h, solvent was removed in vacuo from the pale yellow solution. Subsequent cation exchange, workup as described above, and recrystallization from CH_3CN–EtOH provided 1.50 g (66%) of white crystalline **2** of satisfactory purity.

Anal. Calcd for $C_{56}H_{70}MoN_2O_4Sn_2$: C, 57.56; H, 6.04; N, 2.40. Found: C, 57.47; H, 6.13; N, 2.28.

$[Et_4N]_2[(Ph_3Sn)_2W(CO)_4]$ (3). Method A. From $Na_4W(CO)_4$. A slurry of $Na_4[W(CO)_4]$ was prepared in liquid ammonia from (TMED)$W(CO)_4$ (1.69 mmol) as described previously.[9] All ammonia was removed in vacuo, and the orange product was slurried in 10 mL of THF. To this was added dropwise 1.30 g (3.37 mmol) of Ph_3SnCl in 10 mL of THF over a 1-h period at room temperature to yield a pale yellow solution. The product was then worked up exactly the same as compound **2** to provide 1.08 g (51%) of white crystalline **3** of satisfactory purity. Also 0.43 g (17%) of $[Et_4N][(Ph_3Sn)_3W(CO)_4]$ (**6**) (vide infra) was isolated from fractional recrystallization of the CH_3CN–EtOH soluble products from this reaction.

Anal. Calcd for $C_{56}H_{70}N_2O_4Sn_2W$: C, 53.54; H, 5.62; N, 2.23. Found: C, 53.20; H, 5.58; N, 2.68.

Method B. From (COD)$W(CO)_4$ and Ph_3SnLi. A solution of 0.420 g (1.04 mmol) of (COD)$W(CO)_4$ in 10 mL of THF was added via cannula to a solution containing Ph_3SnLi (2.08 mmol) in 15 mL of THF. After the solution was stirred for 12 h, solvent was removed in vacuo from the golden yellow solution. Subsequent cation exchange as described previously and recrystallization from CH_3CN–EtOH provided 0.42 g (35%) of nearly colorless product which was spectroscopically identical with bona fide **3**.

$[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (4). A solution of $Li_2[(Ph_3Sn)_2Cr(CO)_4]$ (1.96 mmol) was prepared from the reaction of Ph_3SnLi (3.90 mmol) and (TMED)$Cr(CO)_4$ (0.55 g, 1.96 mmol) in 20 mL of THF as indicated above (compound **1**, method B). To this solution was added Ph_3SnCl (0.75 g, 1.96 mmol) in 10 mL of THF, all at once. The mixture was stirred for 18 h, during which time the solution became yellow-orange. The solvent was removed in vacuo, and the residue was carefully triturated with ether (3 × 10 mL). To the resulting solid was added a solution of $[Et_4N]Br$ (1.24 g, 5.90 mmol) in 15 mL of EtOH. Filtration of the solid followed by recrystallization from CH_3CN–EtOH yielded 0.98 g (37%) of shiny pale yellow crystals of **4**.

Anal. Calcd for $C_{66}H_{65}CrNO_4Sn_3$: C, 58.97; H, 4.87; N, 1.04; Sn, 26.49. Found: C, 59.25; H, 5.05; N, 0.85; Sn, 26.32.

$[Et_4N][(Ph_3Sn)_3Mo(CO)_4]$ (5). Solid Ph_3SnCl (0.385 g, 1.00 mmol) was added to a stirred solution of $[Et_4N]_2[(Ph_3Sn)_2Mo(CO)_4]$ (1.17 g, 1.00 mmol) in 15 mL of CH_3CN, and the solution assumed a light yellow color. After 3 h of stirring, its IR spectrum indicated an incomplete reaction. Additional Ph_3SnCl (0.50 g, 1.30 mmol) was added, causing a white precipitate to form after 5 min of stirring. The IR solution spectrum indicated a complete reaction. The solution was filtered, and the solvent was removed in vacuo, leaving a semicrystalline pale yellow solid which was carefully washed with EtOH (3 × 10 mL) to remove $[Et_4N]Cl$ and excess Ph_3SnCl. Recrystallization from CH_3CN–EtOH yielded 0.42 g (30%) of pale yellow crystalline compound **5**.

Anal. Calcd for $C_{66}H_{65}MoNO_4Sn_3$: C, 57.10; H, 4.72; N, 1.01; Sn, 25.65. Found: C, 56.89; H, 4.36; N, 1.07; Sn, 25.34.

