1380 *Inorg. Chem.* **1981**, *20*, 1380–1384

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Seven-Coordinate Alkyl Isocyanide and Mixed-Alkyl Isocyanide–Phosphine Complexes of Tungsten(II)

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Received July 22, 1980

The reactions of the quadruply bonded tungsten dimer $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) with cyclohexyl and *tert*-butyl isocyanides in the presence of KPF_6 lead to the formation of the seven-coordinate homoleptic isocyanide complexes $[W(CNR)_7](PF_6)_2$. The *tert*-butyl isocyanide complex $[W(CNCMe_3)_7](PF_6)_2$ reacts with PR_3 (R = *n*-Pr or *n*-Bu) and 1,2-bis(diphenylphosphino)ethane (dppe) to give the mixed-ligand complexes $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ and $[W(CNCMe_3)_5(dppe)](PF_6)_2$. Cyclic voltammetric studies on $[W(CNR)_7](PF_6)_2$ and the mixed-alkyl isocyanide–phosphine complexes show that they exhibit quasi-reversible one-electron oxidations ($E_{1/2}$ values in the range +1.07 to +0.96 V vs. SCE). Similar electrochemical properties are exhibited by the analogous molybdenum(II) complexes. Bulk electrolysis of dichloromethane solutions of the complexes $[M(CNR)_7](PF_6)_2$ and $[M(CNR)_6(PR_3)](PF_6)_2$ generates the related molybdenum(III) and tungsten(III) cations, which then decompose via ligand loss (CNR or PR_3) to the six-coordinate cations $[M(CNR)_6]^{3+}$.

Introduction

The cleavage of the metal–metal multiple bond of dimers possessing the M_2L_8 skeleton can be an excellent synthetic route to certain classes of monomeric complexes. Of particular note are the reactions of π-acceptor ligands such as CO, NO, and alkyl and aryl isocyanides with dimers possessing the Mo_2^{4+}, Re_2^{6+}, and Re_2^{4+} cores. The phosphine complexes $Re_2X_4(PR_3)_4$ (X = Cl or Br) react with CO to produce $Re(CO)_2X_2(PR_3)_2$,[1] their molybdenum analogues $Mo_2X_4(PR_3)_4$ (X = Cl, Br or NCS) are converted to $Mo(NO)_2X_2(PR_3)_2$ by NO,[2] and while the reactions of alkyl isocyanides (RNC) and aryl isocyanides (ArNC) with $Mo_2(O_2CCH_3)_4$ differ, both give monomeric products ($[Mo(CNR)_7]^{2+}$ and $Mo(CNAr)_6$, respectively.[3,4] With the tertiary phosphine derivatives $Mo_2Cl_4(PR_3)_4$, the seven-coordinate mixed-ligand complexes $[Mo(CNR)_{7-x}(PR_3)_x]^{2+}$ (x = 1 or 2) are produced upon reaction with the alkyl isocyanides.[5] Rhenium(III) dimers such as $Re_2(O_2CR)_4Cl_2$ and $[Re_2Cl_8]^{2-}$ react with alkyl isocyanides in a more complicated fashion than experienced with the isoelectronic molybdenum dimers (i.e., $Mo_2(O_2CR)_4$ and $[Mo_2Cl_8]^{4-}$), but here too the products which have so far been identified[6-8] are in all instances monomeric.

Our explanation for this facile M–M bond cleavage lies in the ability of the π-acceptor ligands to compete effectively for the electron density in the metal-based π-bonding orbitals, thereby weakening the M–M bonds and leading to their disruption.[1,5] If so, we should be able to develop this concept to include other systems which contain multiply bonded metal dimer units. We now describe such a study involving, for the first time, a derivative of the W_2^{4+} core. The results we report are those which stemmed from an investigation of the reactions of $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine)[9] with cyclohexyl and *tert*-butyl isocyanides. During the course of this work we found that the seven-coordinate tungsten(II) cations $[W(CNR)_7]^{2+}$ exhibit a substitution chemistry similar to that of their molybdenum analogues.[5] The electrochemistry of $[M(CNR)_7]^{2+}$ (M = Mo and W) and the mixed-alkyl isocyanide–tertiary phosphine complexes of these metals has also been explored, and the results are discussed herein.

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: $W_2(mhp)_4$[9] and $W(CO)_4I_2$.[10] The samples of the molybdenum(II)–alkyl isocyanide complexes were available from an earlier study.[5] Cyclohexyl isocyanide, *tert*-butyl isocyanide, monodentate tertiary phosphines, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and other reagents and solvents were obtained from commercial sources and were used as received.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere, and all solvents were deoxygenated prior to use by purging with N_2 gas.

A. Reactions of $W_2(mhp)_4$. (i) $[W(CNC(CH_3)_3)_7](PF_6)_2$. A mixture of $W_2(mhp)_4$ (0.529 g, 0.66 mmol) and KPF_6 (0.510 g, 2.77 mmol) in 5 mL of acetone was treated with an excess of *tert*-butyl isocyanide (3 mL). The reaction mixture was refluxed for 3 h, allowed to cool to room temperature, and filtered, and 2-propanol was added to the filtrate. The solution was then chilled to 0 °C for 12 h whereupon a bright yellow solid precipitated. The solid was filtered off, washed with 2-propanol and diethyl ether, and vacuum dried; yield 0.478 g (34%). Anal. Calcd for $C_{35}H_{63}F_{12}N_7P_2W$: C, 39.82; H, 6.02. Found: C, 39.21; H, 5.81.

