Conclusions

The rate data presented in this paper for these $CrCl(AA)(dien)^{2+}$ complexes are difficult to interpret in terms of the dissociative mechanisms that have proved suitable for the Co(III) analogues. Consequently, we believe, along with Swaddle,[14] that the I_a mechanism is more suitable for an understanding of the hydrolysis rate patterns obtained for chloro(amine)chromium(III) complexes.

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Registry No. $CrCl(en)(dien)^{2+}$, 59184-05-3; $CrCl(pn)(dien)^{2+}$, 58806-22-7; $CrCl(tmd)(dien)^{2+}$, 58806-20-5; $CrCl(NH_3)_5^{2+}$, 14482-76-9; $CoCl(NH_3)_5^{2+}$, 14970-14-0; $CoCl(pn)(dien)^{2+}$, 62106-89-2; $CoCl(tmd)(dien)^{2+}$, 46239-66-1; Hg^{2+}, 14302-87-5.

References and Notes

(1) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, **19**, 2051 (1966).
(2) T. K. Huan, J. N. Mulvihill, A. R. Gainsford, and D. A. House, *Inorg. Chem.*, **12**, 1517 (1973).
(3) L. S. Dong and D. A. House, *Inorg. Chim. Acta*, **19**, 23 (1976).
(4) L. S. Dong, M.Sc. Thesis, University of Canterbury, Christchurch, New Zealand, 1976.
(5) Abbreviations used: en, $NH_2(CH_2)_2NH_2$; pn, $NH_2CH(CH_3)CH_2NH_2$; tmd, $NH_2(CH_2)_3NH_2$; Metmd, $CH_3NH(CH_2)_3NH_2$; dien, $NH_2(CH_2)_2NH(CH_2)_2NH_2$; dpt, $NH_2(CH_2)_3NH(CH_2)_3NH_2$.
(6) D. A. House, *Inorg. Nucl. Chem. Lett.*, **12**, 259 (1976).
(7) The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, **28**, 1 (1971). The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order which these are written in the cation formula. The convention adopted here is that the polyamine ligands are coordinated stepwise from one end in the order of the alphabetical letters.
(8) A. R. Gainsford, Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand, 1971; also unpublished work on the crystal structure of the *B*-$[CoCl(pn)(dien)]ZnCl_4$ salt.
(9) A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, **3**, 367 (1969); **5**, 544 (1971).
(10) All calculations were performed on an IBM 360/44 using OMNITAB II, National Bureau of Standards, Washington, D.C., 1971.
(11) A. J. Cunningham, D. A. House, and H. K. J. Powell, *J. Inorg. Nucl. Chem.*, **33**, 572 (1971); see eq 11 and 12.
(12) J. H. Espenson and S. R. Hubbard, *Inorg. Chem.*, **5**, 686 (1966).
(13) A. M. Sargeson, *Pure Appl. Chem.*, **33**, 527 (1973).
(14) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
(15) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 47 (1974).
(16) S. C. Chan and K. Y. Hui, *Aust. J. Chem.*, **20**, 2529 (1967).
(17) M. D. Alexander, *Inorg. Chem.*, **5**, 2084 (1966).
(18) D. A. House, *Inorg. Nucl. Chem. Lett.*, **6**, 741 (1970).
(19) M. C. Couldwell and D. A. House, *Inorg. Nucl. Chem. Lett.*, **7**, 947 (1971).
(20) M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972).
(21) M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, **12**, 627 (1973).
(22) S. C. Chan and S. F. Chan, *Aust. J. Chem.*, **24**, 2071 (1971).
(23) M. L. Tobe, *Acc. Chem. Res.*, **3**, 377 (1970).
(24) C. K. Poon, *Inorg. Chim. Acta, Rev.*, **4**, 123 (1970).
(25) C. S. Garner and D. A. House, *Transition Met. Chem.*, **6**, 211 (1970).

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Chemistry of Metal Carbonyl Anions. 9.[1] Syntheses and Properties of Alkylpentacarbonylmetalate Anions of Chromium and Tungsten

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Reactions of $Na_2M(CO)_5$ (M = Cr in THF and W in 1,2-dimethoxyethane (DME)) with various alkyl halides provide $RM(CO)_5^-$ ($R = CH_3, C_2H_5, NCCH_2, C_6H_5CH_2$) which have been isolated as bis(triphenylphosphine)iminium (PPN^+) salts. Spectral, chemical, and other properties of these new substances are discussed. Also, a new method for the synthesis of $Na_2W(CO)_5$ by the sodium amalgam reduction of $W(CO)_6$ in DME is reported and discussed with respect to other known preparations of this substance.