$[Et_4N][(Ph_3Sn)_3W(CO)_4]$ (6). A pale green THF solution of $Li_2[(Ph_3Sn)_2W(CO)_4]$ was prepared by an 18-h reaction of a solution of (TMED)$W(CO)_4$ (0.809 g, 1.96 mmol) with a solution of Ph_3SnLi prepared from Ph_3SnCl (1.51 g, 3.92 mmol) and Li clippings (0.169 g, 24.4 mmol) in 20 mL of THF. A solution of Ph_3SnCl (1.51 g, 3.92 mmol) in 10 mL of THF was added all at once, and the resulting mixture was allowed to stir for 14 h. After removal of solvent in vacuo, a solution of $[Et_4N]Br$ (1.24 g, 5.90 mmol) in 15 mL of EtOH was added and allowed to stir for 16 h, thereby generating a finely divided white solid in addition to a viscous light green oil. The solvent was removed in vacuo, and the remaining material was triturated with three 20-mL portions of isopentane, leaving a clean white solid. To the solid was added 15 mL of EtOH, and the mixture was filtered. Recrystallization of the isolated solid from CH_3CN–EtOH yielded 0.89 g (33%) of pale yellow crystalline **6**.

Anal. Calcd for $C_{66}H_{65}NO_4Sn_3W$: C, 53.70; H, 4.44; N, 0.95; Sn, 24.12. Found: C, 53.37; H, 4.18; N, 1.25; Sn, 24.37.

$[Et_4N][H(Ph_3Sn)_2Cr(CO)_4]$ (7). Glacial acetic acid (0.107 g, 1.78 mmol) was added all at once to a stirred solution of **1** (1.00 g, 0.89 mmol) in 15 mL of CH_3CN. After being stirred for 45 min, the solution remained clear, and the solvent was removed in vacuo, leaving a white glassy solid. THF (15 mL) was added to dissolve the product, and after filtration from undissolved solid the THF was removed in vacuo. The resulting semicrystalline material was recrystallized from CH_3CN–EtOH, yielding 0.26 g (29%) of white crystalline **7**.

Anal. Calcd for $C_{48}H_{51}CrNO_4Sn_2$: C, 57.92; H, 5.16; N, 1.41. Found: C, 57.77; H, 5.39; N, 1.08.

$[Et_4N][H(Ph_3Sn)_2W(CO)_4]$ (8). By exactly the same procedure as described for compound **7**, the reaction of **3** (1.12 g, 0.89 mmol) with glacial acetic acid (0.107 g, 1.78 mmol) provided 0.31 g (31%) of white crystalline **8** of satisfactory purity. Compound **8** decomposes above 123 °C.

Anal. Calcd for $C_{48}H_{51}NO_4Sn_2W$: C, 51.15; H, 4.56; N, 1.24. Found: C, 50.98; H, 4.68; N, 1.27.

$[Et_4N][(Ph_3Sn)Cr(CO)_4(CH_3CN)]$ (9). Methyl iodide (2.45 g, 17.3 mmol) was added all at once by syringe to a stirred solution of **1** (2.00 g, 1.78 mmol) in 20 mL of CH_3CN, and the solution assumed a light yellow color within 30 min. After 18 h of stirring the solution had a rich yellow color, and the solvent was removed in vacuo, leaving a yellow glass. The crude product was washed with ethanol (3 × 10 mL) to remove $[Et_4N]I$ and was then dissolved in 10 mL of CH_3CN and filtered. The volume of the solution was reduced to 3 mL. The product crystallized upon addition of excess EtOH, yielding 0.75 g (62%) of bright yellow product which analyzed satisfactorily for compound **9**.

Anal. Calcd for $C_{32}H_{38}CrN_2O_4Sn$: C, 56.08; H, 5.59; N, 4.08. Found: C, 56.03; H, 5.56; N, 4.23.

The ethanolic washings and the mother liquor from the crystallization were combined and evaporated. The cream residue was extracted with diethyl ether (3 × 10 mL). Evaporation of the ether extracts provided 0.37 g (57%) of white crystalline product which was identical with bona fide $MeSnPh_3$ (mp 60–61 °C (lit.[29] 59–61 °C).

$[Et_4N][(Ph_3Sn)W(CO)_4(CH_3CN)]$ (10). By the same procedure described for the preparation of compound **9**, the reaction of **3** (2.23 g, 1.78 mmol) with excess CH_3I (1.60 ml, 17.3 mmol) in 20 mL of CH_3CN, after workup, provided 0.87 g (60%) of bright yellow and crystalline **10** of satisfactory purity. Compound **10** decomposes above 141 °C.

Anal. Calcd for $C_{32}H_{38}N_2O_4SnW$: C, 47.03; H, 4.68; N, 3.42. found: C, 46.85; H, 4.79; N, 3.31.

Synthesis of $[Et_4N][(Ph_3Sn)Cr(CO)_5]$ from 9. Carbon monoxide was bubbled through a deep yellow-orange solution of compound **9** (0.080 g, 0.12 mmol) in 8.0 mL of THF. Within 5 min the solution became colorless. Solvent was removed in vacuo. The crystalline white product (0.040 g, 51% yield) had an infrared spectrum superimposable on that of bona fide $[Et_4N][(Ph_3Sn)Cr(CO)_5]$.[10]

$[Et_4N][(Ph_3Sn)Cr(CO)_4(PPh_3)]$ (11). Solid Ph_3P (0.115 g, 0.438 mmol) was added from a side arm to a stirred solution of compound **9** (0.30 g, 0.44 mmol) in 10 mL of CH_3CN. After 18 h of stirring the solvent was removed in vacuo from the yellow solution, leaving a yellow glass. Recrystallization from CH_3CN–EtOH yielded 0.14 g (35%) of compound **11** of satisfactory purity.