(ii) $[W(CNC_6H_{11})_7](PF_6)_2$. A mixture of $W_2(mhp)_4$ (1.036 g, 1.30 mmol) and KPF_6(1.20 g, 6.50 mmol) was dissolved in 15 mL of acetone, and cyclohexyl isocyanide (6 mL) was added to the resulting solution. The reaction mixture was refluxed for 2 days and the volume of the solution then reduced under a stream of nitrogen. When the remaining solution was maintained at 0 °C for 2 days, yellow crystals of the complex precipitated; yield 1.44 g (45%). Anal. Calcd for $C_{49}H_{77}F_{12}N_7P_2W$: C, 47.54; H, 6.27; N, 7.92. Found: C, 47.77; H, 6.46; N, 7.75.

B. Reactions of $W(CO)_4I_2$. (i) $[W(CNC(CH_3)_3)_6I]I$. A quantity of $W(CO)_4I_2$ (0.439 g, 0.80 mmol) was dissolved in 20 mL of methanol, and *tert*-butyl isocyanide (1.5 mL) was added to the solution. This mixture was stirred for 15 min and filtered, and diethyl ether was added to precipitate the product, yield 0.660 g (88%). Anal. Calcd for $C_{30}H_{54}I_2N_6W$: C, 38.48; H, 5.81. Found: C, 38.44; H, 5.98. The spectroscopic properties of this complex were as follows: ^{1}H NMR (in acetone-d_6) δ 1.58 (lit.[11] δ 1.53 in $CDCl_3$); $\nu(C{\equiv}N)$ 2120 s cm^{-1} (lit.[11] 2130 vs); λ_{max} (in dichloromethane) 387, 285, and 243 nm.

(ii) $[W(CNC(CH_3)_3)_7](PF_6)_2$. A quantity of $[W(CNC(CH_3)_3)_6I]I$ (0.147 g, 0.157 mmol), which had been prepared as described in section B(i), was dissolved in 2 mL of methanol, and *tert*-butyl isocyanide (0.1 mL) was added. The resulting solution was stirred for 1 h and then mixed with KPF_6 (0.173 g, 0.942 mmol) dissolved in a minimum

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0020-1669/81/1320-1380$01.25/0

volume of methanol. The solution was cooled to 0 °C, and the yellow solid which separated was filtered off, washed with water, 2-propanol, and diethyl ether, and vacuum dried; yield 0.089 g (54%). This product had the same spectroscopic properties as those of samples of $[W(CNC(CH_3)_3)_7](PF_6)_2$ prepared as in section A(i).

(iii) $[W(CNC_6H_{11})_7](PF_6)_2$. A mixture of $W(CO)_4I_2$ (0.483 g, 0.88 mmol) and KPF_6 (0.340 g, 1.85 mmol) was dissolved in 15 mL of acetone and cyclohexyl isocyanide (2.5 mL) added. The solution was stirred for 5 min and then taken to dryness by use of a stream of nitrogen gas. The solid residue was mixed with ethanol and filtered, and the resulting yellow solid was washed with water, 2-propanol, and ethyl ether and vacuum dried; yield 0.558 g (51%). Its identity as the same complex prepared in section A(ii) was established by infrared and ^1H NMR spectroscopy.

C. Reactions of $[W(CNC(CH_3)_3)_7](PF_6)_2$. (i) $[W(CNC(CH_3)_3)_5(dppe)](PF_6)_2$. The reaction between $[W(CNC(CH_3)_3)_7](PF_6)_2$ (0.394 g, 0.37 mmol) and dppe (0.468 g, 1.17 mmol) in refluxing methanol (30 mL) was carried out for 20 h. The reaction mixture was then reduced in volume under a stream of nitrogen, and diethyl ether was added. After this mixture was kept at 0 °C for 12 h, the yellow crystals which formed were filtered off, washed with diethyl ether, and dried in vacuo. When the filtrate was treated with more diethyl ether, a second batch of crystals was obtained; total yield 0.259 g (38%). This complex can be recrystallized from acetone–diethyl ether mixtures. Anal. Calcd for $C_{51}H_{69}F_{12}N_5P_4W$: C, 47.48; H, 5.39. Found: C, 48.00; H, 5.74.

(ii) $[W(CNC(CH_3)_3)_6(P(C_3H_7)_3)](PF_6)_2$. A quantity of $[W(CNC(CH_3)_3)_7](PF_6)_2$ (0.504 g, 0.48 mmol) was dissolved in 20 mL of methanol and treated with tri-*n*-propylphosphine (2.0 mL). The solution was refluxed for 3 h, during which time it changed color from a yellow to yellow-orange. The reaction mixture was then cooled to room temperature and the volume reduced slowly under a stream of nitrogen gas to afford yellow-orange crystals of the product. These were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.439 g (81%). The product was crystallized from an acetone–diethyl ether mixture. Anal. Calcd for $C_{39}H_{75}F_{12}N_6P_3W$: C, 41.35; H, 6.67. Found: C, 41.14; H, 6.44.