Recently we reported on the first general and high-yield synthesis of the pentacarbonylmetalate dianions of chromium, molybdenum, and tungsten[2] and utilized these highly reactive species in the preparation of group 4 metal and metalloidal derivatives of the general formula $R_3EM(CO)_5^-$.[3] In this paper, an extension of this general procedure (eq 1) for the

$$M(CO)_5^{2-} + RCl \rightarrow RM(CO)_5^- + Cl^- \tag{1}$$

preparation of alkylpentacarbonylmetalate anions of chromium and tungsten is reported. While this work was in progress, a preliminary note appeared on two alternate syntheses (eq

$$W(CO)_5Br^- + RLi \rightarrow RW(CO)_5^- + Br^- \tag{2}$$

$$RCOW(CO)_5^- \xrightarrow{h\nu} RW(CO)_5^- + CO \tag{3}$$

2 and 3) for $RW(CO)_5^-$ species,[4] the second of which parallels Isaacs and Graham's synthesis of silyl-, germyl- and stannylpentacarbonylmetalates of Cr, Mo, and W.[5] Previous attempts to prepare alkylpentacarbonylmetalate monoanions of Cr, Mo, and W by the reaction of dialkylmercury with $M_2(CO)_{10}^{2-}$ [6] or alkyllithium reagents with $M(CO)_6$[7] were unsuccessful; however, the latter reaction provided the corresponding acylpentacarbonylmetalates, the precursors to Fischer carbene complexes.[8]

Related $XM(CO)_5^-$ species containing a noncarbonyl carbon–metal bond reported previous to this work include the X = heptafluoro-1-methylpropenyl complex of eq 4, cyanides (eq 5–7), various acetylides (eq 4, 8), methylenephosphoranes (eq 9), substituted vinyls (eq 10), and diphenylmethoxymethyl (eq 11) (M = Cr, Mo, W).

$$2AgX + M_2(CO)_{10}^{2-} \rightarrow 2XM(CO)_5^- + 2Ag \quad (X = C_4F_7,^{9}\ PhC{\equiv}C^{7}) \tag{4}$$

$$Hg(CN)_2 + M_2(CO)_{10}^{2-} \rightarrow 2NCM(CO)_5^- + Hg \tag*{(5)^{9}}$$

$$M(CO)_6 + N(SiMe_3)_2^- \rightarrow NCM(CO)_5^- + (Me_3Si)_2O \tag*{(6)^{10}}$$

$$Cr(CO)_5^{2-} + CN^- + 2H_2O \rightarrow NCCr(CO)_5^- + 2OH^- + H_2 \tag*{(7)^{11}}$$

$$M(CO)_6 + RC{\equiv}C{:}^- \rightarrow RC{\equiv}CM(CO)_5^- + CO \tag*{(8)^{12}}$$

$$(OC)_5CrC(OMe)Ph + HPPh_2 \rightarrow (OC)_5^-CrC(OMe)Ph(^+PPh_2H) \tag*{(9)^{13}}$$

$$(OC)_5CrC(OMe)Me + n\text{-}BuLi \rightarrow [(OC)_5CrC(OMe)CH_2]^-Li^+ + C_4H_{10} \tag*{(10)^{14}}$$

$$(OC)_5WC(OMe)Ph + PhLi \rightarrow [(OC)_5WC(OMe)Ph_2^-Li^+] \quad \text{(not isolated)} \tag*{(11)^{15a}}$$

In the course of this work we also developed a convenient new method for the synthesis of $Na_2W(CO)_5$ in 1,2-dimethoxyethane (DME). This salt has previously only been available in good yield from the reduction of $W(CO)_6$ by sodium metal in hexamethylphosphoramide (HMPA).[2,3] Considerable difficulty was experienced in the isolation of the moisture-sensitive $RW(CO)_5^-$ from high boiling HMPA, so the new method is of much importance in the preparation of these materials. Further, since HMPA is a potential carcinogen,[15b] the DME method represents a desirable alternative route to $Na_2W(CO)_5$.