Anal. Calcd for $C_{48}H_{50}CrNO_4PSn$: C, 63.59; H, 5.56; N, 1.55. Found: C, 63.52; H, 5.81; N, 1.59.

$[Et_4N][(Ph_3Sn)W(CO)_4(PPh_3)]$ (12). By essentially the same procedure described for the preparation of compound **11**, the reaction of compound **10** (0.358 g, 0.438 mmol) and PPh_3 (0.115 g, 0.438 mmol) in 10 mL of CH_3CN provided, after an acetone–ether recrystallization, 0.22 g (48%) of compound **12** of satisfactory purity. Compound **12** melts at 177 °C.

Anal. Calcd for $C_{48}H_{50}NO_4PSnW$: C, 55.52; H, 4.85; N, 1.35. Found: C, 55.26; H, 4.94; N, 1.38.

$(Ph_3Sn)(CO)_4Cr(CNMe_2)$ (13). THF (30 mL) was added to a solid mixture of compound **1** (1.00 g, 0.89 mmol) and $[Me_2NCCl_2]Cl$ (0.14 g, 0.89 mmol). The resulting slurry was stirred for 20 h at room temperature and filtered. The red filtrate was evaporated, leaving a residue which was redissolved in toluene (5 mL) and filtered. Evaporation of the solvent left an orange solid. This was recrystallized from toluene–heptane to provide

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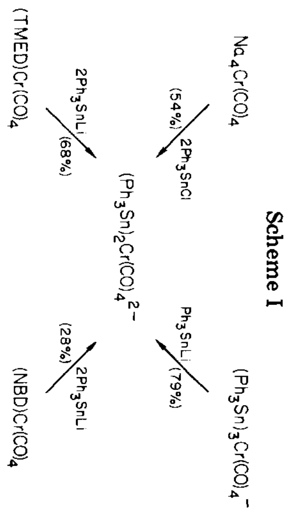
Scheme I



0.25 g (49%) of orange **13** which gave satisfactory analyses. Compound **13** melts at 132 °C.

Anal. Calcd for $C_{25}H_{21}CrNO_4Sn$: C, 52.67; H, 3.71; N, 2.46. Found: C, 52.65; H, 3.91; N, 2.39.

$(Ph_3Sn)(CO)_4W(CNMe_2)$ (14). The same procedure as for the synthesis of compound **13** was used, except that the reaction time was 10 h. The recrystallization from toluene–heptane provided 0.62 g (54%) of orange **14** of satisfactory purity. Compound **14** decomposes above 129 °C.

Anal. Calcd for $C_{25}H_{21}NO_4SnW$: C, 42.78; H, 3.02; N, 2.00. Found: C, 43.00; H, 3.01; N, 2.03.

Results and Discussion

Syntheses of $(Ph_3Sn)_2M(CO)_4^{2-}$ (M = Cr, Mo, W). A variety of methods have been used to synthesize the dianions $(Ph_3Sn)_2M(CO)_4^{2-}$ (M = Cr, Mo, W). In Scheme I these methods are summarized, including isolated yields, for $(Ph_3Sn)_2Cr(CO)_4^{2-}$. These dianions were initially prepared from the reaction of Ph_3SnCl and $Na_4M(CO)_4$.[6] Whether these reactions initially involve the formation of the unknown trianion $Ph_3SnM(CO)_4^{3-}$ is not known. However, both $(Ph_3Sn)_2M(CO)_4^{2-}$ and $(Ph_3Sn)_3M(CO)_4^-$ may be obtained in moderate yields from these reactions for M = Cr and W. For tungsten, this route appears to provide the best yields of the dianion (ca. 50%). However, for the chromium and especially molybdenum dianions, their best syntheses involve the reaction of Ph_3SnLi with complexes of the general formula $L_2M(CO)_4$, where L_2 = TMED, NBD, COD, or ethylenediamine. Generally, the isolated yields of $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$, (M = Cr, Mo) from these reactions range from 60 to 70%. This general method involving displacement of a neutral ligand on $L_nM(CO)_{6-n}$ by X^- has been previously used in the synthesis of other $X_nM(CO)_{6-n}{}^{n-6}$ species, where M = Cr, Mo, or W and X = CN, Cl_3Ge, etc. Examples are shown in eq 1–3.

$$Cr(CO)_4(bpy) + 2CN^- \xrightarrow[-bpy]{} Cr(CO)_4(CN)_2^{2-} \quad (1)^{11}$$

$$Mo(CO)_3(arene) + 3GeCl_3^- \xrightarrow[-arene]{} Mo(CO)_3(GeCl_3)_3^{3-} \quad (2)^{12}$$

$$Cr(arene)_2 + 6GeCl_3^- \xrightarrow[-2arene]{} Cr(GeCl_3)_6^{6-} \quad (3)^{13}$$

The final route to $(Ph_3Sn)_2M(CO)_4^{2-}$ involves the reaction of $(Ph_3Sn)_3M(CO)_4^-$ (vide infra) with Ph_3SnLi. Although the yields are generally high (70–80%), the method is of little synthetic value since the seven-coordinate monoanions are initially prepared from the dianions.

