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Electrochemical and Chemical Oxidation of π-Bonded [Bis(diphenylarsino)methane]chromium and -molybdenum Dicarbonyl Complexes

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Electrochemical oxidation of the complexes $M(CO)_2DAM$ [M = Cr, Mo; DAM = bis(diphenylarsino)methane] in dichloromethane, acetone, and acetonitrile shows some unusual reaction pathways. At mercury electrodes the reversible steps

$$2M(CO)_2DAM + 2Hg \rightleftharpoons 2[HgM(CO)_2DAM]^+ + 2e^-$$

$$2[HgM(CO)_2DAM]^+ \overset{K}{\rightleftharpoons} [Hg(M(CO)_2DAM)_2]^{2+} + Hg$$

are seen in all solvents. Controlled potential electrolyses at a potential corresponding to the limiting current of the reversible polarographic wave generate the mercury cations. Under voltammetric conditions at a platinum electrode $Cr(CO)_2DAM$ undergoes the reversible one-electron oxidation

$$Cr(CO)_2DAM \rightleftharpoons [Cr(CO)_2DAM]^+ + e^-$$

in acetone and dichloromethane under all conditions and in acetonitrile at low temperature. A further irreversible process

$$[Cr(CO)_2DAM]^+ \xrightarrow{-e^-} [Cr(CO)_2DAM]^{2+} \rightarrow \text{products}$$

is also observed. Controlled potential electrolysis at a potential corresponding to the voltammetric one-electron oxidation at 20 °C indicates a two-electron oxidation. However, in acetone or dichloromethane at −78 °C, an n value of 1.0 is obtained at platinum and the cation $[Cr(CO)_2DAM]^+$ is stable on the synthetic time scale at low temperatures. When the temperature is raised, the cation disproportionates to $Cr(CO)_2DAM$ and non-carbonyl-containing species. In contrast to $Cr(CO)_2DAM$, $Mo(CO)_2DAM$ undergoes irreversible oxidation at platinum under all conditions and only non-carbonyl-containing products are obtained from controlled potential electrolysis. Chemical reactions with Hg(II), Ag(I), and iodine are consistent with electrochemical data. In acetonitrile, oxidation with $NOPF_6$ gives the cations $[M(CO)_2(NO)DAM(CH_3CN)_2]^+$ and these can be isolated as hexafluorophosphate salts. For M = Mo, $[Mo(CO)_2NO(CH_3CN)_3]^+$ is also formed. The chemical reactions and electrochemical data can be used to provide a systematic account of reaction pathways for oxidation of the $M(CO)_2DAM$ complexes.

Introduction

Electrochemical and chemical investigations have shown that complexes of the type *cis*-$M(CO)_2(L\text{-}L)_2$ (M = Cr, Mo, W; L-L = DPM (bis(diphenylphosphino)methane), DPE (1,2-bis(diphenylphosphino)ethane)) undergo oxidation to form the paramagnetic cations *trans*-$[M(CO)_2(L\text{-}L)_2]^+$.[1-7] However, under some conditions, seven-coordinate oxidation state II complexes can be obtained.[3,8]

Recently,[9] a mixture of *trans*-$[Cr(CO)_2(DMPE)_2]^+$ and *trans*-$[CrH(CO)_2(DMPE)_2]^+$ has been reported to form from the oxidation of *cis*-$Cr(CO)_2(DMPE)_2$ [DMPE = 1,2-bis(dimethylphosphino)ethane] with $NOPF_6$ in methanol, whereas in acetonitrile, the sole product was *cis*-$[Cr(CH_3CN)(CO)_2(DMPE)_2]^{2+}$, a seven-coordinate dipositive cation, indicating that the solvent played an important role in determining the oxidation product in this type of dicarbonyl complex. This kind of behavior appears to be characteristic of group 6 dicarbonyl complexes.