Experimental Section

General Procedures and Starting Materials. All procedures were carried out under an atmosphere of purified nitrogen or argon further purified by passage through a column of activated BASF catalyst and by dispersion through concentrated sulfuric acid. Solutions were transferred by stainless steel cannulae and syringes. Reagent grade ethyl ether (Fischer), tetrahydrofuran (Aldrich), and dimethoxyethane (Aldrich) were freshly distilled from the benzophenone ketyl of sodium under an argon atmosphere. All liquid alkyl halides (Aldrich) except CH_3I were distilled from anhydrous calcium hydride under an argon atmosphere. Reagent grade acetone and methylene chloride (Aldrich) were degassed for at least 30 min with purified nitrogen passed through a dispersion tube. Tungsten hexacarbonyl (Pressure Chemical), triphenyltin chloride (Ventron), and sodium metal (Fischer Scientific) were used as received from commercial sources. Bis(triphenylphosphine)iminium chloride was prepared according to the method of Ruff and Schlientz,[16] recrystallized from boiling water, and dried for 48 h under high vacuum. Disodium pentacarbonylchromate was prepared by the method of Ellis et al.[3] IR spectra were recorded on a Perkin-Elmer 237B spectrophotometer. Solution spectra were obtained in sealed sodium chloride cells (Barnes Engineering) equipped with stainless steel Luer stopcocks to permit filling via syringe outside the glovebox with essentially complete exclusion of air. All new compounds prepared in this study decompose before melting.

Synthesis of $[(PPh_3)_2N][MeCr(CO)_5]$ (I). Disodium pentacarbonylchromate (0.5 g, 2.1 mmol) was dissolved in 25 mL of THF at room temperature in a flask fitted with a three-way stopcock. With continuous stirring, 0.13 mL (2.1 mmol) of methyl iodide was added dropwise from a syringe throughout a period of 2 min. The resulting yellow solution was transferred via a cannula to a flask containing 1.21 g (2.1 mmol) of bis(triphenylphosphine)iminium chloride dissolved in 25 mL of dichloromethane and the mixture was stirred for 2 h at room temperature. After filtration (medium-fritted disk), the solution was pumped dry, resulting in compound I contaminated with NaI. Addition of ethyl ether (15 mL) to an acetone solution (5 mL) of the crude product caused precipitation of the NaI. Yellow crystalline I (1.10 g, 70% yield) was obtained by removing solvent under vacuum, washing with ether (3 × 10 mL), and drying under vacuum. An analytically pure sample was obtained by further recrystallization from acetone–ether. Anal. Calcd for $C_{42}H_{33}O_5CrNP_2$: C, 67.65; H, 4.46; N, 1.88. Found: C, 67.43; H, 4.47; N, 2.06.

Synthesis of $[(PPh_3)_2N][PhCH_2Cr(CO)_5]$ (II). This material was prepared by the same procedure as given for I using $Na_2Cr(CO)_5$ (0.5 g, 2.1 mmol) in 25 mL of THF and benzyl chloride (0.24 mL, 2.1 mmol). After filtration, the solution was pumped dry providing 0.97 g (56% yield) of II which gave acceptable analyses without further purification. Anal. Calcd for $C_{48}H_{37}O_5CrNP_2$: C, 70.16; H, 4.54; N, 1.70. Found: C, 70.29; H, 4.54; N, 1.67.

Synthesis of $[(PPh_3)_2N][NCCH_2Cr(CO)_5]$ (III). A procedure similar to the above was used for the synthesis of III from $Na_2Cr(CO)_5$ (0.5 g, 2.1 mmol) and $NCCH_2Cl$ (0.14 mL, 2.1 mmol) except best results are obtained if the halide is added at once rather than dropwise. The initial product obtained was a semicrystalline orange-yellow solid (0.65 g, 40% yield). Analytically pure III was obtained by recrystallization from hot ethyl ether. Anal. Calcd for $C_{43}H_{32}O_5CrN_2P_2$: C, 67.02; H, 4.18; N, 3.64. Found: C, 66.34; H, 4.07; N, 4.34.