The crystalline and colorless tetraethylammonium salts, compounds **1–3**, may be handled in air for several hours without deterioration but form quite air sensitive solutions. Infrared spectra (Table I) of $(Ph_3Sn)_2M(CO)_4^{2-}$ are very similar for all three metals and are consistent with compounds of *cis*-$X_2M(CO)_4^{2-}$ geometry. Four infrared-active

Table I. Infrared Spectra in the Carbonyl Stretching Frequency Region and ^{1}H NMR Spectra of Compounds

compds	ν(CO),[a] cm^{-1}	δ[b]
1, $[Et_4N]_2[c\text{-}(Ph_3Sn)_2Cr(CO)_4]$	1918 (m), 1822 (vs), 1782 (s)	*b*
2, $[Et_4N]_2[c\text{-}(Ph_3Sn)_2Mo(CO)_4]$	1948 (m), 1844 (vs), 1791 (s)	*b*
3, $[Et_4N]_2[c\text{-}(Ph_3Sn)_2W(CO)_4]$	1947 (m), 1838 (vs), 1790 (s)	*b*
4, $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$	1956 (m), 1901 (s), 1860 (vs)	*b*
5, $[Et_4N][(Ph_3Sn)_3Mo(CO)_4]$	1999 (m), 1897 (vs), 1832 (w)	*b*
6, $[Et_4N][(Ph_3Sn)_3W(CO)_4]$	1997 (m), 1894 (vs), 1828 (w)	*b*
7, $[Et_4N][H(Ph_3Sn)_2Cr(CO)_4]$	1989 (m), 1960 (s), 1891 (vs)	−4.9 (s, 1 H, CrH), 7.1–7.6 (m, 30 H, Ph_3Sn)
8, $[Et_4N][H(Ph_3Sn)_2W(CO)_4]$	2008 (w-m), 1919 (sh), 1903 (vs)	−2.5 (t, 1 H, WH, J_{W-H} = 10.8 Hz), 7.0–7.4 (m, 30 H, Ph_3Sn)
9, $[Et_4N][c\text{-}(Ph_3Sn)Cr(CO)_4(CH_3CN)]$[c]	1968 (m), 1863 (vs), 1811 (s)	2.0 (s, 3 H, CH_3CN), 7.1–7.6 (m, 15 H, Ph_3Sn)
10, $[Et_4N][c\text{-}(Ph_3Sn)W(CO)_4(CH_3CN)]$[c]	1984 (m), 1863 (vs), 1810 (s)	1.7 (s, 3 H, CH_3CN), 7.1–7.7 (m, 15 H, Ph_3Sn)
11, $[Et_4N][(Ph_3Sn)Cr(CO)_4(PPh_3)]$[d]	1963 (m), 1852 (sh), 1842 (vs)	6.9–7.8 (m, 30 H, Ph_3P, Ph_3Sn)
12, $[Et_4N][c\text{-}(Ph_3Sn)W(CO)_4(PPh_3)]$	1984 (m-s), 1879 (sh), 1863 (vs), 1833 (s)	6.9–7.5 (m, 30 H, Ph_3P, Ph_3Sn)
13, $t\text{-}(Ph_3Sn)(CO)_4Cr(CNMe_2)$[e]	2040 (w), 1974 (s), 1952 (vs)	3.4 (s, 6 H, Me_2NC), 7.3–7.5 (m, 15 H, Ph_3Sn)
14, $t\text{-}(Ph_3Sn)(CO)_4W(CNMe_2)$[e]	2056 (w), 1982 (s), 1954 (vs)	3.4 (s, 6 H, Me_2NC), 7.2–7.5 (m, 15 H, Ph_3Sn)

[a] Medium = CH_3CN for compounds **1–12**; THF for compounds **13** and **14**. [b] Medium = CD_3CN. Signals of Et_4N^+ cations in **1–12** are not included but have very similar positions: δ 3.0–3.1 (q, NCH_2), 1.1 (t of t, NCH_2CH_3). The ^{1}H NMR spectra of compounds **1–6** consist of rather uninformative complex unresolved aromatic proton resonance signals ranging from 6.9 to 7.8 ppm. Integrations of cation to anion signals are satisfactory for the proposed formulations. See Results and Discussion. [c] Nujol mull of compound **9**: ν(CN) 2313 (w), 2265 (w) cm^{-1}; ν(CO) 1966 (s), 1852 (vs), 1837 (vs), 1788 (vs) cm^{-1}. Nujol mull of compound **10**: ν(CN) 2314 (w), 2265 (w) cm^{-1}; ν(CO) 1984 (m-s), 1879 (sh), 1863 (vs), 1833 (s) cm^{-1}. [d] The geometry of the anion in compound **11** may be cis or trans. See Results and Discussion. [e] Compound **13** also shows a band of medium intensity at 1601 cm^{-1}. Compound **14** shows a corresponding band at 1606 (m) cm^{-1}.

