Journal of Organometallic Chemistry, 97 (1975) 79—93

THE CHEMISTRY OF METAL CARBONYL ANIONS

II*. SYNTHESIS AND REACTIONS OF THE PENTACARBONYLMETALLATE DIANIONS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN WITH METALLIC MONOHALIDES

JOHN E. ELLIS*, STEVEN G. HENTGES**, DALE G. KALINA and GARY P. HAGEN

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)

(Received April 15th, 1975)

Summary

Alkali metal amalgam reductions of $M(CO)_6$ in tetrahydrofuran (THF) have provided salts of the pentacarbonylmetallate dianions. Cesium amalgam reacts with $M(CO)_6$ at room temperature to yield $Cs_2M(CO)_5$, while sodium or potassium amalgams provide only (Na or $K)_2Cr(CO)_5$ in good yield in addition to a substantial amount of (Na or $K)_2Cr_2(CO)_{10}$. Molybdenum and tungsten carbonyl give primarily (Na or $K)_2M_2(CO)_{10}$ in THF even after 24 h of reflux; however, infrared evidence indicates the presence of monomeric dianions in these solutions. Reaction of the monomeric dianions with Ph_3MCl (M = Ge, Sn, Pb) provides air- and moisture-stable substituted carbonyl anions of the type $Ph_3MM'(CO)_5^-$ (M' = Cr, Mo, W) which have been isolated as tetraethylammonium salts. Pure $Na_2Cr(CO)_5$, prepared from the interaction of $Cr(CO)_6$ with sodium metal in liquid ammonia or HMPA, has also been used to provide similar substituted carbonyl anions of the type $ECr(CO)_5^-$ where E = Me_3Sn and $C_5H_5Fe(CO)_2$. The triphenyltin derivatives have also been prepared independently by the interaction of Ph_3SnLi with $M'(CO)_6$ in THF at room temperature as well as from the reaction of Ph_3SnCl with $M'_2(CO)_{10}^{2-}$ in THF.

Introduction

Although the pentacarbonylmetallate dianions of Cr, Mo and W have been known for more than ten years [1-3], only recently have facile syntheses of

---

* For Part I see ref. 12.

** National Science Foundation Undergraduate Research Participant for summer 1974.

these substances been reported. These involve either sodium metal reduction of $Cr(CO)_6$ in liquid ammonia, providing up to 95% yields of $Na_2Cr(CO)_5$ [4], or alkali metal reduction of $M(CO)_6$, $M_2(CO)_{10}^{2-}$, and $M(CO)_5(X)^-$ (X = halide) in hexamethylphosphoramide (HMPA), giving essentially quantitative yields of $Na_2M(CO)_5$ (M = Cr, Mo, W) [5].

Sodium and potassium metal amalgam reductions of the neutral hexacarbonyls in ethereal solvents, especially refluxing tetrahydrofuran (THF), have also been claimed to yield salts of $M(CO)_5^{2-}$ [6]. However, the cesium amalgam reduction of $Cr(CO)_6$ in THF is purported to give the unusual binuclear anion $Cs_4Cr_2(CO)_9 \cdot THF$ [7]. Workers have recently shown that the chemical properties of the product(s) of these (Na or K)/Hg reductions are consistent with those expected of the pentacarbonylmetallate dianions; however, no spectral evidence has been published in support of these claims. For example, these products react with 3,4-dichlorocyclobutenes to give from 1% (M = W) to 35% (M = Mo) yields of cyclobutadienetetracarbonylmetal species [8], 3-chloro-2-(chloromethyl)propene to give a 1% yield of trimethylenemethanetetracarbonylmolybdenum (corresponding Cr and W compounds could not be prepared this way) [9] and thiophosgene to give $Cr(CO)_5CS$ (3-5% yield), $Mo(CO)_5CS$ (2-4% yield) and $W(CO)_5CS$ (12-15% yield) [10]. It seems likely, however, that the dimeric dianions, $M_2(CO)_{10}^{2-}$, could also react with these reagents to give the observed products, in addition to $M(CO)_5Cl^-$. For example, in this investigation we have found that chlorotriphenylstannane reacts with $M_2(CO)_{10}^{2-}$ to give salts of $Ph_3SnM(CO)_5^-$ and $M(CO)_5Cl^-$. Also recently, base-stabilized stannylene and germylene complexes have been synthesized from $Cr_2(CO)_{10}^{2-}$ according to the following equation where B = THF or pyridine, R = alkyl group, M′ = Ge, Sn [11].

$$R_2M'Cl_2 + Na_2Cr_2(CO)_{10} + B \rightarrow R_2BM'Cr(CO)_5 + NaCr(CO)_5Cl + NaCl$$

In view of the conflicting reports and confusion on the nature of the species obtained in these alkali metal reductions of Group VI hexacarbonyls, we felt a careful examination of these reactions was in order. In addition, since very little is known about the chemical properties of the pentacarbonylmetallate dianions [12], a systematic examination of the chemistry of these species has been initiated. In this paper we report on the reactions of $M(CO)_5^{2-}$ with various metallic monohalides, particularly main Group IV species which provide new compounds of the type $MM'(CO)_5^-$, where M are various transition and main group metal moieties.

The triphenylmetal derivatives reported herein are particularly noteworthy in that they are air- and moisture-stable carbonyl anions in solution or in the solid state. As such, they are possibly the most oxidatively stable anionic metal carbonyls known. The only previously reported compounds of this type are $MX_3M'(CO)_5^-$ (M = Ge, Sn, X = halide, M′ = Cr, Mo, W) [13-15], all hydrolytically unstable substances.

Experimental

General procedures and starting materials

All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed by using standard Schlenk apparatus [16]. Reagent grade tetrahydrofuran (Aldrich) was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere; hexamethylphosphoramide (Aldrich) was distilled in vacuo from calcium hydride and then subsequently from sodium metal under argon. Chromium hexacarbonyl (Pressure Chemical), molybdenum hexacarbonyl (gift from Climax Molybdenum Co.), tungsten hexacarbonyl (Pressure Chemical), cesium metal (Ventron Corp.), triphenylmetal halides (metal = germanium, tin and lead) (Ventron Corp.), lithium metal wire (Ventron Corp.), trimethyltin chloride (Ventron Corp.), cyclopentadienyliron dicarbonyl iodide (Ventron Corp.), and sodium metal (Fisher Scientific) were used as received from commercial sources. Liquid ammonia was dried with Na metal and distilled before use.