Synthesis of $[(PPh_3)_2N][EtCr(CO)_5]$ (IV). Ethyl bromide (0.16 mL, 2.1 mmol) was added dropwise by syringe to a solution of $Na_2Cr(CO)_5$ (0.5 g, 2.1 mmol) in 25 mL of THF at −78 °C. Yellow crystals rapidly formed which dissolved upon warming to give a deep red solution. After metathesis of ions as described for I a red-brown solid was obtained. This was washed with ether (3 × 10 mL), dried, and dissolved in acetone (30 mL). The resulting yellow solution was filtered and pumped dry. Analytically pure gold-colored IV (0.16 g, 10%) was obtained after washing the residue with ether (5 × 10 mL). Anal. Calcd for $C_{43}H_{35}O_5CrNP_2$: C, 67.98; H, 4.64; N, 1.84. Found: C, 68.00; H, 4.61; N, 2.10.

Synthesis of $Na_2W(CO)_5$ from $W(CO)_6$ in 1,2-Dimethoxyethane (DME). Tungsten hexacarbonyl (0.78 g, 2.22 mmol) and sodium amalgam (5 mL of 0.8% Na in Hg) were stirred at room temperature in 35 mL of DME in a flask containing a stopcock on the side to facilitate the removal of amalgam. After approximately 2 h the solution had assumed a deep red color and infrared spectra in the ν(CO) region (see Figure 1) indicated almost complete reduction to $Na_2W(CO)_5$. Solutions obtained in this manner were used directly in the preparation of various $RW(CO)_5^-$ species described below.

Synthesis of $[(PPh_3)_2N][MeW(CO)_5]$ (V). Gaseous methyl bromide (2.2 mmol) was transferred on a vacuum line to the above solution of $Na_2W(CO)_5$ in DME cooled with liquid nitrogen. After warming of the solution to room temperature with stirring, the product was isolated by the same procedure as shown for I above. Crystalline deep yellow V was thereby obtained in 32% yield (0.60 g). Recrystallization from acetone–ether provided the analytical sample. Anal. Calcd for $C_{42}H_{33}P_5NP_2W$: C, 57.49; H, 3.79; N, 1.60. Found: C, 57.35; H, 3.70; N, 2.21.

Synthesis of $[(PPh_3)_2N][PhCH_2W(CO)_5]$ (VI). This material was prepared by the same procedure as II using $Na_2W(CO)_5$ (2.2 mmol) as prepared above and 1 equiv of benzyl chloride. Purification yielded 0.92 g (45%) of yellow crystalline VI. Anal. Calcd for $C_{48}H_{37}O_5NP_2W$: C, 60.46; H, 3.91; N, 1.47. Found: C, 60.22; H, 4.10; N, 1.31.

Synthesis of $[(PPh_3)_2N][NCCH_2W(CO)_5]$ (VII). This substance was prepared by using 2.2 mmol of $Na_2W(CO)_5$ (vide supra) in 35 mL of DME and 0.14 mL (2.2 mmol) of chloroacetonitrile. A yield of 1.32 g (69%) of yellow crystalline VII was obtained by the same procedure used in the isolation of III. Anal. Calcd for $C_{43}H_{32}O_5N_2P_2W$: C, 57.22; H, 3.57; N, 3.10. Found: C, 57.31; H, 3.66; N, 2.82.

Synthesis of $[(PPh_3)_2N][EtW(CO)_5]$ (VIII). Rather low yields (ca. 16%) of analytically pure, yellow, crystalline VIII were obtained by the reaction of $Na_2W(CO)_5$ (2.2 mmol) and ethyl bromide (2.2 mmol, 0.16 mL) in 35 mL of DME according to the same procedure used for IV. Anal. Calcd for $C_{43}H_{35}O_5NP_2W$: C, 57.93; H, 3.96; N, 1.57. Found: C, 57.28; H, 3.52; N, 1.93.