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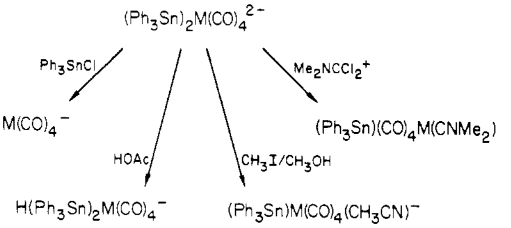
Scheme II



M = Cr, W

ν(CO) bands are expected for such molecules, but often only three are observed.[14] Proton NMR spectra of compounds 1–3 are consistent with the presence of bis(triphenylstannyl)-substituted anions and tetraethylammonium cations in a 1:2 ratio. Chemical shifts and splitting patterns for the Ph_3Sn groups are very similar for all three compounds and contain two discrete groups of signals which correspond to ortho protons and meta–para protons in a 2:3 ratio. Very similar splitting patterns are observed in the ^1H NMR spectrum of Ph_3SnCl.[15]

Reactions of $(Ph_3Sn)_2M(CO)_4^{2-}$. A summary of reactions examined for the substituted dianions in this study appears in Scheme II. These reactions and the properties of the products will now be described.

Syntheses and Properties of $(Ph_3Sn)_3M(CO)_4^-$ (M = Cr, Mo, W). Compounds 1–3 react with Ph_3SnCl in THF to provide, after metathesis, 30–40% yields of pale yellow and crystalline $[Et_4N][(Ph_3Sn)_3M(CO)_4]$ (4–6), which are air stable for days at room temperature. The chromium derivative, compound 4, is noteworthy in that it was the first compound reported to contain seven unidentate ligands attached to a chromium atom.[6] More recently, $H_2Cr(P(OMe)_3)_5$,[16] $Cr(CN\text{-}t\text{-}Bu)_7^{2+}$,[17] $HCr(CO)_3(SnPh_3)_3^{2-}$,[18] and $HCr(CO)_4(SnPh_3)_2^-$ (this study) have been prepared. Subsequently, the seven-coordinate nature of the chromium in $(Ph_3Sn)_3Cr(CO)_4^-$ was confirmed by a single-crystal X-ray diffraction study.[19] By contrast, numerous examples of similar seven-coordinate Mo and W carbonyl complexes exist (e.g., $Mo(CO)_4I_3^-$), for which there are no chromium analogues.[20] However, seven-coordinate chromium complexes containing bidentate ligands (e.g., $[Cr(CO)_2(DIARS)_2Br]Br$, where DIARS = $o\text{-}C_6H_4(AsMe_2)_2$)[21] have been known for many years.

When $(Ph_3Sn)_2M(CO)_4^{2-}$ (M = Cr, Mo, W) react with Ph_3SnCl to form compounds 4–6, all of the infrared bands in the ν(CO) region move to considerably higher energies (Table I). This observation is consistent with an expected decrease in charge on the metal center resulting from the formation of an additional tin–metal bond. Note, however, that the IR spectrum of $(Ph_3Sn)_3Cr(CO)_4^-$ (4) is substantially different from those of the molybdenum and tungsten analogues, compounds 5 and 6, suggesting that the structure of 4[19] may be markedly different from those of 5 and 6. These differences are also present in Nujol mull spectra of the crystalline solids.[22] Proton NMR spectra of 4–6 are similar and indicate the presence of Ph_3Sn and Et_4N groups in a 3:1 ratio.

Syntheses of $H(Ph_3Sn)_2M(CO)_4^-$ (M = Cr, W). Approximately 30% yields of colorless, crystalline compounds having the formula $[Et_4N][H(Ph_3Sn)_2M(CO)_4]$ (M = Cr, W) are obtained from the reaction of the dianions with glacial acetic acid. These reactions are complete within 2 h in acetonitrile at room temperature and provide air-stable products. The presence of a metal hydride group in these compounds is clearly revealed in the ^1H NMR spectra of these species (Table I) which show a singlet at −4.9 ppm for the chromium compound 7 and a "triplet" with well-defined ^{183}W–H satellites (J_{W-H} = 10.8 Hz) at −2.5 ppm for the tungsten species 8. The more negative chemical shift observed for the hydride in 7 vs. that of the tungsten analogue 8 is consistent with similar trends observed for other pairs of homologous chromium and tungsten hydrides. For example, the metal hydride chemical shifts for $H_2Cr_2(CO)_8^{2-}$ (−14.6 ppm)[9] and $HCr(CO)_5^-$ (−6.9 ppm)[23] are more negative than corresponding values for $H_2W_2(CO)_8^{2-}$ (−4.5 ppm)[9] and $HW(CO)_5^-$ (−4.3 ppm).[23] Other ^1H NMR spectral features are also consistent with the presence of seven-coordinate Cr and W in these complexes. It should be noted that reactions of $(Ph_3Sn)_2Mo(CO)_4^{2-}$ (2) with glacial acetic acid and other electrophiles have not been examined.