IR spectra were recorded on a Perkin—Elmer 237B Spectrometer. Solution spectra were obtained in sealed sodium chloride cells equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glove box with essentially complete exclusion of air. Solutions of $Na_2Cr(CO)_5$ in HMPA or THF could be kept for at least 1/2 h in these cells without significant oxidation (to $Na_2Cr_2(CO)_{10}$) occurring. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, or Galbraith Laboratories.

Synthesis of $Cs_2Cr(CO)_5$ (I)

Chromium hexacarbonyl (0.40 g, 1.8 mmol) and cesium amalgam (1.0 g, 7.5 mmol Cs in 7 ml of Hg) are stirred at room temperature in 40 ml of THF in a flask equipped with a stopcock on the side to facilitate removal of amalgam after reaction. The reaction mixture assumed a turbid greyish green color after 15 min; however, after 5 h of stirring a voluminous bright yellow precipitate formed. A yield of 0.40 g (63% yield based on $Cr(CO)_6$) of solid was obtained which gave satisfactory analyses, in spite of the extreme air-sensitivity of this species, after drying under high vacuum at 50°C until virtually all THF was removed. Cesium analysis were carried out by conversion I to $CsBPh_4$ by aqueous

TABLE 1

INFRARED SOLUTION SPECTRA OF SALTS OF $M(CO)_5^{2-}$ AND $M_2(CO)_{10}^{2-}$ IN THE CARBONYL STRETCHING FREQUENCY REGION

Salt	Solvent	Carbonyl stretching frequencies (cm^{-1})		
$Na_2Cr(CO)_5$	HMPA	1760s	1722s	
$Na_2Cr(CO)_5$	THF	1819s	1768s(br)	
$Na_2Mo(CO)_5$	HMPA	1769s	1723s	
$Na_2Mo(CO)_5$	THF	1822s	1757s(br)	
$Na_2W(CO)_5$	HMPA	1775s	1731s	
$Na_2W(CO)_5$	THF	1827s	1757s(br)	
$Cs_2Cr(CO)_5$	HMPA	1779s	1737s	
$Cs_2Mo(CO)_5$	HMPA	1789s	1735s	
$Cs_2W(CO)_5$	HMPA	1789s	1740s	
$Cs_2Cr_2(CO)_{10}$	HMPA	1910m	1881vs	1785ms
$Cs_2Mo_2(CO)_{10}$	HMPA	1926m	1882vs	1788ms
$Cs_2W_2(CO)_{10}$	HMPA	1935m	1881vs	1787ms

$NaBPh_4$. Microanalysis by atomic absorption spectroscopy on pure samples gave virtually identical results (Found: C, 12.2; H, 0.4; Cs, 57.8; Hg, 0.1. $C_5CrCs_2O_5$ calcd.: C, 13.1; H, 0.0; Cs, 58.0; Hg, 0.0%.) The salt is only very slightly soluble in THF; however, dissolution in HMPA gives a red-orange solution. Trace amounts of air caused slurries of $Cs_2Cr(CO)_5$ in THF to rapidly change from yellow to green. The spectrum of this substance is reported in Table 1. Difficulty has been experienced often in preparing samples of I which are substantially free of finely divided mercury metal. However, the avoidance of fast and prolonged stirring helps to minimize mercury contamination of the final product.

Synthesis of $Cs_2Cr_2(CO)_{10}$ (II)

Solid tropylium fluoroborate (Aldrich) (0.32 g, 1.8 mmol) is added to a flask containing I (0.80 g, 1.75 mmol). Addition of THF (20 ml) to this solid mixture caused almost immediate formation of a yellow solution. After stirring for 1 h the solution was filtered from precipitated $CsBF_4$ (identified by its IR spectrum) and the resulting deep yellow filtrate was dried in vacuo. A yield of 0.42 g of yellow crystalline II (71%) was thereby obtained which gave an acceptable cesium analysis without further purification. (Found: Cs, 40.50; $C_{10}Cr_2Cs_2O_{10}$ calcd.: Cs, 40.25%.) The IR-active carbonyl stretching frequencies for this substance in HMPA are shown in Table 1. Additional evidence for the presence of $Cr_2(CO)_{10}^{2-}$ in II was obtained by conversion of II to the known $(Et_4N)_2$-$Cr_2(CO)_{10}$ [17] by treatment of 0.35 g of II (0.54 mmol) with 0.23 g of Et_4NBr (0.54 mmol) in 20 ml of dry acetone. The mixture was stirred for 8 h, filtered to remove CsBr and evaporated in vacuo. An 86% yield (0.30 g) of product having a mull spectrum identical to that previously reported for $(Et_4N)_2Cr_2(CO)_{10}$ was thereby obtained.

Salts of the type $Cs_2M_2(CO)_{10}$ (M = Mo, W) may be synthesized by analogous reactions of $Cs_2M(CO)_5$ [M = Mo (III), W (IV)] with tropylium flouroborate in THF. Alternatively, they and II may be obtained directly and quantitatively in HMPA by reduction of corresponding neutral hexacarbonyls with a twofold excess of cesium amalgam (1 g Cs per 7 ml Hg) for 2 h at room temperature. The IR-active carbonyl stetching frequencies of $Cs_2M_2(CO)_{10}$ (M = Mo, W) in HMPA are also shown in Table 1.

Synthesis of $Cs_2M(CO)_5$. M = Mo (III), W (IV)

These substances are prepared by a method entirely identical to that used for I. For example, 1.8 mmol [0.48 g $Mo(CO)_5$ or 0.63 g $W(CO)_6$] and 7.5 mmol Cs (1.0 g in 7.0 ml Hg) were stirred in 40 ml THF. The molybdenum and tungsten reductions proceed more rapidly than the chromium reaction. Upon work-up, orange solids only very slightly soluble in THF and often heavily contaminated with mercury metal are obtained in 60-80% yields [based on initial weight of $M(CO)_6$]. Because of mercury contamination, carbon analyses were invariably low; however, acceptable cesium analyses on these exceedingly air-sensitive substances were obtained by gravimetric analysis (as $CsBPh_4$) as described for $Cs_2Cr(CO)_5$. III, (found: Cs, 52.2. $C_5Cs_2MoO_5$ calcd.: Cs, 53.0%.) IV, (Found: Cs, 44.6. $C_5Cs_2O_5W$ calcd.: Cs, 45.0%.)