(iii) $[W(CNC(CH_3)_3)_6(P(C_4H_9)_3)](PF_6)_2$. This yellow-orange complex was obtained by a procedure analogous to that in section C(ii); yield 73%. Anal. Calcd for $C_{42}H_{81}F_{12}N_6P_3W$: C, 42.94; H, 6.95. Found: C, 42.77; H, 6.82.

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000-400 cm^{-1} with a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded with a Varian series 634 spectrophotometer. X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950A ESCA spectrometer. A Perkin-Elmer R32 spectrometer was used to obtain the ^1H NMR. Samples were dissolved in acetone-d_6, and resonances were referenced internally to Me_4Si. X-Band ESR spectra of CH_2Cl_2 glasses were recorded at −160 °C with a Varian E-109 spectrometer. Cyclic voltammetry experiments were performed using the set-up described previously.[12]

Results and Discussion

Reactions of $W_2(mhp)_4$ with Alkyl Isocyanides and the Spectroscopic Characterization of the Resultant Products. The reactions of $W_2(mhp)_4$ with alkyl isocyanides in the presence of an excess of KPF_6 provide a quite rapid and convenient route to the homoleptic isocyanide complexes $[W(CNR)_7](PF_6)_2$ (R = C_6H_{11} or CMe_3).[13] The reaction course is thus analogous to that found when these same isocyanide ligands are reacted with $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$[3] and thus substantiates our ideas concerning the ability of π-acceptor ligands to bring about the facile cleavage of M–M quadruple bonds in M_2L_8 systems. Alternative routes to the *tert*-butyl isocyanide cation $[W(CNCMe_3)_7]^{2+}$ have been described by Lippard[11] and San Filippo.[14] The chlorine oxidation of $W(CO)_6$ in the presence of *tert*-butyl isocyanide produces $[W(CNCMe_3)_6Cl]Cl$ which, in the presence of excess isocyanide and $NaPF_6$, is converted to $[W(CNCMe_3)_7](PF_6)_2$ in an overall yield of ~25%.[12] In the presence of a small amount of water, $K_3W_2Cl_9$ reacts with *tert*-butyl isocyanide to afford $[W(CNCMe_3)_7]W_6O_{19}$.[14] The cleavage of the W–W "triple" bond of $[W_2Cl_9]^{3-}$ is thus closely akin to the reaction we observe with the quadruply bonded dimer $W_2(mhp)_4$. While Lippard's method[11] is presumably adaptable to other alkyl isocyanide complexes of tungsten(II), it is not clear whether this is true for the more complicated $K_3W_2Cl_9$ reaction, although San Filippo and co-workers[14] have found that the dimeric molybdenum anions $[Mo_2Cl_9]^{3-}$ and $[Mo_2Cl_8H]^{3-}$ are cleaved by *tert*-butyl isocyanide to generate $[Mo(CNCMe_3)_7]^{2+}$. We have now developed a further procedure which is based upon that used by Lippard[11] but is rapid and appears overall to be somewhat more convenient. In this, the carbonyl iodide complex $W(CO)_4I_2$ is converted directly to $[W(CNR)_7](PF_6)_2$ (yield >50%) in a one-pot reaction, or, alternatively, $[W(CNR)_6I]I$ is first formed and then reacted with additional alkyl isocyanide and with KPF_6 to give $[W(CNR)_7](PF_6)_2$.

The spectroscopic properties of $[W(CNCMe_3)_7](PF_6)_2$ conform to those reported previously by others.[11,14] The ^1H NMR spectrum revealed a single resonance at δ 1.69 in acetone-d_6 (δ 1.58–1.59 in $CDCl_3$)[11,14] while its infrared spectrum (Nujol mull) exhibited a complex $\nu(C{\equiv}N)$ pattern centered at 2142 cm^{-1}. With the new cyclohexyl isocyanide complex $[W(CNC_6H_{11})_7](PF_6)_2$, the corresponding spectral features were multiplets at δ 1.60, 1.95, and 4.52 in the ^1H NMR spectrum (acetone-d_6) and an infrared-active $\nu(C{\equiv}N)$ mode at 2140 (s) cm^{-1} with weaker features at 2185 and 2040 cm^{-1}. The electronic absorption spectra of dichloromethane solutions of these two complexes exhibit absorption maxima at ca. 410, 280 (sh), and 250 nm ($\epsilon > 10^3$) which are very similar to those of their molybdenum analogues.[3,11] The lowest energy absorption at 410 (±2) nm is probably a metal-based transition, assigned[11] to $b_2(yz) \rightarrow a_1(z^2)$ in the case of $[Mo(CNCMe_3)_7]^{2+}$.[15]

Formation of Mixed-Alkyl Isocyanide–Tertiary Phosphine Complexes of Tungsten(II). The treatment of methanol solutions of $[W(CNCMe_3)_7](PF_6)_2$ with the tertiary phosphines P-*n*-Pr_3, P-*n*-Bu_3, and 1,2-bis(diphenylphosphino)ethane (dppe) leads to substitution of one or two isocyanide ligands and the formation of the yellow-orange crystalline complexes $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ (R = *n*-Pr or *n*-Bu) and $[W(CNCMe_3)_5(dppe)](PF_6)_2$. Thus the substitution chemistry of $[W(CNCMe_3)_7](PF_6)_2$ resembles closely that of its molybdenum analogues $[Mo(CNR)_7](PF_6)_2$ (R = CH_3, C_6H_{11}, or CMe_3).[5]

These mixed-ligand complexes exhibit quite complex infrared spectra in the $\nu(C{\equiv}N)$ region,[16] which resemble those of their molybdenum analogues,[5] and electronic absorption spectra (in dichloromethane), which are strikingly similar to the related spectrum of $[W(CNCMe_3)_7](PF_6)_2$. Intense absorption maxima ($\epsilon > 10^3$) are located at 410 ± 10, 280 ± 10 (sh), and 255 nm.