An alternative kind of dicarbonyl complex is possible when a phenyl or arene group π bonds to the metal, and oxidation studies on this kind of complexes have also provided some interesting data.[10-12] For example, Connelly and Johnson[12] have examined the oxidation of $(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2$(alkyne) [$n$ = 0, 1; alkyne = $PhC{\equiv}CPh$, $MeOC_6H_4C{\equiv}CC_6H_4OMe$] with $NOPF_6$, $AgPF_6$, and I_2. In methanol/toluene and dichloromethane, the cationic species $[(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2(\text{alkyne})]^+$ was isolated. However, for alkyne = $MeOC_6H_4C{\equiv}CC_6H_4MeO$ (n = 0, 1), oxidation with $NOPF_6$ gave unstable monocations and the end product was $[(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2NO]^+$.

Furthermore, oxidation of $[(\pi\text{-}C_6Me_6)Cr(CO)_2L]$ (L = phosphine or phosphite)[13] with $NOPF_6$ in methanol/toluene gave a mixture of $[(\pi\text{-}C_6Me_6)Cr(CO)_2NO]^+$ and $[(\pi\text{-}C_6Me_6)Cr(CO)(NO)L]^+$. A reaction scheme was established to explain the data obtained under various conditions.

Work on the oxidation of these various dicarbonyl complexes has provided a wide range of interesting reaction pathways. However, oxidation of the complexes $M(CO)_2DAM$ (M = Cr, Mo; DAM = bis(diphenylarsino)methane),[14] which have an unusual structure[15] (see Figure 1) in the sense that both L and

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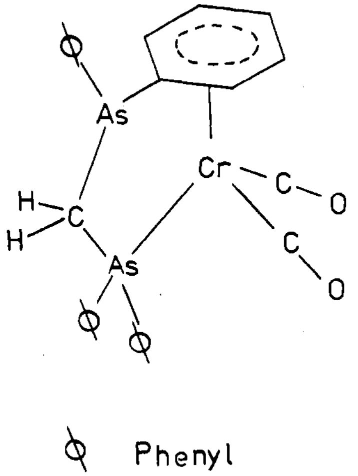

Figure 1. The unusual coordination of DAM in $Cr(CO)_2DAM$.

the π-arene group are contained in the same ligand (DAM), has not been investigated. This work examines the electrochemical and chemical oxidation of these structurally unusual complexes.

Experimental Section

Reagents. $Cr(CO)_2DAM$ and $Mo(CO)_2DAM$. These complexes were prepared as described in the literature.[14] Yields were less than 20%. Their purity was confirmed by microanalysis.

$[Cr(CO)_2(NO)DAM(CH_3CN)_2]PF_6$. Solid $NOPF_6$ (65 mg, 0.37 mmol) was added to a stirred solution of $Cr(CO)_2DAM$ (215 mg, 0.37 mmol) in acetonitrile. The solution rapidly turned red. It was then concentrated under vacuum and, on addition of water, a precipitate was obtained. This orange precipitate was collected and recrystallized several times from dichloromethane/hexane (yield 20%). Anal. Calcd: C, 44.4; H, 3.3; N, 5.0; P, 3.7; As, 17.9; F, 13.6. Found: C, 45.1; H, 3.6; N, 4.9; P, 3.7; As, 17.4; F, 13.6.

$[Mo(CO)_2(NO)DAM(CH_3CN)_2]PF_6$. Solid $Mo(CO)_2DAM$ (435 mg, 0.70 mmol) was dissolved in 40 mL of dichloromethane containing 4 mL of acetonitrile. The solution was flushed with nitrogen, and 123 mg (0.70 mmol) of solid $NOPF_6$ was added and the solution stirred continuously. The initially orange solution turned green and then yellow. The solvent was removed under vacuum and a yellow precipitate remained. This was redissolved in dichloromethane, filtered, and recrystallized from *n*-hexane. Anal. Calcd: C, 42.2; H, 3.2; N, 4.8; P, 3.5; As, 17.0; F, 13.1. Found: C, 42.9; H, 3.4; N, 4.6; P, 3.5; As, 16.5; F, 13.1.