Solution spectra of III and IV in HMPA (Table 1) are practically identical to that of the well characterized and virtually Hg-free $Cs_2Cr(CO)_5$. Finally, the chemical properties of these substances [i.e., their reaction with Ph_3SnCl and $C_7H_7^+BF_4^-$ to give $Ph_3SnM(CO)_5^-$ and $M_2(CO)_{10}^{2-}$, respectively] are entirely consistent with the proposed formulations. These chemical and spectral observations effectively preclude significant contamination of III and IV by soluble mercury derivatives of Mo and W carbonyl anions. Such mercury derivatives occasionally form in moderate yields from alkali metal amalgam reductions of neutral metal carbonyls [19].

Synthesis of $Na_2Cr(CO)_5$ in liquid ammonia (V)

This synthesis is a modification of one reported recently by Behrens and coworkers [4] and is presented in detailed form. Approximately 250 ml of ammonia is condensed into a graduated, three-necked reaction vessel (e.g., Ace Glass No. 7756) containing 0.5 g Na (to remove oxygen and moisture from the ammonia). After the ammonia has assumed a homogeneous blue color, it is distilled under partial vacuum into a 500 ml three-necked round-bottom flask equipped with stopcock, CO_2-acetone condenser, and glass stirring bar (sodium in liquid ammonia attacks teflon-coated stirring bars) and containing 7.5 g (3.4 mmol) $Cr(CO)_6$ and 2.8 g (12.2 mmol) of Na chunks (size is not critical) under an atmosphere of dry nitrogen or argon (argon was used in this particular preparation). Cooling the reaction vessel with dry-ice/acetone facilitates transfer of ammonia. Also, the system must be open to a mercury manometer in order to avoid dangerous build-up of pressure during the transfer step. After completion of the ammonia transfer, the vessel is warmed to approximately the normal boiling point of ammonia and the contents stirred under reflux until the color of the solution changes from blue to orange-yellow (this process generally takes from 3-7 h). The resulting solution is then cooled to —40° to —50°C and transferred via cannula into a jacketed cold medium-porosity fritted disc filter (temperature is held to —40° to —50°C; colder temperatures often result in precipitation of product) and filtered into a 500 ml three-necked round-bottom flask equipped with two stopcocks. This filtration removes most sodium amide and the shock-sensitive disodium acetylenediolate [20] formed as by-products in the reaction. The clear orange-red filtrate is allowed to evaporate overnight through a mercury bubbler. (Best results are obtained if flask is attached directly or via butyl rubber tubing to a vacuum line.) Residues on the frit are pyrophoric and must be disposed of cautiously. The resulting pyrophoric brown-orange solid is dried at room temperature in vacuo ($\leqslant$ 0.01 Torr) to remove all ammonia. In the present experiment, a practically quantitative yield of crude orange-yellow product was obtained (8.1 g). Due to the exceedingly air-sensitive nature of this species it was stored in a Schlenk tube in vacuo in a dry-box until required for recrystallization. A 3 g portion of crude $Na_2Cr(CO)_5$ was dissolved in 125 ml THF at room temperature, stirred for 15 min and filtered (medium-porosity fritted disc). (The filtration step often proceeds slowly and may be hastened with the aid of a magnetic stirring bar.) The resulting clear orange solution was evaporated in vacuo and gave 2.85 g of pure yellow powdery $Na_2Cr(CO)_5$ (95% yield), which has a spectrum in THF virtually identical to that reported by Behrens [4] (see Table 1). Recrystallized $Na_2Cr(CO)_5$ is a pyrophoric solid, soluble in THF and HMPA. The previously unreported and unusual Nujol mull spectrum of this substance is shown in Fig. 1.

Reduction of $Cr(CO)_6$ by Na amalgam in refluxing tetrahydrofuran

Chromium hexacarbonyl (1.70 g, 7.7 mmol) and sodium amalgam (1.78 g, Na, 77 mmol in 13 ml of Hg) were stirred under reflux. The progress of the reduction was monitored by IR spectroscopy in the carbonyl stretching frequency region. After 12 h, intense bands due to $Na_2Cr(CO)_5$, as well as $Na_2Cr_2(CO)_{10}$, were observed (see Fig. 2). Further refluxing did not significantly reduce the amount of $Na_2Cr_2(CO)_{10}$ present.

Preparation of tetraethylammonium(triphenylstannyl)pentacarbonylchromate, $[(C_2H_5)_4N][Cr(CO)_5SnPh_3]$ (VI)

The above solution was cooled to room temperature and triphenyltin chloride (2.98 g, 7.7 mmol) was added, followed by addition of an aqueous solution of tetraethylammonium bromide. A voluminous grey-yellow solid was thereby obtained, filtered, washed with water (2 × 50 ml), dried in vacuo, washed with diethyl ether to remove triphenyltin chloride, and dried in vacuo (4.01 g). This air-stable solid was dissolved in the minimum amount of acetone, filtered, and then recrystallized by adding excess diethyl ether. Shiny crystalline, white, air-stable VI was thereby obtained (3.40 g) in 65% yield.

Preparation of $Ph_3SnCr(CO)_5^-$ (VI) by other methods

(a). From $Na_2Cr(CO)_5$ prepared in liquid ammonia (V). A solution of Ph_3SnCl (0.81 g, 2.1 mmol) in 30 ml THF was added at once via syringe to $Na_2Cr(CO)_5$ (0.50 g, 2.1 mmol) in 40 ml THF. The yellow solution of $Na_2Cr(CO)_5$ become markedly paler in color on addition of the Ph_3SnCl. After stirring the solution for 0.5 h, it was filtered (medium-porosity disc) to remove NaCl and evaporated, yielding a pale yellow, air-stable substance. A solution of this material in THF (5 ml) was treated with 1.4 g of tetraethylammonium bromide in ethanol (25 ml). Subsequent addition of 200 ml of water to the above magnetically stirred solution provided a fine crystalline product which was filtered, washed with additional water and dried in vacuo. A yield of 1.02 g (72%) of crystalline white solid was thereby attained. Recrystallization of this material from acetone/diethyl ether gave 0.80 g (52%) of product identical with that prepared from $Na_2Cr(CO)_5$ derived from sodium amalgam reduction of $Cr(CO)_6$. Excellent yields (80%) of VI may also be obtained by addition of Ph_3SnCl to $Na_2Cr(CO)_5$ generated by the sodium metal reduction of $Cr(CO)_6$ in hexamethylphosphoramide [5].

