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Synthesis and Properties of the Pentacarbonylmetalates of the Group 6 Metals[†]

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Reduction of the amine complexes $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W) with sodium naphthalenide in THF provides a convenient route to the pentacarbonylmetalates of the group 6 metals in an innocuous solvent. The synthetic utility of the method has been demonstrated by reaction of the dianions with Ph_3SnCl to give $[NEt_4][M(CO)_5SnPh_3]$ (M = Cr, Mo, W) in 76, 92, and 62% yield, respectively, after counterion exchange. The sodium salts of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ cannot be handled in the solid state but can be readily separated from the NMe_3 and $C_{10}H_8$ byproducts of the reduction. Naphthalenide reduction has also been used to prepare $[W(CO)_5]^{2-}$ with Li^+ and K^+ counterions, and crystalline salts of $[W(CO)_5]^{2-}$ and $[Mo(CO)_5]^{2-}$ have been prepared by adding pentamethyldiethylenetriamine to $Li_2[W(CO)_5]$ and a cryptand (K-2.2.1) to $Na_2[M(CO)_5]$ (M = Mo, W). Crystals of the encrypted sodium salts are indefinitely stable, and a brief account is given of an X-ray diffraction study which establishes a slightly distorted trigonal-bipyramidal structure for the tungsten anion in the solid state. The IR spectra of the $[Na(K\text{-}2.2.1)]^+$ salts in CH_3CN exhibit the two band patterns expected in the carbonyl stretching region if the anions have D_{3h} structures without counterion contact ion pairing, but ion pairing has a marked effect on solution spectra of simple alkali-metal salts of $[W(CO)_5]^{2+}$. The Li^+ salt exhibits isocarbonyl absorptions indicating interaction with two of the equatorial carbonyls, while $Na_2[W(CO)_5]$ and $K_2[W(CO)_5]$ have high-energy carbonyl stretches indicative of contact ion pairing with direct M–W interaction.

Introduction

Carbonylmetalates have proved to be versatile and reactive intermediates in a wide variety of organotransition metal reactions,[1] and their accessibility has often been a crucial element in the development of the chemistry of particular systems. An example is the extensive exploration of the chemistry of $Na_2[Fe(CO)_4]$ (Collman's reagent), which was stimulated by the development of convenient syntheses of the tetracarbonylferrate dianion.[2] The relatively slow development of the chemistry of the analogous pentacarbonyl dianions of the group 6 metals can be attributed to the limitations of most of the available routes to these species.

The preparation of the $[M(CO)_5]^{2-}$ dianions (M = Cr, Mo, W) was first reported by Behrens and Weber using Na reduction of the hexacarbonyls in liquid ammonia,[3] and this method, as subsequently modified,[4] provides a high yield route to $Na_2[Cr(CO)_5]$. The yields of the Mo and W complexes are, however, low,[1b,5] and the salts obtained are impure. A slow disproportionation of $Na_2[M_2(CO)_{10}]$ (M = Cr, Mo, W) under CO has been reported to afford analytically pure samples of $Na_2[M(CO)_5]$,[6] but there have been no reports of this technically demanding method being used by other workers. Reduction of the hexacarbonyls with cesium amalgam gives the cesium salts $Cs_2[M(CO)_5]$ (M = Cr, Mo, W),[4] but the salts are usually contaminated with Hg and are of limited synthetic utility since they are insoluble in virtually all common organic solvents. Less powerfully reducing sodium and potassium amalgams provide mainly the less highly reduced $[M_2(CO)_{10}]^{2-}$ ions,[4] except in the case of sodium amalgam reduction of $[W(CO)_6]$ in dimethoxyethane. This has been reported to lead to formation of $Na_2[W(CO)_5]$,[7] but in our hands this reaction is not synthetically useful. Infrared spectra of a number of runs showed that $[W_2(CO)_{10}]^{2-}$ was always formed, and, although $[W(CO)_5]^{2-}$ was often present, the relative yield of the monomeric dianion was highly variable and never exceeded ca. 50%.

The most satisfactory synthesis of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ reported to date involves reduction of the hexacarbonyls with sodium in hexamethylphosphoramide (HMPA). This reaction proceeds in high yield,[8] but its application is restricted by the toxicity and low volatility of HMPA.

Our work on the preparation of alkylidene complexes from dianionic complexes by reaction with iminium salts[9] required convenient access to solutions of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ in an innocuous solvent such as tetrahydrofuran (THF), and this led us to explore alternative preparations of these anions. This paper presents the results of that research including details of convenient syntheses of the $[M(CO)_5]^{2-}$ (M = Cr, Mo, W) dianions in solution, the isolation of the first stable crystalline salts of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$, spectroscopic studies of many of the anionic species prepared, and a brief account of a single-crystal X-ray diffraction study of a salt of $[W(CO)_5]^{2-}$ with an encrypted sodium counterion. A preliminary account of some of this work has appeared.[10]

Experimental Section

General Data. All reactions and manipulations were carried out under dry nitrogen using standard Schlenk tube techniques

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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or a Vacuum Atmospheres Dri-Lab. Glassware was flame dried under vacuum or oven dried before use. Combustion analyses were performed by Dornis and Kolb, Mulheim a.d. Ruhr, B.R.D.

Solvents and Reagents. Tetrahydrofuran (THF), dimethoxyethane (DME), and diethyl ether were distilled under nitrogen from sodium–benzophenone ketyl. Pentane was distilled from powdered calcium hydride under nitrogen. Spectrograde dimethylformamide (DMF) was dried by stirring with powdered BaO, filtered, distilled in vacuo, and then stored under nitrogen over 4-Å molecular sieves. Spectrograde acetonitrile was rapidly distilled from a small amount of P_2O_5 onto 4-Å molecular sieves and degassed by the freeze–thaw method before use. Lithium naphthalenide solution was prepared as described previously.[11] Sodium (Fisher) and potssium (Fisher) naphthalenide solutions were prepared in a similar manner from metal samples freshly cut in the glovebox. Group 6 hexacarbonyls were used as received from Pressure Chemical Co. $[W(CO)_5(NMe_3)]$ was prepared photochemically (70% yield) by a modification of the literature method[12] using a Hanovia 450-W medium-pressure Hg lamp in a water-cooled jacket. The product (IR in THF: 2060 vw (A_1), 1931 vs (E), 1899 m cm^{-1} (A_1)) was purified by subliming off $[W(CO)_6]$ at 35 °C in vacuo and recrystallizing the amine complex from pentane at −78 °C. Kryptofix 2.2.1 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane: abbreviated to K-2.2.1 in this paper) was used as obtained from Parish Chemical Co.

Infrared Spectra. IR spectra were routinely obtained on a Perkin-Elmer 457-A spectrometer and rerecorded for publication on a Nicolet 7000 Fourier transform spectrometer by Mr. Gary Lee. Solution spectra were recorded in the range 1600–2100 cm^{-1} using 0.1-mm path length solution cells with sodium chloride windows. The cells were fitted with luer-lock syringe fittings which were tightly capped with small rubber septa (Aldrich) wired into place. Teflon cell spacers and gaskets were used since amalgamated cells tended to separate in use. Solutions of the pentacarbonylmetalate dianions were used to assess the integrity of the solution cells, since the dianions were rapidly oxidized to the dimeric dianions by traces of oxygen. The cells were judged acceptable if no detectable sample oxidation occurred in the time necessary for recording an IR spectrum, although typically samples were unchanged after ca. 1 h on the benchtop. The cells and transfer cannula were purged for at least 5 min with dry nitrogen and then flushed with the sample solution before being filled for measurement of a spectrum. When it was particularly important to be sure that no inadvertent sample oxidation had occurred, IR spectra were obtained on several different samples drawn from the same stock solution. Spectra were calibrated against the 1601 cm^{-1} absorption of a thin polystyrene film.