Results and Discussion

Alkylpentacarbonylchromate Complexes, $[(Ph_3P)_2N][RCr(CO)_5]$. Treatment of tetrahydrofuran solutions of $Na_2Cr(CO)_5$, prepared by sodium metal reduction of $Cr(CO)_6$ in liquid ammonia,[3] with a variety of alkyl halides, provides corresponding $RCr(CO)_5^-$ in 10–70% yields depending on the nature of the alkyl group. These moisture- and air-sensitive species were isolated as bis(triphenylphosphine)iminium (PPN^+) salts to provide additional stability toward oxidation.[17] Low yields were obtained for the ethyl complex due to its thermal instability in solution and resultant difficulty in obtaining a sample of analytical purity. Interestingly, attempts to prepare the unknown (σ-allyl)$Cr(CO)_5^-$ by the reaction of $Na_2Cr(CO)_5$ and allyl chloride led to isolation of 75% yields of the known chloropentacarbonylchromate(0), $ClCr(CO)_5^-$,[18] as the PPN^+ salt. Pentacarbonylchromate(−II) is known to be an extremely strong reducing agent;[19] consequently, the reduction of allyl chloride is not surprising. Similar reactions of other carbonyl anions with allyl halides have been described;[20] however, generally allyl complexes are formed under these conditions.[19] Solubility, spectral, and chemical properties of these salts are very similar to those of corresponding $RW(CO)_5^-$ and will be described below.

Preparation of $Na_2W(CO)_5$ in Dimethoxyethane (DME). Although it is possible to generate $RM(CO)_5^-$ (R = alkyl; M = Cr, Mo, W) almost quantitatively in hexamethylphosphoramide from $Na_2M(CO)_5$[2] and most alkyl halides (allyl chloride is an exception; vide supra), isolation of these moisture-sensitive materials from HMPA (nbp 230 °C) has proven to be an extremely difficult and very low-yield procedure. Accordingly, alternate methods for the synthesis of $Na_2M'(CO)_5$ (M′ = Mo, W), which are not available from the liquid ammonia reductions of $M'(CO)_6$ or $M'_2(CO)_{10}^{2-}$,[19] were sought. It was found that a room-temperature reduction

Table I. Infrared and Proton NMR Spectra of $RM(CO)_5^-$

R	M	Carbonyl str freq,[a] cm^{-1}	Chem shift (ppm),[d,e] multiplicity, and assignment
CH_3	Cr	2019 w, 1926 m, 1888 s, 1842 m	−0.81 (s, 3 H) Cr–CH_3
$C_6H_5CH_2$	Cr	2022 w, 1942 m, 1894 s, 1845 m	1.77 (s, 2 H) Cr–CH_2, 6.33–6.73 (m, 1 H para), 6.73–7.07 (m, 4 H ortho and meta)
$NCCH_2$	Cr[b]	2042 w, 1944 m, 1912 s, 1872 m	0.21 (s, 2 H) Cr–CH_2
CH_3CH_2	Cr	2013 w, 1923 m, 1881 s, 1839 m	0.74 (t, 3 H) –CH_3, 2.67 (q, 2 H) Cr–CH_2
CH_3	W	2031 w, 1922 m, 1887 s, 1836 m	−0.71 (s, 3 H) W–CH_3
$C_6H_5CH_2$	W	2038 w, 1942 m, 1895 s, 1846 m	1.95 (s, 2 H) W–CH_2, 6.21–6.54 (m, 1 H para), 6.74–6.98 (m, 4 H ortho and meta)
$NCCH_2$	W[c]	2050 w, 1940 m, 1903 s, 1867 m	0.60 (s, 2 H) W–CH_2
CH_3CH_2	W	2030 w, 1944 m, 1883 s, 1842 m	0.73 (t, 3 H) –CH_3, 2.49 (q, 2 H) W–CH_2

[a] In THF for M = Cr; in DME for M = W. [b] ν(NC) 2188 cm^{-1}. [c] ν(NC) 2188 cm^{-1}. [d] At 60 MHz recorded in acetone-d_6. [e] Resonances due to cation not shown.