(b). From the reaction of Ph_3SnLi with $Cr(CO)_6$. A deep green solution of Ph_3SnLi, prepared by stirring triphenylstannyl chloride (2 g, 5.2 mmol) in 25 ml of THF with lithium wire (0.37 g, 53 mmol) divided into 1 mm lengths, overnight under a nitrogen atmosphere [21], was filtered into a flask containing $Cr(CO)_6$ (1.15 g, 5.2 mmol) in 50 ml THF. The Ph_3SnLi solution rapidly decolorized on mixing with $Cr(CO)_6$ and became light yellow in color. Removal of solvent in vacuo gave a pale yellow air-stable solid. This was dissolved in acetone, filtered and added to an excess of aqueous tetraethylammonium bromide. Immediate precipitation of white crystals of VI occurred. These were filtered, washed with additional water and then dried in vacuo. Recrystallization of the crude product, which was spectroscopically free of other carbonyl-containing

contaminants, provided 0.98 g (28%) of fine colorless crystals which were identical to genuine VI.

(c). From the reaction of $Cs_2Cr(CO)_5$ (I) with Ph_3SnCl. A mixture of Ph_3SnCl (0.43 g, 1.1 mmol) and $Cs_2Cr(CO)_5$ (0.51 g, 1.1 mmol) was stirred for 1 h in tetrahydrofuran (20 ml). The resulting pale yellow solution was filtered (medium-porosity fritted disc) and evaporated. Metathesis of the resulting salt with tetraethylammonium bromide, as in part (*a*), gave 0.45 g (60% yield) of VI, identical to that prepared by other methods.

(d). From the reaction of $(Et_4N)_2Cr_2(CO)_{10}$ with Ph_3SnCl. A mixture of 1.15 g (1.8 mmol) of $(Et_4N)_2Cr_2(CO)_{10}$ [17] and 0.76 g (2.0 mmol) of Ph_3SnCl was stirred in 40 ml of THF at room temperature. After 1 h all of the slightly soluble dimer dianion had dissolved in the THF. However, only after 12 h did the characteristic red-orange color of the dimer change to the paler orange color of the products. An infrared solution spectrum taken at this time showed all dimer had reacted. Bands at 2057w, 1921s and 1863m cm^{-1}, superimposable with those of genuine $Et_4N[Cr(CO)_5Cl]$ [18], and bands at 2021m, 1898s, and 1881 m(sh) cm^{-1}, superimposable with those of genuine VI, were observed. The only other absorption in the carbonyl stretching frequency region was a weak band at 1980 cm^{-1} attributable to $Cr(CO)_6$. Subsequently, the solvent was removed in vacuo at room temperature, providing a yellow crystalline mixture of $[Et_4N]Cr(CO)_5Cl$ and VI. No attempt was made to isolate the chlorocarbonylmetallate intact; however, it could be easily removed from VI either by treatment of the mixture with water ($Et_4N[Cr(CO)_5Cl]$ is moderately soluble in this medium) or, better, by exposing an acetone solution of the mixture to air for several hours and subsequent filtration of the resulting solution. Since Et_4N-$[Cr(CO)_5Cl]$ is moderately air-sensitive, while VI is essentially air-stable in solution or in the solid state, the latter can be effectively separated from the chloro complex by this method. A yield of 0.45 g (38%) of II was thereby obtained after treatment of the acetone filtrate with an excess of diethyl ether. A quantitative yield of VI corresponds to 0.60 g based on the $(Et_4N)_2Cr_2(CO)_{10}$.

Reduction of $M(CO)_6$ (M = Mo, W) by sodium amalgam in tetrahydrofuran

Tungsten hexacarbonyl (2.05 g, 5.8 mmol) and sodium amalgam (1.34 g Na, 58 mmol in 10.5 ml Hg) were stirred at room temperature. After 16 h bands attributable to $Na_2W(CO)_5$ [1827 and 1757 cm^{-1} (br)] were observed; however, these were much less intense than bands corresponding to $Na_2W_2(CO)_{10}$. Similar reductions of $W(CO)_6$ by Na/Hg in THF under reflux conditions were no more successful in forming $Na_2W(CO)_5$ than those conducted at room temperature. Analogous reductions of $Mo(CO)_6$ in THF at room temperature or under reflux conditions gave similar results: only very weak spikes at 1822 and 1757 cm^{-1} (br) were observed. The general shape and relative intensities of the bands due to $Na_2M(CO)_5$ (M = Mo, W) are very similar to those of $Na_2Cr(CO)_5$ in THF (see Fig. 2).

Preparation of tetraethylammonium (triphenylstannyl)pentacarbonyltungstate, $[(C_2H_5)_4N][W(CO)_5SnPh_3]$ (VII)

(a). From treatment of above tungsten solution with Ph_3SnCl. Triphenyltin chloride (2.30 g, 6.0 mmol) was added to the solution containing reduced

tungsten carbonyl species, followed by addition of an excess of tetraethylammonium bromide (3.80 g, 18 mmol) in water. After removal of the THF in vacuo, a deep red gummy solid was obtained which slowly decolorized in the presence of air. The water was removed by decantation and the solid was dried. After approximately two weeks exposure to air the colored component (mostly $[Et_4N][HW_2(CO)_{10}]$ and $[Et_4N][W(CO)_5Cl]$) disappeared almost completely. The resulting solid was dissolved in acetone and the solution filtered. Addition of excess diethyl ether to the filtrate caused the precipitation of shiny crystalline, very pale yellow VII (2.28 g, 49% yield). This substance was identical to that obtained by the reaction of $W(CO)_5^{2-}$ and Ph_3SnCl in HMPA (see below).

(b). From Ph_3SnCl and $Na_2W(CO)_5$ generated by sodium reduction of $W(CO)_6$ in hexamethylphosphoramide (HMPA). A suspension of $W(CO)_6$ (1.5 g, 4.3 mmol) in 40 ml of dry, oxygen-free HMPA was stirred (glass stirring bar) with small chunks of sodium (0.23 g, 10 mmol) under an argon atmosphere. After 4 h of stirring the solution changed to a deep blue indicating that the reduction was complete (See ref. 5 for figures showing spectral changes in the carbonyl stretching frequency region which occur during this reduction.) Addition of triphenyltin chloride (1.4 g, 4.3 mmol) to the solution caused rapid discoloration. After forty minutes of stirring the HMPA solution was added to an aqueous solution of Et_4NBr (2.3 g, 11 mmol in 350 ml H_2O). The resulting solution and precipitate was cooled in a refrigerator for several days and then centrifuged. The dried centrifugate (2.26 g, 66% yield) was subsequenly recrystallized from acetone/diethyl ether providing 0.6 g (17% yield) of analytically pure VII. The properties of this air-stable, colorless, crystalline salt are virtually identical to those of the chromium analogue.