NMR Spectra. ^{13}C NMR spectra were recorded on a Bruker 300 WB at 75.5 MHz and calibrated relative to the carbonyl resonance at δ 206.0 of acetone-d_6 in a sealed capillary tube inside the NMR tube.

$[Cr(CO)_5NMe_3)]$. A mixture of 2.11 g of $[Cr(CO)_6]$ (9.6 mmol) and 1.5 g of $Me_3NO{\cdot}2H_2O$ (13.5 mmol) was dissolved in 100 mL of THF, and 11 mL of NMe_3 (ca. 122 mmol) was added. The mixture was stirred at room temperature for 70 min and then heated to 40 °C for 1 h. The solvent was removed, and the residue was left at room temperature in vacuo for 1.5 h to sublime away residual $[Cr(CO)_6]$ and then extracted with two 100-mL portions of pentane. The extracts were filtered through a Celite pad; the volume was reduced to near saturation at room temperature (*ca.* 20 mL final volume) and cooled to −60 °C. The product crystallized as long yellow needles which were collected, dried briefly in vacuo, and stored under nitrogen at 0 °C until needed. The complex can be handled briefly in air at room temperature: yield 1.46 g (5.8 mmol ≡ 61%); IR (THF) 2055 vw (A_1), 1932 vs (E), 1902 m cm^{-1} (A_1).

$[Mo(CO)_5(NMe_3)]$. A solution of 5.3 g of $[Mo(CO)_6]$ (20 mmol), 18 mL of NMe_3 (ca. 200 mmol), and 2.8 g of $Me_3NO{\cdot}2H_2O$ (25 mmol) in 150 mL of THF was maintained at 50 °C for 5 h. The solvent was removed on the rotary evaporator and the resulting dark orange-brown solid heated in vacuo to 35 °C to remove unreacted $[Mo(CO)_6]$. The product was extracted with two 200-mL portions of pentane, the extracts were filtered through a Celite pad, and the volume was reduced to 65 mL. After filtration from a small amount of insoluble material, the solution was cooled to −78 °C. The long yellow needles which formed were collected and dried at room temperature in vacuo for 30 min and then stored under nitrogen at 0 °C until needed: yield 4.02 g (13.6 mmol ≡ 68%); IR (THF) 2063 vw (A_1), 1934 vs (E), 1899 m cm^{-1} (A_1).

Preparation of Naphthalene-Free Solutions of $Na_2[Cr(CO)_5]$. A solution of $[Cr(CO)_5(NMe_3)]$ (0.306 g, 1.22 mmol) in 25 mL of THF was cooled to −78 °C and 12.7 mL of a 0.226 M solution of $NaC_{10}H_8$ in THF (2.35 equiv of $NaC_{10}H_8$/equiv Cr) syringed in dropwise over a period of 3 min. The solution IR spectrum of the homogeneous amber solution indicated virtually quantitative conversion of the trimethylamine complex to $Na_2[Cr(CO)_5]$. The THF was removed in vacuo at 0 °C and the product washed at 0 °C with two 25-mL portions of ether and then dried briefly in vacuo at 0 °C. The yellow powder was immediately cooled to −78 °C and covered with 15 mL of cold THF and then allowed to warm to room temperature as it dissolved. A solution IR spectrum of the resulting homogeneous solution indicated that negligible decomposition had occurred during workup.

Preparation of Naphthalene-Free Solutions of $Na_2[Mo(CO)_5]$. A solution of $Na_2[Mo(CO)_5]$ was prepared by $NaC_{10}H_8$ reduction of 0.14 g (0.47 mmol) of $[Mo(CO)_5(NMe_3)]$ in 20 mL of THF at −78 °C, as described above for the Cr isologue. After being warmed to room temperature, an IR spectrum of the homogeneous red-brown solution showed virtually complete reduction to $Na_2[Mo(CO)_5]$. The solution was concentrated in vacuo at −30 °C to a volume of 3–4 mL. Rapid addition of 100 mL of cold (−30 °C) diethyl ether (via 5-mm Teflon cannula) caused immediate precipitation of the light yellow product. The resulting slurry was stirred vigorously for 15 min at −30 °C and then allowed to settle. The ether was decanted off and this washing procedure repeated. The solid was dried briefly in vacuo at −35 °C and immediately redissolved in cold THF (−35 °C). The resulting solution could then be warmed to room temperature with no detrimental effects.

Preparation of Naphthalene-Free Solutions of $Na_2[W(CO)_5]$. A solution of $Na_2[W(CO)_5]$ was prepared by $NaC_{10}H_8$ reduction of 0.388 g of $[W(CO)_5(NMe_3)]$ (1.0 mmol) in 20 mL of THF at −78 °C, as described above for the Cr isologue. The red-orange mixture became suddenly darker and more brown in color when 10.1 mL of 0.20 M $NaC_{10}H_8$ had been added (corresponding to 2.0 equiv of $NaC_{10}H_8$/equiv of tungsten–this visual end point was often useful in determining when sufficient $NaC_{10}H_8$ had been added to complete the reduction). After being warmed to room temperature, a solution IR spectrum of the homogeneous reaction showed the reduction to be virtually complete. The solution was concentrated in vacuo at 0 °C to a volume of 5 mL, the mixture was cooled to −60 °C, and 40 mL of cold (−60 °C) ether was added. The product precipitated as a light yellow powder. The ether was decanted, and the product was washed with a second 40-mL portion of cold ether, dried in vacuo briefly at 0 °C, cooled to −50 °C, and immediately redissolved in cold THF. After being warmed, the solution IR spectrum indicated that no significant decomposition had occurred during the workup procedure.

Preparation of $[Na(K\text{-}2.2.1)]_2[Mo(CO)_5]$. A solution of $[Mo(CO)_5(NMe_3)]$ (0.259 g, 0.878 mmol) in 20 mL of THF was cooled to −78 °C and 7.8 mL of a 0.245 M solution of $NaC_{10}H_8$ in THF syringed in dropwise. The reaction was warmed to room temperature and a solution of 0.59 g of Kryptofix 2.2.1 in 22 mL of THF was added (2.02 equiv of K-2.2.1/equiv of Mo). An orange solid precipitated immediately, leaving a very pale orange mother liquor. The solvent was decanted off and the solid washed with 10 mL of THF and then pumped dry: yield 0.67 g (81%). A mull IR spectrum showed the solid to be predominantly a $[Mo(CO)_5]^{2-}$ salt, with $[Mo_2(CO)_{10}]^{2-}$ as the only detectable CO-containing contaminent. The crude product was dissolved in a minimal amount of acetonitrile to which a few drops of Kryptofix 2.2.1 had been added, centrifuged, and then crystallized by slow addition of THF. A similarly performed final recrystallization gave

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[12] (a) Strohmeier, W.; Gerlach, K.; von Hobe, D. *Chem. Ber.* **1961**, *94*, 164. (b) Strohmeier, W.; Guttenberger, J. F.; Blumenthal, H.; Albert, G. *Chem. Ber.* **1966**, *99*, 3419.