of $W(CO)_6$ by sodium amalgam in DME worked surprisingly well for the synthesis of $Na_2W(CO)_5$. In contrast, the corresponding reduction in THF provided only exceedingly small amounts of the monomeric dianion.[3] Figure 1 shows the infrared spectrum of a $W(CO)_6$ reduction (0.5 g) by sodium amalgam in DME (25 mL) after 2 h at room temperature. The most intense bands (ν(CO) 1827 (s), 1757 (s, b) cm^{-1}) correspond to $Na_2W(CO)_5$ and closely resemble those of $Na_2Cr(CO)_5$ in THF (see Figure 2 in ref 3) in shape and relative intensity. Weaker bands are due to $Na_2W_2(CO)_{10}$ (ν(CO) 1959 (w), 1889 (m), cm^{-1}) which is an intermediate reduction product.[21] Since longer reaction times do not diminish the amount of dimeric dianion, there is undoubtedly an equilibrium between $Na_2W(CO)_5$, $Na_2W_2(CO)_{10}$, solvent, and sodium amalgam under these conditions. To support this claim, we have found these reductions to be very dependent on the nature of the solvent and reducing agent. Thus, cesium amalgam reductions of $M(CO)_6$ (M = Cr, Mo, W), even in THF, proceed to completion, undoubtedly, in part because $Cs_2M(CO)_5$ complexes are only very slightly soluble in this medium.[3,22] Also, DME and HMPA, which are much better coordinating solvents than THF, are significantly more effective than THF in the reduction of $W(CO)_6$ to $Na_2W(CO)_5$. On this basis, we believe that the use of a more electropositive metal, such as potassium, and/or a stronger coordinating solvent than DME, such as diglyme (or DME in the presence of a crown ether), should enable the production of even cleaner preparations of $Na_2W(CO)_5$ and possibly $Na_2Mo(CO)_5$ (vide infra) without resorting to the use of HMPA. Surprisingly, Na/Hg–$Mo(CO)_6$ reductions in DME go no farther than they do in THF; i.e., only very weak spikes at 1822 and 1757 cm^{-1} are observed after long reaction times (e.g., 4 days). Presently, we have not found a satisfactory method for a practical synthesis of reasonably pure $Na_2Mo(CO)_5$, except in HMPA. But other possibilities (vide supra) are presently under investigation.

Alkylpentacarbonyltungstate Complexes, $[(Ph_3P)_2N][RW(CO)_5]$. Sodium amalgam reductions of $W(CO)_6$ in DME provide solutions of $Na_2W(CO)_5$ slightly contaminated with $Na_2W_2(CO)_{10}$[23] from which alkylpentacarbonyltungstate anions may be obtained in 16–70% yields, depending upon the nature of the alkyl group. As in the case of the ethylchromium complex, the corresponding tungsten species is rather thermally unstable in solution and hence obtainable in rather low (ca. 16%) yields. Presently, the nature of the decomposition products from the ethyl complexes is unknown and under investigation.

Salts of the type $[PPN][RM(CO)_5]$ (M = Cr, W) are soluble in dry THF, DME, methylene chloride, HMPA, acetone, and ethanol without decomposition, slightly soluble in diethyl ether, and insoluble in alkanes and unsaturated hydrocarbons. Slow hydrolysis of $RM(CO)_5^-$ occurs in the presence of moisture; stronger acid such as HCl causes rapid decomposition. Infrared spectra of $RM(CO)_5^-$ in the carbonyl stretching frequency region (Table I) exhibit four bands. While only three infrared-active bands are expected for a $LM(CO)_5^-$ molecule of C_{4v} symmetry, a rather weak band at ca. 1940 cm^{-1} in related complexes has been assigned as the formally infrared-inactive B_1 mode.[24] This fourth band is also observed in many other $XM(CO)_5^-$ species.[25] As the alkyl group in $RM(CO)_5^-$ becomes more electronegative, one might expect the carbonyl stretching frequencies to increase. For $RM(CO)_5^-$ and M = Cr or W the energies of corresponding bands change according to the R group as follows: Me–CH_2 < H–CH_2 < Ph–CH_2 < NC–CH_2. This is reasonable in terms of the electronegativities of the substituents. Proton NMR spectra of these species (Table I) are also consistent with their proposed formulations.

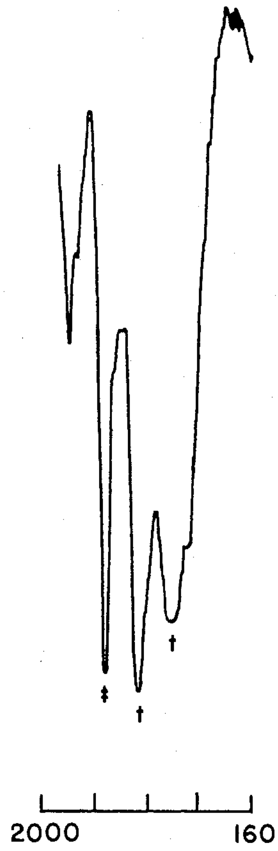

Figure 1. Infrared spectrum of products from a 2-h reduction of $W(CO)_6$ by 1% sodium amalgam in 1,2-dimethoxyethane at room temperature. Identity and position of bands: ‡ = $W_2(CO)_{10}^{2-}$, 1889 cm^{-1} (principal); † = $W(CO)_5^{2-}$, 1827 (s), 1757 (s) cm^{-1}.