The room-temperature ^1H NMR spectra are quite normal, the monosubstituted derivatives exhibiting their *tert*-butyl resonance as a singlet at ca. δ 1.68 which overlaps the reso-

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[13] We have also studied the reaction of $W_2(mhp)_4$ with methyl isocyanide and isolated $[W(CNCH_3)_7](PF_6)_2$ (identified by infrared and X-ray photoelectron spectroscopic techniques). Unfortunately, the yield of this product is very low for reasons we do not yet understand.

[14] LaRue, W. A.; Liu, A. T.; San Filippo, J., Jr. *Inorg. Chem.* **1980**, *19*, 315.

[15] In ref 11, the table of electronic absorption spectral data (Table VI) lists λ_{max} values for $[W(CNCMe_3)_7](PF_6)_2$ of 376, 287 and 249 nm. In our hands, we find that the position of the lowest energy band of $[W(CNCMe_3)_7](PF_6)_2$ is at 410 nm. Professor S. J. Lippard has informed us that the cause of this spectroscopic discrepancy lies in the occurrence of the dealkylation reaction $[W(CNCMe_3)_7](PF_6)_2 \rightarrow [W(CNCMe_3)_6CN]PF_6$. Accordingly, the 376-nm band characterizes the $[W(CNCMe_3)_6CN]^+$ cation while that at 410 nm is due to $[W(CNCMe_3)_7]^{2+}$.

[16] Infrared absorptions (Nujol mulls) between 2250 and 2000 cm^{-1} are as follows: $[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$, 2205 m, ~2170 sh, 2120 s, 2055 sh; $[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 2200 m, 2132 s, 2110 sh, 2055 sh; $[W(CNCMe_3)_5(dppe)](PF_6)_2$, 2186 m, 2120 s, 2055 sh.

Table I. $E_{1/2}$ Values for Alkyl Isocyanide and Mixed-Alkyl Isocyanide–Tertiary Phosphine Complexes of Molybdenum(II) and Tungsten(II)[a]

complex	$E_{1/2}$, V	complex	$E_{1/2}$, V
$[Mo(CNCH_3)_7](PF_6)_2$	+1.01	$[W(CNCMe_3)_7](PF_6)_2$	+1.03
$[Mo(CNC_6H_{11})_7](PF_6)_2$	+1.12	$[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$	+0.96
$[Mo(CNCMe_3)_7](PF_6)_2$	+1.12	$[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$	+1.02
$[W(CNC_6H_{11})_7](PF_6)_2$	+1.05	$[W(CNCMe_3)_5(dppe)](PF_6)_2$	+1.07

[a] In volts vs. SCE with a Pt-bead working electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.

nances due to the PR_3 ligands (δ ca. 1–2). Integration of the phenyl (δ 7.70, multiplet) and *tert*-butyl (δ 1.34, singlet) resonances of $[Mo(CNCMe_3)_5(dppe)](PF_6)_2$ is in accord with the known stoichiometry of this complex. The resonances assigned to the C_2H_4 group of the dppe ligand (singlets at δ 2.91 and 3.12) are consistent with both phosphorus atoms of the bidentate dppe ligand being coordinated, comparable features in the ^1H NMR spectrum of $[Mo(CNCMe_3)_5(dppe)](PF_6)_2$ being at δ 2.88 and 3.11.[5]

The W $4f_{7/2}$ binding energies in the X-ray photoelectron spectra (XPS) of $[W(CNR)_7](PF_6)_2$ (R = C_6H_{11} or CMe_3), $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ (R = *n*-Pr or *n*-Bu), and $[W(CNCMe_3)_5(dppe)](PF_6)_2$ are essentially constant at 32.1 ± 0.2 eV, values which are very similar to those of (π-allyl)tungsten(II) species.[17] Two P 2p binding energies are present in the XPS of the mixed-ligand complexes, the one at higher energy (135.5 ± 0.2 eV) being due to the PF_6^- anions, while that arising from the tertiary phosphine ligands is at 131.1 ± 0.3 eV.[18] The relative intensities of the two P 2p peaks are in agreement with the proposed stoichiometries of the complexes. The XPS of the iodide complex $[W(CNCMe_3)_6I]I$ is of particular note since the I 3d binding energies of the inner- and outer-sphere iodine atoms are quite different. The bound iodine atom has a I $3d_{5/2}$ energy of 619.2 eV, while for the iodide anion the value is 618.2 eV. Such a difference is in accord with earlier work in this laboratory[19] in which the XPS technique has been used successfully to distinguish such inner- and outer-sphere coordination environments.