Table I. Principal C≡O Stretching Absorptions in the Infrared of Pentacarbonylmetalate Salts of the Group 6 Metals

complex	medium	ν(C≡O), cm^{-1}
$Na_2[W(CO)_5]$	THF	1828 vs, 1772 vs
$Li_2[W(CO)_5]$	THF	1812 vs, 1764 s, 1690 s, 1658 m
$[Li(PMDT)_x]_2[W(CO)_5]$	THF	1826 vs, 1784 s, 1762 s, 1713 sh, 1697 s, 1665 sh
$K_2[W(CO)_5]$	THF	1816 vs, 1743 vs
$[Na(K\text{-}2.2.1)]_2[W(CO)_5]$	CH_3CN	1787 vs, 1741 vs
$[Na(K\text{-}2.2.1)]_2[W(CO)_5]$	Nujol mull	1771 vs, 1722 vs
$Na_2[Mo(CO)_5]$	THF	1832 s, 1772 s, 1750 sh
$[Na(K\text{-}2.2.1)]_2[Mo(CO)_5]$	CH_3CN	1789 vs, 1741 vs
$[Na(K\text{-}2.2.1)]_2[Mo(CO)_5]$	Nujol mull	1770 vs, 1722 vs
$Na_2[Cr(CO)_5]$	THF	1817 vs, 1766 vs

analytically pure material as red-orange crystals. Extreme caution must be exercised during the recrystallization to avoid oxidation and consequent loss of material: IR (Nujol mull) 1770 vs, 1722 vs, 1363 m, 1350 m, 1299 m, 1289 sh, 1275 m, 1261 w, 1252 w, 1233 w, 1166 w, 1112 s, 1093 sh, 1082 s, 1068 sh, 1027 m, 935 m, 809 w, 714 w cm^{-1}. Anal. Calcd for $C_{37}H_{64}N_4O_{15}Na_2Mo$: C, 46.94; H, 6.81. Found: C, 46.89; H, 6.78.

Preparation of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$. A solution of $Na_2[W(CO)_5]$ was prepared by syringing dropwise 5.0 mL of 0.206 M $NaC_{10}H_8$ in THF (1.03 mmol) into a magnetically stirred solution of $[W(CO)_5(NMe_3)]$ (0.18 g, 0.48 mmol) in THF (10 mL) to give a deep red-brown solution. This was treated with a solution of Kryptofix-2.2.1 (0.32 g, 0.97 mmol) in 5 mL of THF to give an orange precipitate. The suspension was warmed to room temperature and the mother liquor filtered off. The solid was washed with THF (2 × 10 mL) and dried under vacuum to give an orange powder in which the principal carbonyl-containing species was $[W(CO)_5]^{2-}$, contaminated by a trace of $[W_2(CO)_{10}]^{2-}$ (mull IR; yield of $[Na{\cdot}K\text{-}2.2.2]_2[W(CO)_5]$ 0.4 g, 0.39 mmol ≡ 80%). The complex was recrystallized (yield 60%) by dissolving it in twice the minimum volume of DMF and adding THF dropwise over a period of 10–20 min to give blood red tabular crystals of the pure compound: IR (Nujol mull) 1771 vs, 1722 vs, 1351 m, 1299 m, 1290 sh, 1276 m, 1263 w, 1255 w, 1234 w, 1164 w, 1111 s, 1083 s br, 1027 m, 932 m, 811 w, 732 w cm^{-1}; ^{13}C NMR δ 257.4. Anal. Calcd for $C_{37}H_{64}N_4Na_2O_{15}W$: C, 42.94; H, 6.23. Found: C, 43.08; H, 6.70.

Preparation of Pentamethyldiethylenetriamine (PMDT) Complex of $Li_2[W(CO)_5]$. A solution of $Li_2[W(CO)_5]$ was prepared by syringing dropwise 25.7 mL of 0.234 M $LiC_{10}H_8$ in THF (6.01 mmol) into a solution of $[W(CO)_5(NMe_3)]$ (1.0 g, 2.61 mmol) in THF (40 mL) containing 1.05 mL (0.87 g, 50 mmol) of PMDT at −78 °C. The resulting homogeneous red solution was warmed to room temperature, and it was observed that an orange precipitate appeared at intermediate temperatures and then redissolved at ca. −10 °C. The solution was concentrated to ca. 40 mL under vacuum, at which volume the solution was close to saturation at room temperature, and cooled slowly (~12 h) to −78 °C. Long (2 mm) orange needles precipitated. These were collected by decantation and washed with 3 × 20 mL of THF at −78 °C. The wet needles were redissolved in THF and the solution IR and ^{13}C NMR spectra recorded. The solution IR (Table I) was similar to that of $Li_2[W(CO)_5]$; ^{13}C NMR δ 251.6.

Results

Reduction of $[M(CO)_6]$ and $[M(CO)_5(NMe_3)]$ (M = Cr, Mo, W). Initial attempts to develop a better route to the pentacarbonyl dianions focussed on modification of Ellis' reported reduction of $[W(CO)_6]$ with sodium amalgam in DME.[7] Since $[W(CO)_6]$ (T_{1u}, 1976 vs cm^{-1}), $Na_2[W(CO)_5]$ (see Table I), and $Na_2[W_2(CO)_{10}]$ (E, 1896 vs cm^{-1}) have distinctive principal CO stretching frequencies, solution IR provided a sensitive means of monitoring the reductions, and it was readily determined that the primary product of reduction under most conditions was $Na_2[W_2(CO)_{10}]$. Under no conditions did we see $Na_2[W(CO)_5]$ as the principal product, nor formation of a reproducible mixture of $[W(CO)_6]$, $Na_2[W_2(CO)_{10}]$, and $Na_2[W(CO)_5]$. Variations attempted included the addition of 5% v/v HMPA, the use of diglyme as the solvent, and reduction under irradiation. Reduction with potassium in DME gave $K_2[W_2(CO)_{10}]$, and reduction with potassium metal in THF in the presence of 0.1 molar equiv of benzophenone[2] gave a black, DME- and HMPA-insoluble powder which was not further characterized. Reduction with sodium in the presence of benzophenone at room temperature gave principally $Na_2[W_2(CO)_{10}]$.