TABLE 2

INFRARED SPECTRA OF $[Et_4N][RM(CO)_5]$ IN THE CARBONYL STRETCHING FREQUENCY REGION

R	M	Medium	Carbonyl stretching frequencies (cm^{-1})
Ph_3Ge	Cr	CH_2Cl_2	2023m, 1936(sh), 1894s
		Nujol mull	2021m, 1941m, 1889s, 1878(sh)
Ph_3Ge	Mo	CH_2Cl_2	2039m, 1909vs, 1878(sh)
		Nujol mull	2038m, 1953m, 1898vs, 1881vs
Ph_3Ge	W	CH_2Cl_2	2038m, 1900vs, 1877(sh)
		Nujol mull	2038m, 1947ms, 1892s, 1874s
Ph_3Sn	Cr	THF	2019m, 1900vs, 1883(sh)
		Nujol mull	2020m, 1937m, 1896s, 1876s
Ph_3Sn	Mo	THF	2035m, 1912vs, 1887ms
		Nujol mull	2036m, 1914vs, 1893(sh), 1875vs
Ph_3Sn	W	THF	2036m, 1908vs, 1882ms
		Nujol mull	2035m, 1908ms, 1870s
Ph_3Pb	Cr	THF	2025m, 1943(sh), 1909s, 1882(sh)
		Nujol mull	2025m, 1948m, 1882vs(br)
Ph_3Pb	Mo	CH_2Cl_2	2045m, 1920vs, 1888(sh)
		Nujol mull	2040m, 1924s, 1902s, 1880(sh)
Ph_3Pb	W	CH_2Cl2	2043m, 1910vs, 1880(sh)
		Nujol mull	2039m, 1914s, 1893s, 1866s
Me_3Sn	Cr	CH_2Cl_2	2003m, 1880s(br)
		Nujol mull	2003m, 1870s, 1848s
$C_5H_5Fe(CO)_2$	Cr	THF	2016m, 1942(sh), 1919vs, 1904s, 1878s
		Nujol mull	2017m, 1909s(br), 1868s(br), 1820ms(br)

(c). From Ph_3SnCl and $(Et_4N)_2W_2(CO)_{10}$. This reaction was carried out quite analogously to that described earlier for $(Et_4N)_2Cr_2(CO)_{10}$. A mixture of 0.95 g (1.0 mmol) $(Et_4N)_2W_2(CO)_{10}$ [17] and 0.40 g (1.04 mmol) Ph_3SnCl was stirred for 3 h at room temperature. Evaporation of the solution, followed by recrystallization of the product from acetone/ether provided 1.09 g of a mixture of $Et_4N[W(CO)_5Cl]$ and VII. Exposure of acetone solutions of this mixture to air for ca. 1 week caused virtually complete decomposition of $Et_4N[W(CO)_5Cl]$ and provided, after filtration, a pale yellow solution from which 0.52 g (33%) of pale yellow, crystalline VII was obtained (maximum yield of 50% expected from this method).

Preparation of $[(C_2H_5)_4N][C_5H_5Fe(CO)_2Cr(CO)_5]$ (VIII)

A solution of $Na_2Cr(CO)_5$ (1.00 g, 4.20 mmol) in 30 ml THF was slowly added by dropping funnel to a solution of $IFe(CO)_2C_5H_5$ (1.27 g, 4.20 mmol) in 30 ml THF over a period of 2 h at room temperature. During this period the originally brown-black solution of $IFe(CO)_2C_5H_5$ changed to a deep red color. The solution was stirred for an additional 0.5 h and then filtered (medium-porosity fritted disc) and evaporated to dryness. The solid was taken up in a minimum

TABLE 3

DATA FOR $[Et_4N][RM(CO)_5]$[a]

R	M	Yield (%)	M p. (°C)	Elemental analysis[g] found (calc.) (%)		
				C	H	N
Ph_3Ge	Cr	80[d]	242-243	59.13 (59 46)	5.72 (5.63)	2.31 (2.24)
Ph_3Ge	Mo	51[e]	154-155	55 31 (55.56)	5.14 (5 26)	2 40 (2.09)
Ph_3Ge	W	38[e]	191-192 (dec)	48.87 (49.12)	4.54 (4.65)	1.76 (1.85)
Ph_3Sn	Cr	77[b], 28[c], 73[d], 80[e], 60[f], 38[h]	200-202	55 37 (55 38)	5.41 (5.25)	2 11 (2.08)
Ph_3Sn	Mo	20[e]	136-138	52.08 (51.98)	5 04 (4 93)	
Ph_3Sn	W	49[b], 58[c], 66[e], 33[h]	140-142	46.08 (46.30)	4.15 (4.39)	
Ph_3Pb	Cr	51[d]	139-140(dec.)	49.03 (48.94)	4.72 (4.64)	
Ph_3Pb	Mo	33[e]	140-141 (dec.)	46.15 (46 27)	4.21 (4.38)	
Ph_3Pb	W	45[c]	135-136 (dec.)	41.86 (41.71)	4.07 (3 95)	
Me_3Sn	Cr	54[d]	Dec. above 130	39.17 (39 53)	5 80 (6.01)	2.97 (2.88)
$C_5H_5Fe(CO)_2$	Cr	50[d]	Dec. above 180	47.75 (48.11)	4.95 (5.05)	2.64 (2 81)

[a] Empirical formulas for R = Ph_3M': $C_{31}H_{35}M'MNO_5$; R = Me_3Sn: $C_{16}H_{29}CrNO_5Sn$; R = $C_5H_5Fe(CO)_2$, $C_{20}H_{25}CrFeNO_7$. [b] From $M(CO)_6$ + Na/Hg. [c] From $M(CO)_6$ + Ph_3SnLi. [d] From $Na_2Cr(CO)_5$ (generated in NH_3) + RX. [e] From $Na_2M(CO)_5$ (generated in HMPA) + RX. [f] From $Cs_2Cr(CO)_5$ (from $Cr(CO)_6$ + Cs/Hg). [g] Samples from methods b and e were used for elemental analysis determinations for R = Ph_3Sn, M = Cr and R = Ph_3Sn, M = W, respectively. [h] From Ph_3SnCl + $(Et_4N)_2M_2(CO)_{10}$ in THF.

amount of ethanol (20 ml). To this solution was added Et_4NBr (2.66 g, 12.6 mmol in 10 ml EtOH). Addition of 200 ml of H_2O caused precipitation of additional red-orange solid. This was filtered (coarse frit) and dried in vacuo. Three tetrahydrofuran/heptane recrystallizations provided a product that was spectroscopically free of $(C_5H_5Fe(CO)_2)_2$, a by-product in the reaction. Also only very weak bands attributable to $Et_4N[Cr_2H(CO)_{10}]$ were present. Yield: 1.03 g (50%) of deep red crystalline VIII.