Electrochemical Oxidations of $[W(CNR)_7]^{2+}$ and the Mixed-Alkyl Isocyanide–Tertiary Phosphine Complexes of Tungsten(II) and a Comparison with the Analogous Molybdenum Systems. The electrochemical properties of $[M(CNR)_7](PF_6)_2$ (M = Mo or W and R = CH_3, C_6H_{11}, or CMe_3), $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ (PR_3 = P-*n*-Pr_3 or P-*n*-Bu_3), and $[W(CNCMe_3)_5(dppe)](PF_6)_2$ were investigated by cyclic voltammetry and coulometry techniques. The voltammetric half-wave potentials vs. SCE for dichloromethane solutions of these complexes are given in Table I. In all instances, the complexes exhibit a single oxidation, $[M(CNR)_7]^{2+} \rightarrow [M(CNR)_7]^{3+} + e^-$, where M = Mo or W, or $[W(CNR)_{7-x}(PR_3)_x]^{2+} \rightarrow [W(CNR)_{7-x}(PR_3)_x]^{3+} + e^-$. The $E_{1/2}$ values are between +1.12 and +0.96 V and thus lie within the range of +1.18 to +0.90 V, which was encountered in an earlier electrochemical study[5] on the analogous mixed-alkyl isocyanide–tertiary phosphine complexes of molybdenum(II) of the types $[Mo(CNR)_6(PR_3)]^{2+}$, $[Mo(CNR)_5(PR_3)_2]^{2+}$, $[Mo(CNR)_5(dppm)]^{2+}$, and $[Mo(CNR)_5(dppe)]^{2+}$. The peak current ratios $i_{p,a}/i_{p,c} \simeq 1$ and the ratio $i_p/v^{1/2}$ were constant for sweep rates (v) between 50 and 400 mV/s. The potential separation between the anodic and cathodic peaks, ΔE_p, in the cyclic voltammograms was greater than 60 mV, being in the range 70–110 mV for a sweep rate of 200 mV/s. ΔE_p increased slightly with increase in sweep rate; for example, ΔE_p = 80 mV for v = 50 mV/s and ΔE_p = 90 mV for v = 300 mV/s in the case of $[Mo(CNCH_3)_7](PF_6)_2$, an observation which is in accord with these being quasi-reversible electron-transfer processes.[20,21]

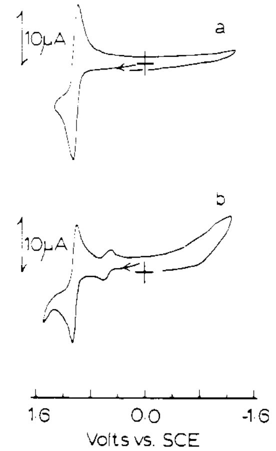

Figure 1. Cyclic voltammogram in 0.2 M TBAH–dichloromethane of $[Mo(CNCH_3)_7](PF_6)_2$ (a) before and (b) after electrolysis at +1.2 V.

There is an irreversible electrochemical reduction close to the solvent limit ($E_{p,c} \sim -1.7$ V) for the molybdenum(II) complexes $[Mo(CNR)_7](PF_6)_2$. This probably arises from a two-electron reduction followed by a rapid chemical process, which results in the disruption of the complex.

Exhaustive electrolyses at potentials anodic of the oxidation waves (i.e., in the vinicity of +1.1 V) generated solutions of the corresponding seven-coordinate Mo(III) and W(III) cations. When these electrolyzed solutions were monitored over a period of several hours by cyclic voltammetry, it was apparent that a chemical product was formed following this oxidation. While all the complexes listed in Table I were studied in this way, together with the mixed-alkyl isocyanide–tertiary phosphine molybdenum(II) complexes which were available from the study described in ref 5, our discussion will emphasize the results for the complexes $[Mo(CNCH_3)_7](PF_6)_2$ and $[Mo(CNCH_3)_6(PEt_3)](PF_6)_2$.

The change which occurs following exhaustive electrolysis of the yellow dichloromethane solutions of $[Mo(CNCH_3)_7](PF_6)_2$ is shown in Figure 1. A new couple appears with an $E_{1/2}$ value of +0.55 V, and coulometry shows this to correspond to a reduction. The amount of this product increases with time (as measured by peak currents) at the expense of $[Mo(CNCH_3)_7]^{3+}$. Since the back-reduction of some of the $[Mo(CNCH_3)_7]^{3+}$ to $[Mo(CNCH_3)_7]^{2+}$ also occurs during the time that the product is being formed, the rate of its formation is enhanced if the potential of the solution is maintained at approximately +1.1 V.[22] By this means, solutions could be obtained in which the majority species was that characterized by $E_{1/2}$ = +0.55 V. Such solutions differed little in color from that of the parent $[Mo(CNCH_3)_7]^{2+}$. Similar results were obtained for the corresponding cyclohexyl and *tert*-butyl iso-

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(22) Separate experiments showed that it is the trivalent ions which decompose since solutions of $[Mo(CNR)_7]^{2+}$ and the other molybdenum(II) complexes can be maintained for prolonged periods without the appearance of the product waves in their cyclic voltammograms.