The variability in the ratio of $Na_2[W_2(CO)_{10}]$ to $Na_2[W(CO)_5]$ under many of these conditions, together with the inability of any of the reagents examined to reduce $Na_2[W_2(CO)_{10}]$, led us to suspect that the problem in the reduction was kinetic rather than thermodynamic. It has been reported that electrochemical reduction of $[M(CO)_6]$ (M = Cr, Mo, W) to $[M_2(CO)_{10}]^{2-}$ occurs via $[M(CO)_5]^{-}\cdot$,[13] and if the same intermediate is involved in reduction to the $[M(CO)_5]^{2-}$ dianions, the use of a reductant with a low barrier to electron transfer could result in $[M(CO)_5]^{2-}$ formation before intermediate $[M(CO)_5]^{-}\cdot$ can dimerize. This reasoning led us to investigate the use of alkali-metal salts of fused polyaromatic anions, which are readily available by direct reaction of the metals with polyarenes in etheric solvents such as THF. The anions are powerful reductants with electrode potentials vs. SCE ranging as low as −2.50 V for naphthalene in CH_3CN.[14] Ellis has previously used sodium naphthalenide in carbonylmetalate chemistry to reduce $[M_4(CO)_{12}]$ to $[M(CO)_3]^{3-}$ (M = Rh, Ir).[16]

Clean reduction of $[W(CO)_6]$ to $Na_2[W(CO)_5]$ can be achieved by adding $NaC_{10}H_8$ to $[W(CO)_6]$ in THF at −78 °C. This procedure is, however, tedious, since the limited solubility of the carbonyl in THF at this temperature necessitates a very slow addition of the naphthalenide solution, and the more soluble complex $[W(CO)_5(NMe_3)]$ is the preferred substrate. Reduction gives slightly cloudy solutions which can be shown by IR to contain $Na_2[W(CO)_5]$ as the major carbonyl-containing product (Figure 1a).

The quantity of naphthalenide consumed is very sensitive to the purity of the solution used. With rigorous exclusion of air and H_2O and using $NaC_{10}H_8$ which contains no residual base (determined as described previously[11]), the reaction consumes 2.0 equiv of reductant, but the "end point" of the reaction, as indicated by a sharp change from a clear amber solution to a much darker, and often cloudy, solution, more typically comes after consumption of 2.2–2.3 equiv of reductant. Addition of larger excesses of reductant gives solutions which, at −78 °C, exhibit the characteristic dark green of the naphthalenide ion.

Attempts to reduce $[W(CO)_5(NMe_3)]$ at −78 °C with sodium anthracenide, a less powerfully reducing polyarene

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[14] Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. Although the reduction potentials of the arenes have not been reported in THF, similar potentials have been reported in DMF and dioxane.[15]

[15] Hoytink, G. J. *Adv. Electrochem. Electrochem. Eng.* **1970**, *7*, 221.

[16] Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

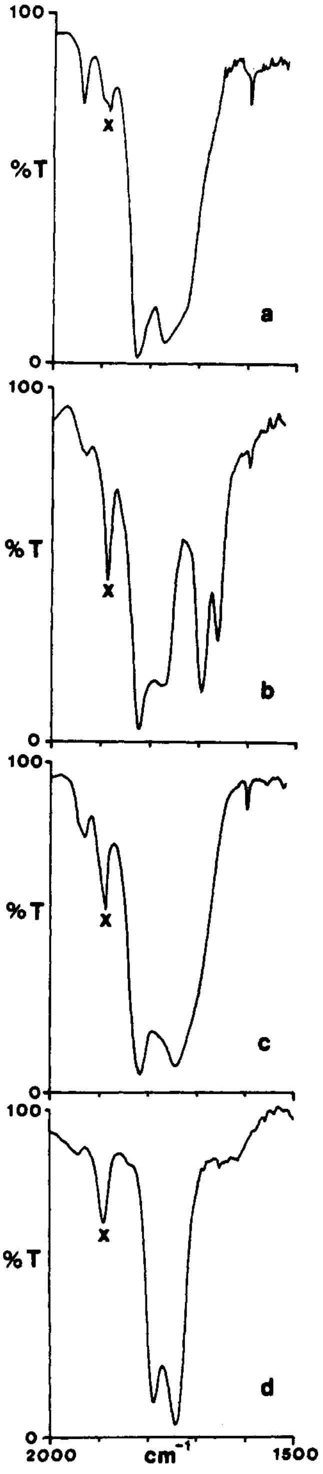

Figure 1. Solution infrared spectra in the C≡O stretching region of $[W(CO)_5]^{2-}$ salts. Peaks marked X arise from small quantities of $[W_2(CO)_{10}]^{2-}$ or $[W(CO)_5H]^-$ impurities. Contamination by these species is a particular problem in the case of solutions of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ (and its molybdenum analogue), which are exceptionally sensitive in solution, but the adventitious origin of the X peak in this sample is established by the increase in its relative intensity with time in the IR cell and its complete absence from spectra of Nujol mulls of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$. The samples are as follows: (a) $Na_2[W(CO)_5]$ in THF; (b) $Li_2[W(CO)_5]$ in THF; (c) $K_2[W(CO)_5]$ in THF; (d) $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ in CH_3CN.

anion (−1.97 V reductant vs. SCE in acetonitrile[14]), led to exclusive formation of $Na_2[W_2(CO)_{10}]$ as shown by solution IR.

Reduction of the Cr and Mo isologues of the trimethylamine complex with $NaC_{10}H_8$ at −78 °C provided clean routes to $Na_2[Cr(CO)_5]$ and $Na_2[Mo(CO)_5]$. Reduction of $[Mo(CO)_5(NMe_3)]$ provides the only convenient alternative to Ellis' preparation of $Na_2[Mo(CO)_5]$ in HMPA, and even in the case of $Na_2[Cr(CO)_5]$, which can be prepared by sodium reduction of $[Cr(CO)_6]$ in liquid NH_3,[1b,4] we find naphthalenide reduction to provide a more convenient route to the anion in most situations. The only significant difference between the route to $Na_2[W(CO)_5]$ and those to $Na_2[Mo(CO)_5]$ and $Na_2[Cr(CO)_5]$ is that the Cr and Mo amine complexes are more conveniently prepared from the hexacarbonyls by oxidation with $Me_3NO{\cdot}2H_2O$ in the presence of excess NMe_3 (eq 1) than by photolysis. Both complexes can be prepared photochemically,[12b] but in the case of the Mo complex in particular we have found that competitive disubstitution significantly reduces yields. Amine oxides have been used previously for oxidative substitution of CO in metal carbonyls.[17]

$$[M(CO)_6] \xrightarrow[THF]{Me_3NO/NMe_3} [M(CO)_5(NMe_3)] + CO_2 \quad (1)$$

$$M = Cr, Mo$$

Chemical Derivatization of $Na_2[M(CO)_5]$ Samples. Although IR spectra indicated that −78 °C reduction of $[M(CO)_5(NMe_3)]$ complexes resulted in essentially quantitative formation of the pentacarbonyl dianions, the qualitative character of the data led us to confirm the high yields by chemical derivatization. This was done by Ellis' method[4,18] in which solutions of the anions were treated with Ph_3SnCl to give the $[M(CO)_5SnPh_3]^-$ monoanions (eq 2). The $[NEt_4]^+$ salts of the monoanions were recrystallized from acetone/ether and identified by comparison of their IR spectra with those in the literature.[4] The ^1H NMR spectra of the complexes (CD_3CN) showed only absorptions assignable to the aromatic groups at δ 7.1–7.2 (m, 9 H) and 7.5 (m, 6 H), and the characteristic absorptions of the $[NEt_4]^+$ cation (in CD_3CN: δ 1.18 (tt, 12 H) and 3.13 (q, 8 H)).

$$Na_2[M(CO)_5] \xrightarrow[-NaCl]{Ph_3SnCl} Na[M(CO)_5SnPh_3] \xrightarrow{[NEt_4]Br} [NEt_4][M(CO)_5SnPh_3] \quad (2)$$

The derivatizations proceeded in 76, 92, and 62% yield for Cr, Mo, and W, respectively, and since these yields are based on the quantity of $[M(CO)_5(NMe_3)]$ used and hence represent cumulative yields after reduction, reaction with Ph_3SnCl, counterion exchange, and recrystallization, they clearly establish that the reductions do indeed proceed in a high yield[19] and provide eminently practical routes to the pentacarbonyl dianions.