Synthesis of other salts of the type $EM(CO)_5^-$

All of those species shown in Table 3 were prepared by methods very similar to those outlined above. The yields and methods used for these compounds are indicated in Table 3.

Results and discussion

Alkali metal and alkali metal amalgam reductions

Alkali metal reductions of $M(CO)_6$ *in ammonia and HMPA.* Previously, it has been established that sodium reductions of $M(CO)_6$ in HMPA provide a facile and clean route to $Na_2M(CO)_5$ [5]. A representative preparation using this method is shown in the experimental section (compound VII part *b*). Although complete reduction of $M(CO)_6$ to $Na_2M(CO)_5$ generally requires about four hours at room temperature, considerably faster reductions can be effected by using sodium sand. In as much as alkali metal (but not tetraalkyl or arylonium) salts of $M_2(CO)_{10}^{2-}$ and $M(CO)_5(X)^-$ (X = halide) are also reduced to $M(CO)_5^{2-}$ under these conditions, the HMPA method is presently the most general route to these species. Interestingly, all tetraalkyl or arylonium ions investigated have been shown to react with $M(CO)_5^{2-}$ to give products such as $HM(CO)_5^-$, $M_2(CO)_{10}^{2-}$ and others which are presently under investigation [22].

It has not proven possible thus far to isolate solid solvated or unsolvated $Na_2M(CO)_5$ from HMPA solutions. Addition of petroleum ether to these solutions results in the separation of a viscous deep red oil which contains $Na_2M(CO)_5$. Hexamethylphosphoramide is one of the strongest donor solvents known and binds tightly to metal cations [23], hence it is not surprising that our attempts to remove HMPA completely from these salts have been unsuccessful. Indeed, it is possible that the deep red oils correspond to liquid salts of composition $[Na(HMPA)_x]_2M(CO)_5$. The existence of solvated salts of carbonylmetallate anions, such as $[Na(Et_2O)_x]Co(CO)_4$ [24], which are liquid at room temperature, is well established.

The presence of HMPA is not detrimental when it can be easily removed from products; for example, by precipitation of the product on addition of an excess of water in which HMPA is completely miscible. However, this procedure is limited to products such as $[Et_4N][Ph_3MM'(CO)_5]$ (M = Ge, Sn, Pb, M' = Cr, Mo, W) which are insoluble in and stable towards water.

Other more difficult procedures are necessary for isolating hydrolytically unstable derivatives of $M(CO)_5^{2-}$ such as $RM(CO)_5^-$ where R = alkyl; these will be the subject of future communications [22].

Because of the general difficulty of removing HMPA (n.b.p. = 232°C) from products, it has proved useful in the case of $Na_2Cr(CO)_5$ to prepare the unsolvat-

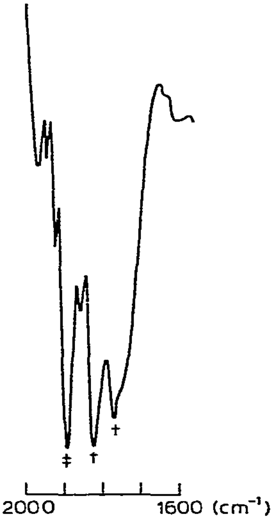

Fig. 1. Infrared Nujol mull spectrum of $Na_2Cr(CO)_5$, recrystallized from THF, in carbonyl stretching frequency region (1925w, 1802s, 1770s, 1644s).

Fig. 2. Infrared spectrum in THF of products from a 12 h reduction of $Cr(CO)_6$ by 1% sodium amalgam in refluxing THF. Identity and position of bands: ‡ = $Cr_2(CO)_{10}^{2-}$, 1885 (principal); † = $Cr(CO)_5^{2-}$, 1819, 1768 cm^{-1} (br)

ed reactant in liquid ammonia. Accordingly, a detailed preparation of the chromium salt in liquid ammonia is presented which provides up to 95% yields of yellow powdery and pyrophoric $Na_2Cr(CO)_5$. The solution spectrum of this substance in HMPA is consistent with that of a D_{3h} carbonyl anion (see Table 1) [5]. However, its Nujol mull spectrum (Fig. 1) is unusual in that it shows a broad intense absorption centered at 1644 cm^{-1} which probably arises via interaction of Na^+ with an oxygen on the carbonyl anion. [The $Na_2Cr(CO)_5$ used for the spectrum was recrystallized from THF and is free of $NaNH_2$ and NH_3 which also absorp in this region.] Such "isocarbonyl" interactions [12] are known to cause shifting of carbonyl stretching frequencies to substantially lower energies [25]; however, to our knowledge no interactions of Na^+ with terminal carbonyl groups have been suggested previously.

Surprisingly, the corresponding reductions of $Mo(CO)_6$ and $W(CO)_6$ in liquid ammonia provide only poor yields of the monomeric dianions [5]. In these cases HMPA is clearly superior to liquid ammonia as a medium for reduction of metal carbonyls.

Sodium amalgam reductions of $M(CO)_6$ in THF. Sodium and potassium amalgam reductions of $Cr(CO)_6$ in THF behave similarly; however, in the case of sodium amalgam, the THF solution of $Cr(CO)_6$ must be refluxed for many hours before a significant amount of the intermediate $Cr_2(CO)_{10}^{2-}$ is reduced to $Cr(CO)_5^{2-}$. Fig. 2 shows that after 12 h substantial amounts of $Cr(CO)_5^{2-}$ (1819, 1768 cm^{-1}) coexist with $Cr(CO)_{10}^{2-}$ (principal band at 1885 cm^{-1}). Further reflux of the reaction mixture does not result in formation of more $Na_2Cr(CO)_5$. Small amounts of dry air instantaneously convert $Cr(CO)_5^{2-}$ to $Cr_2(CO)_{10}^{2-}$ The concentration ratios of $Cr(CO)_5^{2-}$ to $Cr_2(CO)_{10}^{2-}$ in these solutions are not known. Since R_2SnCl_2 [11], Ph_3SnCl (see later) and presumably other covalent halides evidently react with $Cr_2(CO)_{10}^{2-}$ and $Cr(CO)_5^{2-}$ to form the same products in many cases [in addition to $Cr(CO)_5Cl^-$ in the case of $Cr_2(CO)_{10}^{2-}$] it is not possible to determine this ratio on the basis of product yields; quantitative IR analysis is required.