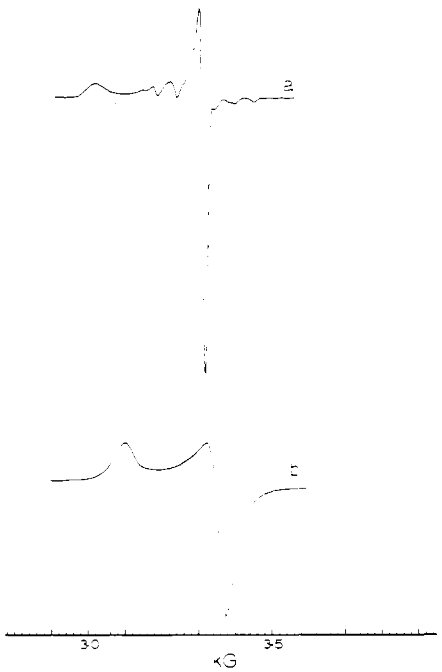

Figure 2. X-Band ESR spectra of dichloromethane solutions (−160 °C) of (a) $[Mo(CNCH_3)_7](PF_6)_2$ and (b) $[W(CNCMe_3)_7](PF_6)_2$ following oxidation at +1.2 V.

cyanide complexes, the $E_{1/2}$ values of the products being +0.57 and +0.60 V, respectively.

With the mixed-alkyl isocyanide–tertiary phosphine complexes of the type $[Mo(CNR)_6(PR_3)](PF_6)_2$, where R = CH_3 when PR_3 = PEt_3 and R = CMe_3 when PR_3 = PEt_3 or P-*n*-Pr_3, exhaustive electrolysis led to the evolution of free phosphine and the appearance of this same reversible couple at an $E_{1/2}$ value of +0.55 V (R = CH_3) or +0.60 V (R = CMe_3). When the electrolyzed solutions were maintained at a potential anodic of the oxidation to $[Mo(CNR)_6(PR_3)]^{3+}$, the rate of product formation was enhanced. Since the products which are formed following the oxidation of $[Mo(CNR)_7]^{2+}$ and $[Mo(CNR)_6(PR_6)]^{2+}$ have the same $E_{1/2}$ values, we can assume that they are in fact the same chemical species. This is supported by ESR spectral measurements as described below.

The X-band ESR spectra of dichloromethane glasses (−160 °C) of the oxidized solutions showed that the seven-coordinate molybdenum(III) species were ESR inactive under these conditions, while the decomposition product ($E_{1/2}$ = +0.55–0.60 V) displayed a very characteristic signal. The ESR spectrum of an oxidized solution of $[Mo(CNCH_3)_7](PF_6)_2$, in which the dominant species was that exhibiting its half-wave voltammetric potential at +0.55 V, is shown in Figure 2a, the *identical* spectrum being obtained for $[Mo(CNCH_3)_6(PEt_3)](PF_6)_2$ following its exhaustive electrolysis. The intensity of this signal increased as the concentration of the product increased in the electrolyzed solution. Integration of the signal confirmed that it was associated with a major solution species rather than with trace amounts of an impurity. The signal was unaffected upon reducing any remaining $[Mo(CNCH_3)_7]^{3+}$ back to $[MoCNCH_3)_7]^{2+}$ (at a potential of +0.70 V), but it disappeared upon reducing the solution at +0.20 V; i.e., it correlates with the product in its oxidized form.

We believe that the product of the decomposition of $[Mo(CNR)_7]^{3+}$ and $[(Mo(CNR)_6(PR_3)]^{3+}$ is the six-coordinate 15-electron molybdenum(III) species $[Mo(CNR)_6]^{3+}$. Unfortunately, our attempts to isolate such a complex were thwarted by its decomposition during the work-up of the electrolyzed solution. This appears to occur via a disproportionation reaction in which the parent seven-coordinate cation is re-formed (characterized by cyclic voltammetry) together with other unidentified species. Accordingly, our conclusion concerning its formulation rests upon the following experimental evidence. (1) Cyclic voltammetry shows that treatment of an electrochemically generated solution containing the product in its reduced form (i.e., $[Mo(CNR)_6]^{2+}$) with an excess of alkyl isocyanide regenerates $[Mo(CNR)_7]^{2+}$. For this particular experiment, we used the product from the electrolysis of $[Mo(CNC_6H_{11})_7]^{3+}$. (2) If, as we believe, the product is $[Mo(CNR)_6]^{3+}$, then its formation from $[Mo(CNR)_7]^{3+}$ and $[Mo(CNR)_6PR_3)]^{3+}$ is consistent with the same simple ligand loss mechanism. (3) The ESR spectrum of the product resulting from the electrolysis of $[MonCNCH_3)_7]^{2+}$ (Figure 2a) is consistent with, although it does not prove, the presence of octahedral molybdenum(III).[23] The *g* values of 2.16 and 1.96 are higher than those usually encountered with molybdenum(V) species (the only other oxidation state likely to give an ESR signal under these conditions).[24] Unfortunately there is a dearth of ESR data in the literature on well-defined molybdenum(III) species,[25] the studies of most relevance to ours being powder data (77 K) on K_3MoCl_6 and $K_3Mo(NCS)_6{\cdot}4H_2O$.[26] The former complex has *g* values of 2.01 and 1.96 while for $K_3Mo(NCS)_6{\cdot}4H_2O$ these are between 1.8 and 2.0 with molybdenum hyperfine associated with the principal *g* value,[26] a feature which is present in the ESR spectrum displayed in Figure 2a. (4) There is no evidence for the formation of alternative high oxidation state molybdenum isocyanide complexes, such as oxomolybdenum(IV) species.[27] (5) We have, in a separate study, recently isolated and characterized[28] pure samples of the analogous chromium(II) complexes $[Cr(CNR)_7](PF_6)_2$ and $[Cr(CNR)_6](PF_6)_2$, where R = C_6H_{11} or CMe_3, and have shown[28] that the oxidation of $[Cr(CNR)_7]^{2+}$ to $[Cr(CNR)_7]^{3+}$ (at ca. +1.15 V) is followed by the loss of a CNR ligand to produce $[Cr(CNR)_6]^{3+}$. We therefore propose that the same mechanism applies to the molybdenum complexes but that any differences which exist are governed by the stability order $[Mo(CNR)_7]^{3+} \gg [Cr(CNR)_7]^{3+}$.