Purification of $Na_2[M(CO)_5]$ Solutions. In many cases, the solutions of the pentacarbonyl dianions can be used as prepared without further purification. The solutions do, however, contain NMe_3 and naphthalene as side products of the reduction, and for some purposes (including reactions of the dianions with iminium salts[9]) it is desirable to free the solutions from these contaminants

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(19) The $[M_2(CO)_{10}]^{2-}$ dianions also form $[M(CO)_5SnPh_3]^-$ complexes when treated with Ph_3SnCl,[4] but this reaction cannot be a significant source of the tin complexes in these cases since solution IR established the absence of $[M_2(CO)_{10}]^{2-}$ anions from the reduced solutions.

by precipitation of the salts followed by washing with a non-polar solvent.

This procedure is complicated in practice by the thermal behavior of the solid salts. Precipitation of the Na^+ salts of the pentacarbonyl dianions from concentrated THF solutions by addition of diethyl ether at low temperatures (<-40 °C) gives fine yellow powders which will freely redissolve in THF to give solutions with the characteristic IR spectra of the pentacarbonyl dianions. At room temperature, however, the powders darken in color to give dull orange or brown powders which will not redissolve in THF nor in DME; the rapidity of this reaction can be judged from an experiment in which the bulk of a sample of $Na_2[W(CO)_5]$ was insoluble in THF after 10 min at ambient temperatures.

These observations were initially taken to imply that the salts are thermally unstable in the solid state, in surprising conflict with Behrens' reports.[6,20] Decomposition may not, however, be as complete as initially supposed, since a sample of $Na_2[W(CO)_5]$ maintained at ambient temperatures for 20 h, although essentially insoluble in THF, will partially (~35%) redissolve in a more polar solvent like DMF to give a solution in which the principal carbonyl containing species is $[W(CO)_5]^{2-}$ (IR: see Discussion).

Although the nature of the THF-soluble solids precipitated at low temperatures has not been unambiguously established, their precipitation does provide a practical route for the purification of the pentacarbonyl anions. The best compromise between the instability of the solids and the inconvenience of working at low temperatures is achieved by handling $Na_2[Cr(CO)_5]$ and $Na_2[W(CO)_5]$ at 0 °C and $Na_2[Mo(CO)_5]$ at -30 °C. Once precipitated as detailed in the Experimental Section, the solids can be washed with ether to remove the last traces of naphthalene and redissolved in cold THF or DME to give spectroscopically pure $Na_2[M(CO)_5]$ solutions. Such solutions are stable for periods of weeks at ambient temperatures; although we use fresh solutions of the salts for most reactions, this largely reflects the storage problems associated with solutions which are extremely O_2 and H_2O[21,22] sensitive.

Salts of the Pentacarbonyl Dianions with Li^+, $[Li(PMDT)]^+$, K^+, and $[Na(K\text{-}2.2.1)]^+$ Counterions. The nature of the naphthalenide reduction allows easy access to the pentacarbonyl dianions with other alkali-metal counterions, and the desirability of finding salts of the anions which could be handled and stored as solids led us to examine the preparation of $[W(CO)_5]^{2-}$ with a range of alternative counterions.

Reduction of $[W(CO)_5(NMe_3)]$ with THF solutions of lithium or potassium naphthalenide proceeds smoothly at -78 °C in a manner analogous to the $NaC_{10}H_8$ reduction. The only complications are that the $LiC_{10}H_8$ reduction is particularly sensitive to the presence of residual base and that the IR spectrum of $Li_2[W(CO)_5]$ (Table I and Figure 1b) differs markedly from that of $Na_2[W(CO)_5]$, exhibiting four principal bands, two of which are at the unusually low frequencies of 1690 and 1658 cm^{-1}. The IR spectrum of $K_2[W(CO)_5]$ in THF, which is similar to that of $Na_2[W(CO)_5]$ in THF, is tabulated in Table I and shown in Figure 1c.

The alkali-metal salts of $[W(CO)_5]^{2-}$ have similar handling characteristics. They are all thermally stable in solution, but solid samples will only partially redissolve, even in the polar solvent DMF, after being maintained at ambient temperatures. The rapidity of this change in the solubilities decreases in the order $Li^+ > Na^+ > K^+$: this parallels the decreasing order of charge:radius ratios for the cations and also the solubility order ($Li^+ > Na^+ > K^+$).

The availability of $Li_2[W(CO)_5]$ suggested an approach to the preparation of a tractable salt modeled on recent results obtained by Jonas and co-workers,[23] in which the addition of polychelate nitrogen donors such as tetramethylethylenediamine (TMEDA) to solutions of anionic complexes gave stable crystalline salts containing TMEDA coordinated lithium bonded to transition metals (as in $[Li(TMEDA)]_2[Ni(cyclodocatriene)]$[23,24]). Attempts to prepare similar salts of $Li_2[W(CO)_5]$ met with limited success. Reduction in the presence of pentamethyldiethylenetriamine (PMDT) gave solutions with IR spectra (Table I) similar to those of $Li_2[W(CO)_5]$. The material was less soluble than $Li_2[W(CO)_5]$ and could be crystallized at low temperatures as orange needles. These crystals were collected wet at -78 °C and are stable indefinitely at ambient temperatures provided they remain in contact with the mother liquor. Attempts to dry the crystals, however, resulted in immediate collapse, and we were unable to mount crystals for X-ray examination even in the presence of the mother liquor. Although the instability of the dry crystals precluded elemental analysis or mass balance determination, the IR data and the obviously reasonable yield suggested that the complex was the desired $[Li(PMDT)]_2[W(CO)_5]$ adduct or a solvate thereof.

The crystalline nature of the PMDT adduct suggested that it might be profitable to examine complete inhumation of the alkali-metal cation. Addition of the cryptand[25] Kryptofix 2.2.1 (see Experimental Section; abbreviated to K-2.2.1 in formulas) to a THF solution of $Na_2[W(CO)_5]$ precipitated $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ as an orange solid. This can be recrystallized from DMF/THF as orange octahedra which, although extremely air and water sensitive, are stable indefinitely at ambient temperatures. The cryptand salt is only soluble in polar solvents such as DMF and CH_3CN and reacts with both protic solvents and halocarbons such as CH_2Cl_2. The molybdenum analogue was prepared similarly by using an alternative CH_3CN/THF recrystallization and has similar solubility and handling characteristics. The full mull IR spectra of the cryptand salts are listed in the Experimental Section, the solution IR spectra are tabulated in Table I, and the solution spectrum of $[Na(K\text{-}2.2.1)]_2[W(CO))_5]$ is reproduced in Figure 1d.