Chemical Reactivities of $RM(CO)_5^-$. In contrast to $RFe(CO)_4^-$,[26] and although moisture- and air-sensitive, $RM(CO)_5^-$ (M = Cr, W) are rather unreactive nucleophiles in the presence of alkyl halides, presumably because of the reluctance of the metal to become seven-coordinate. For example, benzylpentacarbonyltungstate anion in DME does not react perceptibly with benzyl chloride or other alkyl halides after 18 h at room temperature. In contrast, however, $RM(CO)_5^-$ complexes react rapidly with several organometallic electrophilic species including Ph_3SnCl and Ph_3PAuCl. Chlorotriphenylstannane reacts with $PhCH_2W(CO)_5^-$ rapidly to provide 70–75% yields of $PhCH_2SnPh_3$. During this process a deep red intermediate forms at −78 °C which we believe is a seven-coordinate adduct. This quickly decomposes on warming to room temperature to the observed tin species, $W(CO)_6$ and $W(CO)_5Cl^-$. Interestingly, the much less reactive $Ph_3SnW(CO)_5^-$ [3] fails to react with benzyl chloride, even at reflux, in DME.[23] By the same procedure we have also shown that $EtM(CO)_5^-$ ions provide the known $EtSnPh_3$ complexes in similar yields, thus confirming our formulation of these solvolytically unstable species.

Although our preliminary studies on the reactivities of $RM(CO)_5^-$ suggest that these species will not be useful as stoichiometric organic reagents in the same sense as are corresponding alkylcarbonylferrates,[24] we are confident that they will serve as useful precursors to novel organometallic compounds and we shall report on these studies in due course.

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Registry No. I, 62197-85-7; II, 62197-83-5; III, 62228-09-5; IV, 62197-81-3; V, 62197-79-9; VI, 62197-78-8; VII, 62197-77-7; VIII, 62197-75-5; $Na_2Cr(CO)_5$, 51233-19-3; methyl iodide, 74-88-4; benzyl chloride, 25168-05-2; $NCCH_2Cl$, 107-14-2; ethyl bromide, 74-96-4; $Na_2W(CO)_5$, 57127-91-0; $W(CO)_6$, 14040-11-0; methyl bromide, 74-83-9.