Electrochemical and ESR spectral measurements reveal that the tungsten complexes $[W(CNR)_7](PF_6)_2$ (R = C_6H_{11} or CMe_3) and $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ (PR_3 = P-*n*-Pr_3 or P-*n*-Bu_3) behave similarly to their molybdenum analogues. Oxidation to the trivalent ions is followed by the slow loss of ligand (RNC or PR_3), the resulting product ($E_{1/2}$ value close to +0.48 V) having the X-band ESR spectrum displayed in Figure 2b.[29] From a close comparison with $[Mo(CNR)_7]^{3+}$ (vide supra) and $[Cr(CNR)_7]^{3+}$,[28] it is clear that the overall stability within the $[M(CNR)_7]^{3+}$ series is W $\gtrsim$ Mo $\gg$ Cr.

The final complexes to be considered are those of the types $[Mo(CNR)_5(PR_3)_2]^{2+}$, in which the phosphine ligands are monodentate (PEt_3 or P-*n*-Pr_3), $[Mo(CNR)_5(dppm)](PF_6)_2$, and $[M(CNR)_5(dppe)](PF_6)_2$ (M = Mo or W). In the case of $[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$ and $[Mo(CNC_6H_{11})_5(PEt_3)_2](PF_6)_2$, electrolysis at +1.1 V produces some $[Mo(CNR)_6]^{3+}$ together with unidentified product(s) characterized

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[23] An additional spectroscopic characterization of these solutions was the measurement of their electronic absorption spectra. For example, a dichloromethane solution containing $[Mo(CNC_6H_{11})_6]^{3+}$ exhibits its lowest energy absorption at 375 nm, thereby distinguishing it from both $[Mo(CNC_6H_{11})_7]^{2+}$ and $[Mo(CNC_6H_{11})_7]^{3+}$.

[24] Stiefel, E. I. *Prog. Inorg. Chem.* **1976**, *22*, 1.

[25] See, for example: Averill, B. A.; Orme-Johnson, W. H. *Inorg. Chem.* **1980**, *19*, 1702.

[26] Boyd, P. D. W.; Smith, P. W.; Wedd, A. G. *Aust. J. Chem.*, **1969**, *22*, 653.

[27] Novotny, M.; Lippard, S. J. *Inorg. Chem.* **1974**, *13*, 828.

[28] Mialki, W. S.; Wood, T. E.; Walton, R. A., *J. Am. Chem. Soc.* **1980**, *102*, 7105.

[29] We find *g* values of 2.10 and 1.93 for the ESR spectrum displayed in Figure 2b.

by irreversible reductions exhibiting $E_{p,c}$ values close to –0.3 and –0.8 V. On the other hand, the decomposition, which follows electrolytic oxidation of $[Mo(CNR)_5(dppm)](PF_6)_2$ (R = CH_3 or C_6H_{11}), $[Mo(CNR)_5(dppe)](PF_6)_2$ (R = CH_3, C_6H_{11}, or CMe_3), and $[W(CNCMe_3)_5(dppe)](PF_6)_2$, produces no significant quantities of $[M(CNR)_6]^{3+}$ as demonstrated by the cyclic voltammograms of the solutions and ESR spectral measurements.[30] The only reproducible product waves in these cyclic voltammograms are ones at $E_{p,c} \sim -0.25$ and –0.75 V of unknown origin. It seems likely that loss of the bidentate chelating dppm and dppe ligands does not occur following oxidation. On the other hand, with $[Mo(CNCH_3)_5(P\text{-}n\text{-}Pr_3)_2]^{3+}$ and $[Mo(CNC_6H_{11})_5(PEt_3)_2]^{3+}$, loss of CNR and/or loss of monodentate phosphine are viable decomposition pathways; the free isocyanide which is released could then explain why $[Mo(CNR)_6]^{3+}$ is formed, as we have detected in the cyclic voltammograms of these latter systems.

Acknowledgment. Support from the National Science Foundation through Grant No. CHE79-09233 is gratefully acknowledged. The Varian E-109 ESR spectrometer was purchased with a grant from the National Science Foundation (BMS 75-19127). We thank Dr. Thomas E. Wood for supplying several of the samples of the molybdenum complexes whose electrochemical properties we investigated.