Discussion

Mechanism of the Naphthalenide Reductions. The electrochemical studies of Pickett and Pletcher[13] suggest that $[Cr(CO)_5]^{-\cdot}$ has a lifetime of several seconds at room temperature in CH_3CN.[13b] The simplest mechanistic interpretation of the naphthalenide reductions is that this relatively stable radical anion and the isologous species, formed as shown in eq 3 and 4, are key intermediates and

$$[M(CO)_5L] \xrightarrow{e^-} [M(CO)_5L]^{-\cdot} \tag{3}$$

$$[M(CO)_5L]^{-\cdot} \xrightarrow{-L} [M(CO)_5]^{-\cdot} \tag{4}$$

$$[M(CO)_5]^{-\cdot} \xrightarrow{e^-} [M(CO)_5]^{2-} \tag{5}$$

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[20] The absence of spectroscopic data for Behrens' materials[6] prevents a detailed comparison.

[21] Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

[22] Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

[23] Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *19*, 520 and references therein.

[24] Brauer, D. J.; Krüger, C.; Sekutowski, J. C. *J. Organomet. Chem.* **1979**, *178*, 249.

[25] (a) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1. (b) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.

are directly reduced at −78 °C, as shown in eq 5. If this is the case naphthalene probably catalyzes the reduction, since the reduction potential of $C_{10}H_8^-$ is −2.50 V in CH_3CN,[14] while only one electron was transferred to the hexacarbonyls in controlled potential coulometry at potentials significantly more cathodic than this (−2.9 V for $[W(CO)_6]$ and $[Mo(CO)_6]$; −2.7 V for $[Cr(CO)_6]$).[13a] Alternative mechanisms involving addition of a second electron directly to a 19-electron $[M(CO)_5L]^{-\cdot}$ species (L = CO or NMe_3) seem unlikely in view of the instability of the 19-electron radical anions which are presumably the initial products of the electrochemical reductions.[13]

The failure to prepare $Na_2[W(CO)_5]$ by reduction of $[W(CO)_5(NMe_3)]$ with sodium anthracenide, a reaction which gives exclusively $Na_2[W_2(CO)_{10}]$, allows us to estimate that the potential required to reduce $[W(CO)_5]^{-\cdot}$ must lie between the reduction potential of anthracene (−1.97 V vs. SCE in CH_3CN[14]) and that of napthalene (−2.50 V vs. SCE in CH_3CN[14]). This magnitude would be consistent with the variable results which we have observed for sodium amalgam reduction of $[W(CO)_6]$: saturated (0.6%) sodium amalgam has a potential of −2.17 V vs. SCE,[26] and small variations in the reduction potentials of amalgam samples would fall within a range critical to the course of the reaction.

Solution and Solid-State Structures of Salts of the Pentacarbonyl Dianions and the Infrared and ^{13}C NMR Spectra of the Salts. The structure of neutral carbonyl complexes can often be readily determined from vibrational spectra of the molecules in solution by the application of straightforward symmetry considerations.[27] In the case of carbonylmetalates this process is considerably complicated by solution ion-pairing, which affects vibrational spectra because anion–cation interactions change the symmetry of the effective force field in the molecular ion and hence change the nature, symmetry, and activity of the normal modes of the ion.[28] We have taken advantage of the availability of the dianions with a range of counterions to make a preliminary analysis of these effects in the case of $[W(CO)_5]^{2-}$ and to deduce the probable structures of the dominant species in solution.

As demonstrated recently by Edgell and Chanjamsri[28p] encrypting an alkali-metal cation can considerably simplify the observed IR spectra of a carbonylmetalate by eliminating contact ion pairing and reducing the effect of solvent separated ion pairing on the vibrational spectra. In the case of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ and $[Na(K\text{-}2.2.1)]_2[Mo(CO)_5]$ the IR spectra in CH_3CN solutions (Table I and Figure 1d) contain two bands whose outlines can be well approximated by Lorentzian line functions. This would suggest that the spectrum is that of a single species with minimal solute-solvent interaction[28d,29] although the increase in the frequencies of the bands when compared with spectra obtained in Nujol mulls (Table I) implies that there is some solvent-separated ion pairing in CH_3CN.[30] As emphasized recently[28m,s] this has little obvious effect on the IR spectra of carbonylmetalates since, unlike most contact ion pairing, it does not significantly reduce the symmetry of the effective force field. The spectra in CH_3CN are similar to those reported for $Na_2[W(CO)_5]$ and $Na_2[Mo(CO)_5]$ in HMPA[32] and correlate well with those expected if the anions have trigonal-bipyramidal structures. This geometry has been suggested previously for the dianions in HMPA[8] and is the same as that established for the isoelectronic $[Mn(CO)_5]^-$[33] and $[Fe(CO)_5]$[34] com-

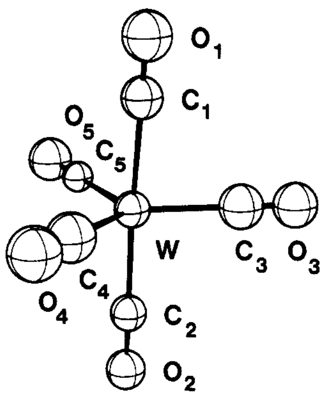

Figure 2. Structure of the $[W(CO)_5]^{2-}$ anion in $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$. The geometry is basically that of a trigonal bipyramid, with a significant distortion of the equatorial angles (C_3–W–C_4) = 111°, C_3–W–C_5 = 111°, and C_4–W–C_5 = 138°). The structure refined to an *R* value of 6.4% for 1376 reflections (see ref 36 for details).

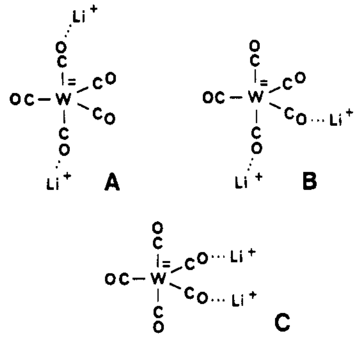

Figure 3. Possible structures for $Li_2[W(CO)_5]$ in THF solution. Nonlinear CO/Li^+ isocarbonyl interactions are suggested on the basis of the arguments presented by Darensbourg.[28n]

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(26) Calculated from the critically selected data in: Balej, J. *Electrochim. Acta* **1976**, *21*, 953.

(27) (a) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: London, 1975. (b) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley-Interscience: New York, 1971; Chapter 10.

(28) (a) Edgell, W. F.; Yang, M. T.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 2563. (b) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403. (c) Edgell, W. F.; Lyford, J. *J. Am. Chem. Soc.* **1971**, *93*, 6407. (d) Edgell, W. F.; Barbetta, A. *J. Am. Chem. Soc.* **1974**, *96*, 415. (e) Pribula, C. D.; Brown, T. L. *J. Organomet. Chem.* **1974**, *71*, 415. (f) Burlitch, J. M.; Theyson, T. W. *J. Chem. Soc., Dalton Trans.* **1974**, 828. (g) Darensbourg, M.; Borman, C. *Inorg. Chem.* **1976**, *15*, 3121. (h) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, A. *J. Am. Chem. Soc.* **1976**, *98*, 3127. (i) Pannell, K. H.; Jackon, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443. (j) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23. (k) Pannell, K. H.; Chen, Y.-S.; Belknap, K. L., Wu, C. C.; Bernal, I.; Creswick, M. W.; Huang, H. N. *Inorg. Chem.* **1983**, *22*, 418. (l) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297. (m) Edgell, W. F.; Hegde, S.; Barbetta, A. *J. Am. Chem. Soc.* **1978**, *100*, 1406. (n) Darensbourg, M. Y.; Barros, H. L. C. *Inorg. Chem.* **1979**, 18, 3286. (o) Schramm, C.; Zink, J. *J. Am. Chem. Soc.* **1979**, *101*, 4454. (p) Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 147. (q) Braterman, P. S.; Leslie, A. E. *J. Organomet. Chem.* **1981**, *214*, C45. (r) Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82. (s) Darensbourg, M. Y.; Jiminez, P.; Sackett, J. R.; Hanckel, J. M. Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

(29) Seshadri, K. S.; Jones, R. N. *Spectrochim. Acta* **1963**, *19*, 1013.