Infrared studies of corresponding sodium and potassium amalgam reductions of $M(CO)_6$ (M = Mo, W) in THF show that only small amounts of $M(CO)_5^{2-}$ are formed; the principal product is $M_2(CO)_{10}^{2-}$ even after 24 h under reflux or at room temperature. On this basis, it seems likely that most of the cyclobutadienetetracarbonylmolybdenum (yield: 35%) obtained from 3,4-dichlorocyclobutene and products from the reduction of $Mo(CO)_6$ and Na/Hg in THF arose from the interaction of the dihalide with $Mo_2(CO)_{10}^{2-}$ rather than $Mo(CO)_5^{2-}$ [8].

Cesium amalgam reductions of $M(CO)_6$ in THF and HMPA. A previous report indicated that $Cr(CO)_6$ was reduced in THF by cesium amalgam to a green solid of stoichiometry $Cs_4Cr_2(CO)_9 \cdot THF$ [7]. Since the spectrum of this substance in HMPA (see Fig. 4 and Table III in ref. 7) was quite similar in appearance to those of partially oxidized HMPA solutions of $Na_2Cr(CO)_5$ we had observed (without subtraction of HMPA bands, see later), this reaction was reexamined under the same conditions as reported previously. We obtained a bright yellow solid, only very slightly soluble in THF, which in HMPA gave a spectrum extremely similar to that of $Na_2Cr(CO)_5$ (see Fig. 3a, bands due to HMPA subtracted by "solvent compensation;" i.e., an infrared cell of same pathlength containing pure HMPA was placed in the reference beam) and after removal of coordinated THF gave analyses consistent with the formulation $Cs_2Cr(CO)_5$. After a brief exposure of the HMPA solution to dry air, a spectrum similar to the aforementioned one in ref. 7 results (see Fig. 3b, the relative intensities of the two bands at lowest energies are reversed if an HMPA band practically superimposable with the lowest energy band is not subtracted by solvent comparison. Such a reversal may be seen in the "solvent uncompensated" spectrum of $Na_2W(CO)_5$ in HMPA in ref. 5. It appears that the spectrum in ref. 7 under consideration also contains the superimposed HMPA band which causes considerable broadening of the lowest energy band). The bands, however, are all at ca. 20 cm^{-1} higher wavelength than reported previously, and are due to $Cs_2Cr_2(CO)_{10}$ (1910, 1881 and 1785 cm^{-1}) and $Cs_2Cr(CO)_5$ (1779, 1737 cm^{-1}). The 1785 and 1779 cm^{-1} bands of the dimer and monomer are unresolved in Fig. 3b. Further exposure of the solution to air results in complete disappearance of $Cs_2Cr(CO)_5$ and only bands due to $Cs_2Cr_2(CO)_{10}$ and an uncharacterized carbonyl species (weak band at 1854 cm^{-1} present in Figs. 3b and 3c) are present.

The chemical properties of the yellow product I from the Cs/Hg reduction of $Cr(CO)_6$ are consistent with its formulation as $Cs_2Cr(CO)_5$. Thus, the reactions

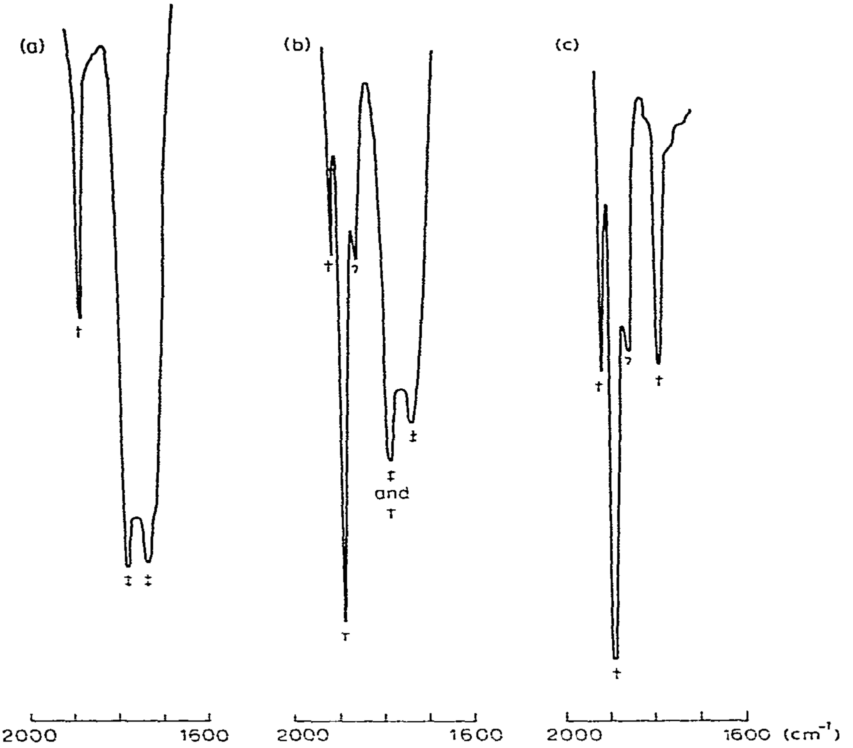

Fig. 3. Infrared spectrum of $Cs_2Cr(CO)_5$ in HMPA (HMPA bands subtracted via solvent compensation). (a). Trace of $Cs_2Cr_2(CO)_{10}$ present. (b). Brief exposure of solution to dry air. (c) Longer exposure of solution to dry air. Identity and position of bands ‡ = $Cs_2Cr(CO)_5$, 1779, 1737; † = $Cs_2Cr_2(CO)_{10}$, 1910, 1881, 1785; ? = unknown species absorbing at 1854 cm^{-1}

of I with $C_7H_7{}^+BF_4{}^-$ and Ph_3SnCl provide good yields of $Cs_2Cr_2(CO)_{10}$ and $Ph_3SnCr(CO)_5{}^-$. In marked contrast to I, $Cs_2Cr_2(CO)_{10}$ is very soluble in THF. The insolubility of $Cs_2Cr(CO)_5$ in THF undoubtedly plays an important role in the ability of Cs amalgam to cause virtually complete reduction of $Cr(CO)_6$ to I. Thus, cesium amalgam reductions of $Cr(CO)_6$ in HMPA provide only the dimeric dianion after seven hours at room temperature. In HMPA both $Cs_2Cr_2(CO)_{10}$ and I are soluble. Also, a similar driving force for quantitative formation of $Cr(CO)_5{}^{2-}$ does not exist in the Na or K amalgam reductions of $Cr(CO)_6$ in THF since $(Na\ or\ K)_2Cr(CO)_5$ is soluble in this medium.