Syntheses and Substitution Reactions of $[(Ph_3Sn)M(CO)_4(CH_3CN)]^-$ (M = Cr, W). Attempts were also made to prepare $Me(Ph_3Sn)_2M(CO)_4^-$ by the reaction of $(Ph_3Sn)_2M(CO)_4^{2-}$ with methyl iodide. In acetonitrile these reactions lead to the formation of $MeSnPh_3$ (50–60% isolated yields) and approximately 60% yields of new acetonitrile complexes *cis*-$Ph_3SnM(CO)_4(CH_3CN)^-$ isolated as tetraethylammonium salts. It is possible that compounds 9 and 10 are formed by the reductive elimination of $MeSnPh_3$ from $Me(Ph_3Sn)_2M(CO)_4^-$, followed by incorporation of CH_3CN, but we have no evidence for the existence of this possible seven-coordinate precursor. What is known about this reaction is summarized in eq 4.

$$(Ph_3Sn)_2M(CO)_4^{2-} + MeI + CH_3CN \xrightarrow{CH_3CN} MeSnPh_3 + Ph_3SnM(CO)_4(CH_3CN)^- + I^- \quad (4)$$

Infrared and ^1H NMR spectra, elemental analyses, and chemical reactivity patterns are compatible with the presence of cis-octahedral units in compounds 9 and 10. Infrared spectra of 9 and 10 in the ν(CO) region in CH_3CN (Table I) are very similar to those of *cis*-$(Ph_3Sn)_2M(CO)_4^{2-}$ except the bands are shifted to substantially higher energies. Nujol mull infrared spectra of 9 and 10 reveal two very weak absorptions at ca. 2313 and 2265 cm^{-1} attributable to the ν(CN) of coordinated acetonitrile. Proton NMR spectra of these compounds in CD_3CN show singlets at 2.0 and 1.7 ppm, respectively. The former value is identical with that of free CH_3CN in CD_3CN. Thus, the coordinated CH_3CN in compound 9 appears to exchange rapidly with free CD_3CN. This result is consistent with our observation that 9 reacts completely within 5 min at room temperature in CH_3CN with CO to form $[Et_4N][Ph_3SnCr(CO)_5]$. Under similar conditions in THF, 9 also reacts rapidly with CO to form the same product. From this reaction, a 51% yield of crystalline product, identical

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with bona fide $[Et_4N][Ph_3SnCr(CO)_5]$,[10,25] was obtained. In contrast, the coordinated CH_3CN in compound **10** exchanges much more slowly with CD_3CN. Only after 20 h in CD_3CN at room temperature, does the ^1H NMR spectrum of **10** show no signal due to coordinated CH_3CN. Also the reaction of **10** with CO at atmospheric pressure and room temperature in CH_3CN requires about 5 h to proceed to completion. IR spectra show that **10** is converted entirely to $[Et_4N][Ph_3SnW(CO)_5]$[10,25] in this reaction. In THF, the same reaction requires only 1 h at room temperature. These results suggest that the rate-determining step for this carbonylation reaction is dissociative in character. It is reasonable to expect that compound **9** should be more labile than compound **10** in this regard.

In contrast, triphenylphosphine appears to react slowly with both **9** and **10** in acetonitrile to provide, after 18 h, a 35% yield of $[Et_4N][(Ph_3Sn)Cr(CO)_4(PPh_3)]$ (**11**) and a 49% yield of $[Et_4N][(Ph_3Sn)W(CO)_4(PPh_3)]$ (**12**). Infrared spectra of **11** and **12** in the ν(CO) region are somewhat different. While **12** is presently assigned a *cis*-$(Ph_3Sn)W(CO)_4(PPh_3)^-$ structure on the basis of the four observed bands in the ν(CO) region, it is not clear whether the chromium complex **11** is a cis or trans isomer. Since only two major bands in the ν(CO) region are present in the infrared spectra in the correct intensity ratios for the trans isomer, it is tempting to assign this as the geometry. However, there is the possibility that the somewhat broad band at 1842 cm^{-1} may envelope more than one carbonyl stretching frequency, so the trans assignment is at best tentative at this time. The only previously well-characterized compound analogous to **11** and **12** appears to be $[Et_4N][(Ph_3Sn)W(CO)_4(P(iPr)_3)]$,[24] which has an infrared spectrum in the ν(CO) region (1978 (s), 1858 (vs), 1823 (s) cm^{-1}) very similar to that of **12**. On the basis of these infrared spectra, it is highly unlikely that an impure product obtained previously from the photolysis of $Ph_3SnMo(CO)_5^-$ in the presence of PPh_3 is $[Ph_3SnMo(CO)_4PPh_3]^-$.[25] The substitution reactions with compounds **9** and **10** discussed herein are summarized in eq 5.

$$\mathrm{Ph_3SnM(CO)_5^-} \xleftarrow{\mathrm{CO}} \mathrm{(Ph_3Sn)M(CO)_4(CH_3CN)^-} \xrightarrow{\mathrm{PPh_3}} \mathrm{(Ph_3Sn)M(CO)_4(PPh_3)^-} \quad (5)$$