Instrumentation. Electrochemistry. Polarograms and cyclic voltammograms were recorded on either a PAR electrochemistry system, Model 170, or a PAR polarographic analyzer, Model 174A. For studies in dichloromethane, 0.07 M tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte, and Ag/AgCl (saturated LiCl in dichloromethane) was used as the reference electrode. In acetone and acetonitrile, 0.1 M TEAP was used as the supporting electrolyte and Ag/AgCl (saturated LiCl in acetone) as the reference electrode. A three-electrode system employing positive feedback circuitry was used on all occasions with a platinum wire as the auxiliary electrode. The working electrode was either a platinum wire or a dropping mercury electrode. For the cyclic voltammograms at the DME, the potential scan was commenced 1 s after the start of the drop. This and other timing sequences for this technique were controlled by a PAR linear sweep accessory module, Model 174/51. All voltammograms were recorded at a scan rate of 500 mV/s. Pulse voltammograms were recorded by using a pulse width of 57 ms and a sampling duration of 15 ms with the pulse being applied at 0.5-s intervals. Further details of operating conditions are given at appropriate places in the text and figures. Solutions were thoroughly degassed with argon prior to recording a polarogram or voltammogram. Unless otherwise stated, results were obtained at 20 °C.

Controlled potential electrolysis experiments were performed at mercury pool and platinum gauze electrodes by using a PAR Model 173 potentiostat in conjunction with a Model 9600 coulometry cell system and Model 179 digital coulometer. A three-electrode system was used with platinum gauze as the auxiliary electrode separated from the test solution by a porous Vycor sinter. The supporting electrolyte solutions and the reference electrodes were the same as for the polarography and voltammetry except at −78 °C where the supporting electrolyte solution was 0.2 M $t\text{-}Bu_4NClO_4$. The test solution was stirred during the course of the experiment and a stream of argon was passed over the solution at all times. The platinum working electrode was thoroughly cleaned in 6 M nitric acid and washed with solvent before each use.

Table I. Electrochemical Data for DAM[a] at 20 °C

solvent	polarography[b,c] $E_{1/2}$	CV at Hg[c,d] redcn	oxidn	$E_{1/2}$
acetone	0.57	0.58	0.65	0.63
		0.75	0.82	
dichloromethane	0.58	0.60	0.76	0.72
		0.78	0.96	
acetonitrile	0.59	0.56	0.64	0.61

[a] Concentration of DAM 10^{-1} M. All measurements are in volts. [b] Drop time 0.5 s. [c] First oxidation process only. [d] Scan rate 500 mV/s.

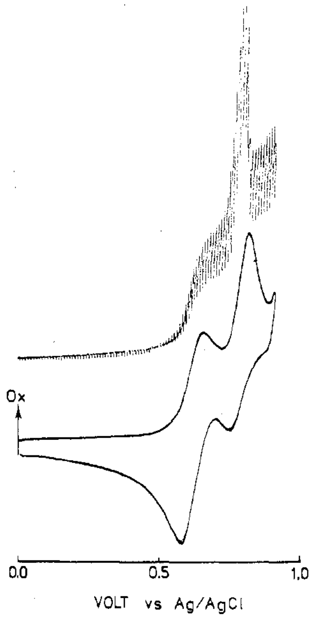

Figure 2. Polarogram and cyclic voltammogram at Hg (scan rate 500 mV/s) of 10^{-3} M DAM in acetone.

Other Instrumentation and Experimental Details. Infrared spectra between 1600 and 2400 cm^{-1} were recorded on a Unicam SP 1200 grating infrared spectrophotometer. Conductivity data were obtained with a Philips PR 9500 conductivity meter in 60/40 acetone/dichloromethane. NMR spectra were recorded on a Varian HA 100 NMR system with tetramethylsilane as an internal reference. ESR spectra were recorded on a Varian 450/15 spectrometer. All analytical data were obtained from the Australian Microanalytical Service, Melbourne.

Results and Discussion

Interpretation of the electrochemical oxidation of the $M(CO)_2DAM$ complexes requires that the electrochemistry of the ligand DAM itself be known. Results from this investigation are therefore presented first.