(30) The variable effects of cryptands on ion pairing in solutions of carbonylmetalates are illustrated by the conductometric evidence that $Na_2[Fe(CO)_4]$ solutions in *N*-methylpyrollidinone with 2 equiv of added cryptand contain free $[Fe(CO)_4]^{2-}$,[31] while $[Na(K\text{-}2.2.1)][Co(CO)_4]$ exhibits significant solvent separated ion pairing in tetrahydropyran and 2-methyltetrahydrofuran but not in tetrahydrofuran or 1,2-dimethoxyethane.[28p]

(31) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.

(32) Bands at 1775 (s) and 1731 (s) cm^{-1} and 1769 (s) and 1723 (s) cm^{-1}, respectively;[8] it is well established that this exceptionally polar solvent inhibits contact ion pairing of carbonylmetalate salts.[28h,n,r,s]

(33) Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 1109.

(34) Beagley, B.; Schmidling, D. *J. Mol. Struct.* **1974**, *22*, 466 and references therein.

plexes. The higher energy bands can be assigned to the A''_2 stretches of the axial ligands[35] while the more intense lower energy bands can be assigned to the E′ stretching modes of the equatorial ligands.[35] The bands have relative intensities similar to those of the corresponding bands in the spectra of the solvent separated $Na^+[Mn(CO)_5]^-$ ion pairs[28h] and show appropriate shifts to lower energies.

The geometry of $[W(CO)_5]^{2-}$ has been confirmed to be essentially trigonal bipyramidal in the solid state by a single-crystal X-ray diffraction study of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ (Figure 2),[36] although there is noticeable distortion of the equatorial carbonyl groups (see caption to Figure 2).

The most noticeable difference between the spectrum of $Li_2[W(CO)_5]$ in THF (Figure 1b) and that of the cryptand-complexed Na^+ salt is the presence of the low-energy absorptions at 1690 and 1658 cm^{-1} suggestive of contact ion pairing of the isocarbonyl type[1a,37] involving direct coordination of the cation to the oxygen of a carbonyl ligand. The presence of two isocarbonyl absorptions in solutions of $Li_2[W(CO)_5]$ suggests that both of the Li^+ ions interact with the anion, raising the possibility that $Li_2[W(CO)_5]$ in THF has one of the three structures shown in Figure 3. Structure A can be immediately ruled out since only the A_2'' isocarbonyl stretching mode would be IR active in this D_{3h} molecule. The two-band pattern could be consistent either with structure B or with structure C, but the observation of two distinct absorptions in the normal carbonyl stretching region is more consistent with structure C than with structure B.[38] The diequatorial structure should have only two strongly active carbonyl stretching modes as observed: one of the A_1 modes formally active under C_{2v} corresponds to the in-phase stretching combination of the axial ligands and would only give rise to a small dipole moment change. This should produce a weak high-energy absorption, and all preparations of $Li_2[W(CO)_5]$ exhibit precisely such an absorption at 1932 cm^{-1}.[39]

The preference for equatorial rather than axial isocarbonyl interaction is consistent both with the experimental observation of equatorial contact ion pairing in solutions of trigonal-bipyramidal $[Mn(CO)_4L]^-$ [28h] and $[Fe(CO)_4H]^-$ [28l] salts and with the general preference of d^8 trigonal-bipyramidal complexes for equatorial coordination of the best π-acceptor ligands in their coordination sphere: a $C{\equiv}O\cdots Li^+$ ligand can be regarded as a better π-acceptor than a $C{\equiv}O$ ligand.[28r]

IR spectra of $Na_2[W(CO)_5]$ in THF (Table I and Figure 1) indicate that there are dramatic differences between the ion pairing of $[W(CO)_5]^{2-}$ with Li^+ and that with Na^+. The $Na_2[W(CO)_5]$ spectrum contains none of the low-energy absorptions characteristic of isocarbonyl interactions, but the carbonyl stretching absorptions observed occur at markedly higher frequencies than in solutions or mulls of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$, indicating a strong interaction between the dianion and the Na^+ counterion which reduces the effective electron density at the metal center. This probably involves direct interaction of the Na^+ with the W: metal–metal contact is less common for carbonylmetalates than isocarbonyl ion pairing or contact interactions involving simultaneous interaction of a counterion with the oxygens of several carbonyl ligands,[41] but IR studies have established that it does occur in solutions of $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$[28i] and $Tl[Co(CO)_4]$.[28f] The spectrum of $K_2[W(CO)_5]$ in THF (Figure 1c and Table 1) is qualitatively similar to that of $Na_2[W(CO)_5]$, indicating similar contact ion pairing, but the absorptions are at significantly lower energies consistent with the lower polarizing power of the larger K^+ cation.

IR spectra of $Na_2[W(CO)_5]$ (and of $K_2[W(CO)_5]$) are consistent with maintenance of the basic trigonal-bypyramidal structure of $[W(CO)_5]^{2-}$ in solution.[42] The higher energy absorption at 1829 cm^{-1} would then be assigned to the out-of-phase (A_2'') stretch of the axial carbonyls, while the complex absorption at 1772 cm^{-1} would be derived from the equatorial E′ mode. These assignments suggest that equatorial coordination of one or both Na^+ counterions reduces the effective symmetry of the anion and splits the E′ band, while reducing back-donation to all the carbonyls and shifting both the A_2'' and E′ absorptions to higher energies.

The IR spectra of $Na_2[Mo(CO)_5]$ and $Na_2[Cr(CO)_5]$ in THF (Table I) are very similar to those of the tungsten salt, implying similar structures for the isologous molecular ions and that all three sodium salts undergo similar ion pairing in THF.

The dramatic counterion dependent changes in electron density at the metal in $[W(CO)_5]^{2-}$ observed by vibrational spectroscopy correlate closely with the changes in the ^{13}C NMR spectra of $[W(CO)_5]^{2-}$ as the counterion is changed. Like $[Fe(CO)_5]$, $[W(CO)_5]^{2-}$ is rapidly fluxional on the ^{13}C NMR time scale and exhibits a single absorption at all temperatures (down to 215 K for the $[Na(K\text{-}2.2.1)]^+$ salt, 240 K for the Li^+ salt, 205 K for the Na^+ salt). It is well established[46] that increasing the electron donation from a transition metal to a carbonyl ligand will shift the corresponding ^{13}C resonance downfield by an amount proportional to the change in the approximate force constant. Consistent with this, $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$ has the most deshielded ^{13}C absorption at 257.3 ppm while $Na_2[W(CO)_5]$ has the most shielded ^{13}C absorption at 247.4 ppm. The Li^+ salt, in which the two isocarbonyl ligands carry con-

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(35) (a) Bigorgne, M. *J. Organomet. Chem.* **1970**, *24*, 211. (b) Edgell, W. F.; Wilson, W. E.; Summitt, R. *Spectrochim. Acta* **1963**, *19*, 863.