Synthesis of (Dimethylamino)carbyne Complexes $(Ph_3Sn)(CO)_4M(CNMe_2)$ (M = Cr, W). Lappert and co-workers previously established that binary metal carbonyl dianions react with (dichloromethylene)dialkylammonium halides to provide *C*-chlorocarbene complexes as shown in eq 6.[26] Subsequent removal of the chloro

$$\mathrm{M(CO)_x^{2-} + [R_2N{=}CCl_2]Cl \rightarrow R_2N(Cl)C{=}M(CO)_x + 2Cl^-} \quad (6)$$

$$\mathrm{M = Cr, Fe}$$

group with silver cation provided ((dialkylamino)carbyne)metal cations $(R_2NC)M(CO)_x^+$. To determine whether substituted carbonyl dianions might behave similarly, the dianions $(Ph_3Sn)_2M(CO)_4^{2-}$ were reacted with $[Me_2NCCl_2]Cl$. Surprisingly, a slow reaction occurred according to eq 7. In this case, one of the coordinated

$$\mathrm{(Ph_3Sn)_2M(CO)_4^{2-} + [Me_2NCCl_2]^+ \rightarrow (Ph_3Sn)(CO)_4M(CNMe_2) + Ph_3SnCl + Cl^-} \quad (7)$$

triphenyltin groups evidently functions as a chloride acceptor, thereby leading directly to the substituted (dimethylamino)carbyne complexes. It seems possible that the first product in this reaction is a *C*-chlorocarbene complex analogous to those prepared by Lappert, although we have no spectroscopic evidence for such an intermediate. This rather sterically encumbered seven-coordinate species then loses, perhaps in separate steps, Ph_3Sn and Cl groups to provide the observed products. This proposal is summarized in eq 8.

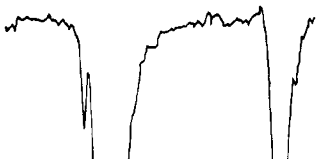

Figure 1. Infrared spectrum of *t*-$(Ph_3Sn)(CO)_4W{\equiv}CNMe_2$ (**14**) in THF from 1400 to 2200 cm^{-1}. Values of band positions are shown in Table I.

$$\mathrm{(Ph_3Sn)_2M(CO)_4^{2-} + [Me_2NCCl_2]^+ \xrightarrow{-Cl^-} [(Ph_3Sn)_2(CO)_4M{=}C(Cl)NMe_2] \rightarrow (Ph_3Sn)(CO)_4M{\equiv}CNMe_2 + Ph_3SnCl} \quad (8)$$

Similar chromium compounds have been prepared previously in Fischer's group by the reaction shown in eq 9. An X-ray structure analysis of the tin derivative showed

$$\mathrm{[(CO)_5Cr{\equiv}CNEt_2]^+ + Ph_3E^- \xrightarrow[-CO^-]{25\ ^\circ C} (Ph_3E)(CO)_4Cr{\equiv}CNEt_2} \quad (9)$$

$$\mathrm{E = Sn,^{27}\ Pb^{28}}$$

the molecule to have trans geometry but with a marked perturbation of the idealized C_{4v} molecular symmetry.[27] This perturbation is also reflected in the rather complex IR spectrum of $(Ph_3Sn)(CO)_4Cr(CNEt_2)$ in the ν(CO) region in octane (2045 (m), 1982 (s), 1963 (vs), 1952 (s) cm^{-1}) which is more characteristic of a *cis*-$XYCr(CO)_4$ complex than of one having trans geometry. Infrared spectra (Table I) of compounds **13** and **14** (Figure 1) are very similar to those reported by Fischer, both in THF and as Nujol mulls,

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suggesting that they are also trans isomers. However, the rather broad, lowest energy band in **13** and **14** was not resolved into two bands as in the case of Fischer's compounds. As is normally observed in analogous tunsten and chromium carbonyl complexes, the ν(CO) values of the tungsten complex **14** are higher than the corresponding values of the chromium complex **13**. There is also observed a band of medium intensity at ca. 1600 cm^{-1} which Fischer has attributed earlier[28] to a CN stretching frequency. The relative position of this ν(CN) mode emphasizes that the $CNMe_2$ unit in these complexes is best described as having both carbene and carbyne character; i.e., the following resonance forms are both of importance in describing their ground electronic states.

$$\{(Ph_3Sn)(CO)_4M{\equiv}C{-}NMe_2 \leftrightarrow (Ph_3Sn)(CO)_4\bar{M}{=}C{=}\overset{+}{N}Me_2\}$$

Proton NMR spectra of **13** and **14** are also entirely consistent with the proposed formulations. On the basis of these results, we suggest that other highly nucleophilic organotin derivatives of carbonyl anions may also be useful precursors to analogous carbyne complexes.