References and Notes

(1) Part 8: J. E. Ellis and M. C. Palazzotto, *J. Am. Chem. Soc.*, **98**, 8264 (1976).
(2) J. E. Ellis and G. P. Hagen, *J. Am. Chem. Soc.*, **96**, 7825 (1974).
(3) J. E. Ellis, S. Hentges, D. Kalina, and G. P. Hagen, *J. Organomet. Chem.*, **97**, 79 (1975).
(4) C. P. Casey, S. W. Polichnowski, and R. L. Anderson, *J. Am. Chem. Soc.*, **97**, 7375 (1975).
(5) E. E. Isaacs and W. A. G. Graham, *Can. J. Chem.*, **53**, 467 (1975).
(6) W. J. Schlientz and J. K. Ruff, *Synth. Inorg. Met.-Org. Chem.*, **1**, 215 (1971).
(7) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).
(8) E. O. Fischer, *Pure Appl. Chem.*, **24**, 407 (1970).
(9) W. J. Schlientz and J. K. Ruff, *J. Organomet. Chem.*, **33**, C64 (1971).
(10) R. B. King, *Inorg. Chem.*, **6**, 25 (1967).
(11) H. Behrens and J. Köhler, *Z. Anorg. Allg. Chem.*, **306**, 94 (1960).
(12) J. K. Ruff, *Chem. Commun.*, 1363 (1969); W. J. Schlientz and J. K. Ruff, *J. Chem. Soc. A*, 1139 (1971).
(13) F. R. Kreissl, C. G. Kreiter, and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 643 (1972).
(14) C. P. Casey and R. L. Anderson, *J. Am. Chem. Soc.*, **96**, 1230 (1974).
(15) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973); (b) J. A. Zapp, *Chem. Eng. News*, **54** (5), 3 (1976).
(16) J. K. Ruff and W. J. Schlientz, *Inorg. Synth.*, **15**, 84 (1974).
(17) This protecting ability of PPN^+ has been qualitatively established for a wide range of organometallic anions and has recently been the subject of a quantitative study: M. Darensbourg and C. Borman, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept. 1976; No. INOR 18.
(18) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
(19) For a review on the syntheses and properties of $M(CO)_5^{2-}$ see J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).
(20) For example, $C_5H_5Cr(CO)_3^-$ is oxidized by allyl chloride to neutral dimer: R. B. King, *Inorg. Synth.*, **7**, 104 (1963).
(21) Spectra taken after 1 h show that practically all $W(CO)_6$ is reduced to $Na_2W_2(CO)_{10}$; weak spikes due to $Na_2W(CO)_5$ are also present. On further reaction, the strong bands of the dimeric dianion become less intense as bands due to $Na_2W(CO)_5$ grow in.
(22) We have also shown $Cs_2M_2(CO)_{10}$ to be an intermediate in the cesium amalgam reduction of $M(CO)_6$ in THF.
(23) No quantitative infrared spectroscopy has been done on these solutions to determine the exact $W(CO)_5^{2-}$:$W_2(CO)_{10}^{2-}$ ratio, but up to 85% yields $Ph_3SnW(CO)_5^-$ are obtained from these preparations: J. E. Ellis and R. A. Olson, unpublished results.
(24) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Nucl. Chem.*, **8**, 1 (1966).
(25) For example: in $M(CO)_5ECl_3^-$ (E = Ge, Sn), J. K. Ruff, *Inorg. Chem.*, **6**, 1502 (1967); in $M(CO)_5F^-$ (M = Cr, W), J. L. Cihonski and R. A. Levenson, *ibid.*, **14**, 1717 (1975); in $M(CO)_5EPh_3^-$ (E = Ge, Sn, Pb), ref 3.
(26) M. P. Cooke, *J. Am. Chem. Soc.*, **92**, 6080 (1970).

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Manganese Schiff Base Complexes. 5. Synthesis and Spectroscopy of Some Anion Complexes of *N,N'*-Ethylenebis(acetylacetone iminato)manganese(III)

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The synthesis of the series of new five-coordinate Mn(III) complexes of the type [Mn(acen)X] where acen is the dianion of the tetradentate ligand *N,N'*-ethylenebis(acetylacetone imine) and X^- = Cl^-, Br^-, NO_2^-, SCN^-, I^-, N_3^-, NCO^-, CN^-, and $C_2H_3O_2^-$ is reported. Two hydrated forms, $[Mn(acen)I]\cdot 2H_2O$ and $[Mn(acen)C_2H_3O_2]\cdot H_2O$, were also isolated. The green-brown crystalline solids show normal high-spin magnetic moments in chloroform solution at room temperature. The infrared spectra of the solids have been measured in the range 4000–100 cm^{-1} and band assignments suggested. The electronic absorption spectra of the materials in chloroform, ethanol, and pyridine have been determined and tentative band assignments made to ligand field, charge-transfer, and ligand transitions. The solid-state structure of [Mn(acen)Cl] has been determined by single-crystal x-ray diffraction techniques and is described.

Introduction

Although a large number of Mn(III) and Mn(II) complexes of a tetradentate Schiff base *N,N'*-ethylenebis(salicylaldiminato) dianion (salen), have been synthesized,[3] analogous complexes of the well-known and ubiquitous ligand *N,N'*-ethylenebis(acetylacetone imine) have not been reported. Complexes of this type of ligand have been extensively studied for the latter transition metals, especially for the oxygen-carrying cobalt system.[4] Since the two classes of ligands have different donor strengths and steric requirements, it is of interest to determine whether the coordination chemistry of their Mn(III) and Mn(II) chelates can be related to the properties of the tetradentate Schiff base. Attempts to prepare [Mn(acen)X] using the standard technique of refluxing a mixture of Mn(II) salts and the ligand in ethanol with aeration lead only to the formation of polynuclear Mn(II) complexes.[5] Another approach to the synthesis of the desired complexes was then sought and an Mn(III) salt, manganic acetate, was