Registry No. $[W(CNCMe_3)_7](PF_6)_2$, 66687-57-8; $[W(CNC_6H_{11})_7](PF_6)_2$, 76705-37-8; $[W(CNCMe_3)_6I]I$, 66652-48-0; $[W(CNCMe_3)_5(dppe)](PF_6)_2$, 76721-72-7; $[W(CNCMe_3)_6(P\text{-}n\text{-}Pr_3)](PF_6)_2$, 76721-74-9; $[W(CNCMe_3)_6(P\text{-}n\text{-}Bu_3)](PF_6)_2$, 76721-76-1; $[Mo(CNCH_3)_7](PF_6)_2$, 66632-84-6; $[Mo(CNC_6H_{11})_7](PF_6)_2$, 72155-82-9; $[Mo(CNCMe_3)_7](PF_6)_2$, 41982-05-2; $W_2(mhp)_4$, 67634-84-8; $W(CO)_4I_2$, 40813-52-3.

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(30) While the ESR spectrum of a dichloromethane glass (–160 °C) that contains the products from the oxidation of $[Mo(CNCH_3)_5(dppm)]^{2+}$ shows a weak signal, it differs from that which we attribute to $[Mo(CNCH_3)_6]^{3+}$ (Figure 2a).

Contribution from the Institutt for Uorganisk Kjemi, Norges Tekniske Høgskole, Universitetet i Trondheim, N-7034 Trondheim-NTH, Norway, and the F. J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado 80840

Spectroscopic Study of the Coordination of Titanium Chlorides in Fused Chloroaluminates and Alkali Chloride Mixtures

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Received September 26, 1980

The spectra and the coordination chemistry of titanium chlorides in some fused salt solvents are reported. Spectra of Ti(III) and Ti(II) have been obtained in $AlCl_3$–KCl melts ($1.00 \geq X_{AlCl_3} \geq 0.49$) at temperatures 471–894 K and in the LiCl–KCl eutectic melt at temperatures 658–1185 K. Ti(III) is found to be octahedrally coordinated in pure $AlCl_3$(l) and in $AlCl_3$–KCl melts with $X_{AlCl_3} \geq 0.67$ while octahedral–tetrahedral coordination equilibria are established at lower $AlCl_3$ contents. Ti(II) has octahedral coordination at compositions $1.00 \geq X_{AlCl_3} \geq 0.51$, but a disproportionation equilibrium is observed for $X_{AlCl_3} \leq 0.60$, culminating at $X_{AlCl_3} = 0.49$ where Ti(II) is unstable and the spectrum of Ti(III) in an octahedral–tetrahedral coordination equilibrium is found. In the LiCl–KCl eutectic Ti(III) is also present in an octahedral–tetrahedral coordination equilibrium. Ti(II) has octahedral coordination in this solvent, but a disproportionation equilibrium is established.

Introduction

High-temperature equilibria between titanium and aluminum chlorides may play an important part in ore processing by chlorination such as production of TiO_2 from ilmenite and production of $AlCl_3$ from clay. However, the literature on these equilibria are scarce, mainly due to the considerable experimental difficulties encountered from the oxygen and water sensitivity of the systems.

A previous publication[1] discussed the complexation and redox equilibrium of titanium chlorides in gaseous $AlCl_3$, while the present paper will deal with the coordinations of the different oxidation states of titanium in molten chloroaluminates and alkali chloride mixtures based on spectroscopic evidence.

The spectrophotometer is a sensitive instrument for characterization of the different oxidation states of titanium with various ligand coordinations, as the electronic transitions that arise usually lie within the wavelength span of a UV–vis–near IR spectrophotometer. The intensity of the electronic transitions in dilute solutions normally follows Beer's law (eq 1)

$$\epsilon_i = A_i/cl \qquad (1)$$

and the law of additivity (eq 2) which states that at a fixed

$$A = \sum_i A_i \qquad (2)$$

wavelength, *i*, the molar absorptivity, ϵ (L/(mol·cm)), is a constant independent of the concentration, *c* (mol/L), and optical path length, *l* (cm), and that in a solution of more than one light-absorbing species each contributes additively to the total absorbance at wavelength *i*. The absorption *A* is defined as log (I_0/I), where I_0 and *I* are the radiation intensities which enter and are transmitted through the sample, respectively.

Experimental Section

Instrumentation. Spectra were recorded with a Cary Model 17H spectrophotometer (Cary Instruments, Monrovia, CA). An interfacing device built at this university[2] transferred the spectrometer signals to a magnetic tape recorder (Model 1600, Kennedy Co., Altadena, CA) for temporary storage prior to computer processing of the spectra.

The furnace was specially built to fit into the Cary 17H sample compartment. The heating element was made of a cross-shaped pythagoras tubing with the light beam passing through the arms of the cross. It consisted of three separate heating zones, each controlled by a Eurotherm PID regulator (Eurotherm Ltd., Sussex, England). The upper and lower zone were regulated differentially from the one in the middle, as this arrangement made it easier to establish the required temperature gradient along the cell.

Spectrometric Cells. In order to withstand the high internal pressures, the cells were made from square-base (10 × 10 mm internal

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(1) M. Sørlie and H. A. Øye, *Inorg. Chem.*, **17**, 2473 (1978).

(2) O. Borgen, T. Bruvoll, and H. Petersen, Technical Report 70, Division of Physical Chemistry, University of Trondheim, Trondheim-NTH, Norway, 1976.

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