(36) $[Na(K\text{-}2.2.1)]_2{}^+[W(CO)_5]^{2-}$ crystallizes in the orthorhombic space group $Pna2_1$, with a = 19.640 (6) Å, b = 22.193 (5) Å, and c = 10.405 (3) Å. X-ray data were collected on a Nicolet/Syntex $P2_1$ diffractometer using Mo Kα X-rays. The structure was solved by standard Patterson and heavy-atom techniques and refined to a final R factor of 6.4% for 1376 reflections. The structure determination was complicated by disorder of the $[Na(K\text{-}2.2.1)]^+$ cations, especially those of the ethylene carbons, many of which did not refine well. However, the $[W(CO)_5]^{2-}$ anion is well-defined and did refine properly, yielding the following molecular parameters: $W\text{–}C_1 = 2.00$ Å, $W\text{–}C_2 = 2.00$ Å, $W\text{–}C_3 = 1.88$ Å, $W\text{–}C_4 = 1.91$ Å, $W\text{–}C_5 = 1.87$ Å, $C_1\text{–}O_1 = 1.17$ Å, $C_2\text{–}O_2 = 1.21$ Å, $C_3\text{–}O_3 = 1.25$ Å, $C_4\text{–}O_4 = 1.28$ Å, $C_5\text{–}O_5 = 1.21$ Å; $C_1\text{–}W\text{–}C_2 = 172°$, $C_3\text{–}W\text{–}C_4 = 111°$, $C_3\text{–}W\text{–}C_5 = 111°$, $C_4\text{–}W\text{–}C_5 = 138°$, $W\text{–}C_1\text{–}O_1 = 177°$, $W\text{–}C_2\text{–}O_2 = 174°$, $W\text{–}C_3\text{–}O_3 = 176°$, $W\text{–}C_4\text{–}O_4 = 172°$, $W\text{–}C_5\text{–}O_5 = 172°$.

(37) Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469.

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(39) The intensity of this band is such that it is impossible to rule out the possibility that it is produced by a small quantity of a persistent impurity, and it has accordingly been omitted from Table I.

(40) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365 and references therein.

(41) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434.

(42) This seems reasonable since structural studies of $[Fe(CO)_4]^{2-}$ have shown that the distortions induced by interactions with monovalent counterions do not destroy the basic tetrahedral shape of the dianion.[41,43] More polarizing divalent cations, however, have been shown to produce more dramatic geometry changes when forming oligomers with $[Fe(CO)_4]^{2-}$.[44,45]

(43) Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

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siderable electron density, has an intermediately positioned absorption at 251.7 ppm.

The gross positions of the $[W(CO)_5]^{2-}$ absorptions are also consistent with electron density arguments: $[W(CO)_6]$ resonates at 192.1 ppm,[46] and this resonance is shifted downfield by ca. 30 ppm in the W(1−) complex $Na_2[W_2(CO)_{10}]$ with axial absorptions at 220.3 ppm and equatorial absorptions at 222.4 ppm.[47] It seems reasonable that further reduction to W(2−) should result in a further 30 ppm shift downfield as observed.

Solid-State Stability of Alkali-Metal Salts of $[M(CO)_5]^{2-}$ Anions. The nature of the THF-insoluble solids formed when solid samples of alkali-metal salts of $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ are left at ambient temperatures remains unclear. Mull IR spectra of "$Na_2[W(CO)_5]$" show ill-defined bands, centered at ca. 1850 and 1650 cm^{-1}, which do not correspond to the stretching absorptions of known carbonyltungstates. These are at approximately the frequencies which one would expect for contact ion paired $Na_2[W(CO)_5]$ with isocarbonyl interactions; it seems possible that at ambient temperatures $Na_2[W(CO)_5]$ initially forms a solid containing discrete cation/anion pairs which may then undergo a further slow reaction. This could involve formation of an anionic cluster[48] or, alternatively, might simply involve a solid state rearrangement to form a polymeric structure of distinctly lower solubility (cf. the oligomers of $[Fe(CO)_4]^{2-}$ with divalent cations such as Cd^{2+} [44,45]). This would explain why the PMDT adduct of $Li_2[W(CO)_5]$ is more tractable in the solid state than $Li_2[W(CO)_5]$, since PMDT coordination presumably prevents Li^+ coordinating to more than one carbonyl at a time.

The stability sequence for alkali metal salts of $[W(CO)_5]^{2-}$ parallels that reported by Ellis[18b] for the isoelectronic $[V(CO)_5]^{3-}$ anion (although the latter is significantly less stable) and presumably the species may be undergoing similar reactions. There is, however, one surprising difference: while the encrypted salts of $Na_2[W(CO)_5]$ and $Na_2[Mo(CO)_5]$ are indefinitely stable at room temperature, Ellis was unable to isolate salts of $[V(CO)_5]^{3-}$ with noncoordinating cations.[18b] Since the stability of the group 6 encrypted salts is what one would anticipate if a polymerization or other solid-state reaction is Lewis acid promoted, a partial explanation of the discrepancy may be that the vanadium salts are unstable with respect to decomposition pathways which are characteristic of the noncoordinating cations examined. Ellis has reported, for example, that the bis(diphenylphosphine)nitrogen(1+) (PPN^+) and PPh_4^+ salts of $[V(CO)_5]^{3-}$ decompose to give $[V(CO)_5(PPh_3)]^-$, and this may indicate that electron transfer reactions are occurring.[49] The intractability of the encrypted salts is more puzzling, but we have noted, for example, that $[Na(K\text{-}2.1.1)]_2[W(CO)_5]$, which has a crystal habit which differs from that of $[Na(K\text{-}2.2.1)]_2[W(CO)_5]$, is more difficult to handle as a solid than the 2.2.1-cryptand analogue.[47]

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Registry No. $[Cr(CO)_5(NMe_3)]$, 15228-26-9; $[Cr(CO)_6]$, 13007-92-6; $[Mo(CO)_5(NMe_3)]$, 15152-84-8; $[Mo(CO)_6]$, 13939-06-5; $Na_2[Cr(CO)_5]$, 52154-81-1; $Na_2[Mo(CO)_5]$, 54099-81-9; $Na_2[W(CO)_5]$, 54099-82-0; $[W(CO)_5(NMe_3)]$, 15228-32-7; $Na{\cdot}K\text{-}2.2.1]_2[Mo(CO)_5]$, 96997-09-0; $[Na{\cdot}K\text{-}2.2.1]_2[W(CO)_5]$, 79199-37-4; $Li_2[W(CO)_5]$, 75706-82-0; $K_2[W(CO)_5]$, 96913-74-5; $[Li(PMDT)]_2[W(CO)_5]$, 96913-75-6; $[NEt_4][Cr(CO)_5SnPh_3]$, 55997-66-5; $[NEt_4][Mo(CO)_5SnPh_3]$, 55971-56-7; $[NEt_4][W(CO)_5SnPh_3]$, 55971-72-7; Ph_3SnCl, 639-58-7.

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