Extremely air-sensitive orange solids formulated as $Cs_2M(CO)_5$ (M = Mo and W), also only very slightly soluble in THF, are obtained by analogous cesium amalgam reductions of corresponding $M(CO)_6$. These are often heavily contaminated with metallic mercury; however, their infrared spectra in the carbonyl region in HMPA (Table 1) and chemical properties so closely coincide with those of well defined $Cs_2Cr(CO)_5$ that there is no doubt as to the correctness of their formulation. The high expense of cesium metal, however, severely limits the utility of these salts as reactants in syntheses.

Reactions of metallic monohalides with $M(CO)_5{}^{2-}$ and $M_2(CO)_{10}{}^{2-}$. One or more equivalents of Ph_3MCl (M = Ge, Sn, Pb) react with $M'(CO)_5{}^{2-}$ (M′ = Cr, Mo,

W) generated in THF, HMPA or ammonia to provide generally good yields of $Ph_3MM'(CO)_5^-$. The products are air- and moisture-stable for indefinite periods; however, they slowly darken on exposure to sun or fluorescent light. The interaction of Ph_3SnLi with $M'(CO)_6$ at room temperature in THF gives identical tin derivatives in 20-60% yields. The latter species may also be obtained from the reaction of Ph_3SnCl and $M_2(CO)_{10}^{2-}$ according to the equation:

$$Ph_3SnCl + M_2(CO)_{10}^{2-} \xrightarrow{THF} Ph_3SnM(CO)_5^- + ClM(CO)_5^-$$

Infrared analysis supports the premise that the two anions are formed in approximately equal amounts. Such a reaction is not surprising in view of reports that the M—M bond of $M_2(CO)_{10}^{2-}$ is cleaved by halides [26], cyanogen [26], SnI_2 [27], GeI_2 [27], SO_2 [27], Hg [28], R_2SnCl_2 [11], and perfluoropropyl iodide [17]. Indeed, it seems likely that most covalent halides can cleave the rather weak M—M bond in these dianions.

Similar, but air-sensitive derivatives of $Cr(CO)_5^{2-}$, have been prepared by reaction of the chromium monomer with Me_3SnCl and $C_5H_5Fe(CO)_2I$. In order to achieve good yields of $C_5H_5Fe(CO)_2Cr(CO)_5^-$ it is necessary to add a solution of the anion slowly to a stirred solution of $C_5H_5Fe(CO)_2I$. Inverse addition causes formation of mainly $[C_5H_5Fe(CO)_2]_2$ and $Cr_2(CO)_{10}^{2-}$.

Infrared spectra of these monohalide derivatives are shown in Table 2; their solution spectra are all consistent with that expected of anions having local C_{4v} symmetry about the Group VIb metal.

The chemical properties of these novel metallic monohalide derivatives of $M(CO)_5^{2-}$ are currently under investigation and will be discussed in a future paper in this series.

Acknowledgement

The authors express their appreciation to the donors of the Petroleum Research Fund (PRF 2670-G3), administered by the American Chemical Society, the University of Minnesota Graduate School, and the NSF-Undergraduate Research Participation Program for partial support of this work.

References

1 H. Behrens and R. Weber, Z. Anorg. Allg Chem , 291 (1957) 122.
2 H. Behrens and W. Haage, Chem. Ber., 94 (1961) 312
3 H. Behrens and J. Vogl, Chem. Ber., 96 (1963) 2220.
4 E. Lindner, H. Behrens and D. Uhlig, Z. Naturforsch. Sect. B, 28 (1973) 276.
5 J.E. Ellis and G.P. Hagen, J. Amer. Chem. Soc., 96 (1974) 7825.
6 H.E. Podall, H.B. Prestridge and H. Shapiro, J. Amer. Chem. Soc , 83 (1961) 2057.
7 W.C. Kaska, J. Amer. Chem. Soc , 90 (1968) 6340.
8 R.G. Amiet, P.C. Reeves, and R Pettit, Chem. Commun. (1967) 1208.
9 J.S. Ward and R. Pettit, Chem. Commun., (1970) 1419.
10 B.D. Dombeck and R.J. Angelici, J. Amer. Chem. Soc., 95 (1973) 7516.
11 T.J. Marks, J. Amer. Chem. Soc., 93 (1971) 7090.
12 J.E. Ellis, J. Organometal. Chem., 86 (1975) 1.
13 J.K. Ruff, Inorg. Chem., 6 (1967) 1502.
14 T. Kruck and W. Molls, Z. Naturforsch. Sect. B, 29 (1974) 198.
15 T. Kruck, F.-J. Becker, H. Breuer, K. Ehlert, and W. Rother, Z. Anorg. Allg. Chem., 405 (1974) 95.

16 S. Herzog, J. Dehnert and K. Luhder, in H.B. Jonassen (Ed.), "Technique of Inorganic Chemistry", Vol. VII, Interscience, New York, NY, 1968.
17 R G. Hayter, J. Amer. Chem. Soc., 88 (1966) 4376.
18 E.W. Abel, I.S. Butler and J.G. Reid, J. Chem. Soc., (1963) 2068.
19 R.B. King, J. Inorg. Nucl. Chem., 25 (1963) 1296.
20 V.M. Sinclair, R.A. Davies and J.L. Drummond, Chem. Soc. Special Pub., No. 22 (1967) 260.
21 C. Tamborski, F E. Ford and E.J. Soloski, J Org. Chem., 28 (1963) 181.
22 J.E. Ellis and G.P. Hagen, unpublished research in progress
23 V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett., 2 (1966) 257.
24 W. Hieber, O. Vohler and G. Braun, Z. Naturforsch. Sect. B, 13 (1958) 192.
25 D.F. Shriver, Acc. Chem. Res., 3 (1970) 231.
26 H. Behrens and H. Zizlsperger, Z. Naturforsch. Sect. B, 16 (1961) 349.
27 J.K. Ruff, Inorg. Chem., 6 (1967) 2080.
28 H. Behrens, H.D. Feilner and D. Uhlig, Z. Naturforsch. Sect. B, 26 (1971) 990.