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Registry No. **1**, 67202-48-6; **2**, 67202-50-0; **3**, 67202-52-2; **4**, 67202-54-4; **5**, 86129-00-2; **6**, 86129-01-3; **7**, 86129-03-5; **8**, 86129-05-7; **9**, 86129-07-9; **10**, 86129-09-1; 11, 86129-11-5; **12**, 86129-13-7; **13**, 86129-14-8; **14**, 86129-15-9; $Na_4[Cr(CO)_4]$, 67202-62-4; Ph_3SnCl, 639-58-7; Et_4NBr, 71-91-0; Ph_3SnLi, 4167-90-2; $(TMED)Cr(CO)_4$, 21136-10-7; $(NBD)Mo(CO)_4$, 12146-37-1; $Na_4[W(CO)_4]$, 67202-46-4; $(COD)W(CO)_4$, 12129-70-3; $Li_2[(Ph_3Sn)_2Cr(CO)_4]$, 86129-16-0; $Li_2[(Ph_3Sn)_2W(CO)_4]$, 86129-17-1; $(TMED)W(CO)_4$, 15024-58-5; CH_3I, 74-88-4; CH_3CN, 75-05-8; $[Et_4N][(Ph_3Sn)Cr(CO)_5]$, 55997-66-5; Ph_3P, 603-35-0; $[Me_2NCCl_2]Cl$, 33842-02-3; Sn, 7440-31-5; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7.

Electron Spin Resonance and Photoelectron Studies of Neutral Bis(η-arene)metal Compounds (Metal = Ti, V, Nb, Ta, Mo, and W)[†]

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The electronic structure of several bis(η-arene)metal complexes, synthesized by the metal vapor method, has been examined by electron spin resonance (ESR) and photoelectron spectroscopy (PES). The ESR spectra of $Nb(\eta\text{-arene})_2$ and $Ta(\eta\text{-}C_6H_6)_2$ in frozen toluene at 77 K are axial and show $g_\parallel \approx 2$ and $g_\perp$ = 1.94–1.98 consistent with a $^2A_1$ ground state. The spectra show structure arising from coupling to the protons and highly anisotropic coupling to the metal nuclei. The extent of delocalization onto the ring protons is little affected by the arene in the series $Nb(\eta\text{-arene})_2$ (arene = benzene, toluene, mesitylene), but a substantial increase is observed in the proton coupling down the series $V(\eta\text{-}C_6H_6)_2$, $Nb(\eta\text{-}C_6H_6)_2$, and $Ta(\eta\text{-}C_6H_6)_2$ (A^H = 4.1, 5.1, and 6.1 G, respectively). Additionally, solution ESR spectra at 300 K show considerable increases in the metal $(n + 1)$s electron density down the group. The PE spectra were assigned with the aid of comparisons between He I and He II spectra. The spectra of the d^6 complexes $W(\eta\text{-arene})_2$ (arene = benzene, toluene, mesitylene) are consistent with a $^2A_1$ ground state for the cation (IE = 5.2–5.4 eV) with a $^2E_{5/2}/^2E_{3/2}$ doublet appearing ~1.2 eV to higher energy. The first ionizations of the d^5 complexes $Nb(\eta\text{-arene})_2$ are assigned to $^1A_1$ ion states with $^3E_2$ and $^1E_2$ states appearing at higher IE. The ion ground state of $Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)$ is shown to be the $^3E_2$ state, while the lowest ionization of its molybdenum analogue consists of overlapping bands from the $^3E_2$ and $^1A_1$ ion states. The PE spectra of $Ti(\eta\text{-}C_6H_6)_2$ and $Ti(\eta\text{-}C_6H_5Me)_2$ are consistent with a $^1A_1$ ground state leading to a $^2E_2$ ion ground state. Evidence is presented for a back-bonding interaction of e_{2g} symmetry between the metal and the arene ring.

Introduction

A variety of new bis(η-arene)metal complexes of titanium and of the second- and third-row metals of groups 5 and 6 have recently become available through metal-vapor synthesis.[1-3] In this paper we examine the electronic structure of these complexes by using electron spin resonance (ESR) and photoelectron spectroscopy (PES). The electron spin resonance spectra of several d^5 bis(arene) compounds of V and Cr have been reported in solution, in glasses, and doped into related diamagnetic hosts.[4-7] The spectra are typically axial with $g \approx 2.00$ and $g \approx 1.98$, and show very anisotropic metal hyperfine coupling (e.g., $V(\eta\text{-}C_6H_6)_2$, $A_\perp{}^V$ = 92.1, $A_\parallel{}^V$ = 6 G; $Cr(\eta\text{-}C_6H_6)_2{}^+$, $A_\perp{}^{Cr}$ = 26.9, $A_\parallel{}^{Cr}$ = 0.5 G).[5,7] The proton hyperfine splitting is often highly resolved and is closer to isotropic (e.g., $V(\eta\text{-}C_6H_6)_2$, $A_\parallel{}^H$ = 3.75, $A^H{}_{av}$ = 4.12; $Cr(\eta\text{-}C_6H_6)_2{}^+$, $A_\parallel{}^H$ = 3.1,

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