Electrochemistry of DAM. Electrochemical data for the oxidation of DAM is summarized in Table I. In acetone, two oxidation waves are observed for DAM at a dropping mercury electrode as shown in Figure 2. One is a well-defined wave with a half-wave potential $E_{1/2} = 0.57$ V; the other, which is associated with a maximum, occurs at 0.75 V and very close to the oxidation of mercury. The limiting current magnitude per unit concentration of the first wave was similar to that for the known one-electron oxidation of *cis*-$Cr(CO)_2(DPM)_2$.[3]

Table II. Electrochemical Data for $Cr(CO)_2DAM^a$ at 20 °C

	electrode process 1				electrode process 2	
	CV at Pt^b			polarography^c	CV at Pt^b	
solvent	redcn	oxidn	$E_{1/2}$	$E_{1/2}$	redcn	oxidn
acetone	0.50	0.58	0.55	0.53		1.21
dichloromethane	0.57	0.65	0.60	0.55		1.27
acetonitrile	irr^d	0.59	0.54	0.50	not observed	
acetonitrile (−43 °C)	0.44	0.57	0.53			1.40 (broad)
acetonitrile (at Hg)	0.46	0.57	0.54			

^{a} Concentration 10^{-3} M. All measurements are in volts. ^{b} Scan rate 500 mV/s. ^{c} Drop time 0.5 s. ^{d} irr = irreversible.

Controlled potential electrolysis on the first wave confirmed a one-electron oxidation. A polarogram of this oxidized solution gave a reduction wave with $E_{1/2} = 0.57$ V and an oxidation wave at a similar potential to the second wave of the starting material. Addition of Hg(I) or Hg(II) salts to solutions of DAM produced electrochemistry identical to that obtained after the controlled potential electrolysis experiment. Cyclic voltammograms at mercury indicated that both oxidation processes are chemically reversible (Figure 2) but that the second wave is essentially an adsorption-controlled process. The shape of the first wave at low concentrations is consistent with a diffusion-controlled reversible one-electron step. Studies of limiting currents of dc polarograms as a function of concentration showed that the second wave predominates at low concentrations and becomes less well defined as the concentration increases because of maxima. Electrocapillary curves confirm the presence of substantial adsorption.

In accordance with the above, the first oxidation pathway is consistent with the overall equations

$$2Hg + 2DAM \rightleftharpoons 2[Hg^{I}DAM]^+ + 2e^- \qquad (1)$$

$$2[Hg^{I}DAM]^+ \overset{fast}{\rightleftharpoons} [Hg(DAM)_2]^{2+} + Hg \qquad (2)$$

This reaction scheme is the same as that reported for the oxidation of mercury in the presence of YPh_3 (Y = P, As) to generate $[Hg(YPh_3)_2]^{2+}$.[16]

The chemistry associated with the second process is unknown, and, because it is not required for interpretation of the electrochemistry of the $M(CO)_2DAM$ complexes, detailed studies to identify the mechanism completely were not pursued.

Oxidation of DAM in dichloromethane is completely analogous to the acetone result, whereas in acetonitrile, only the first reversible one-electron oxidation wave is observed. At platinum, oxidation of DAM can only be observed in acetonitrile. In this solvent a broad, irreversible oxidation wave occurred at 1.82 V. Mechanistic details of this electrode process have not been considered.

Electrochemical Oxidation of $Cr(CO)_2DAM$

All relevant data are summarized in Table II.

A. Electrochemistry at Platinum. (i) Acetone and Dichloromethane. Figure 3 shows a cyclic voltammogram of $Cr(CO)_2DAM$ at 20 °C. On the first anodic scan an oxidation wave occurs at 0.58 V. If the scan is then reversed, a reduction wave occurs at 0.50 V. These two waves form a chemically reversible couple (electrode process 1). If the anodic scan is continued, another irreversible wave is observed at more positive potentials (electrode process 2) and electrode process 1 no longer appears chemically reversible. A further very sharp oxidation wave near the solvent limit is also found but is not discussed. The limiting current magnitude per unit concentration of electrode process 1 under conditions of normal pulse voltammetry was equal to that for the known one-electron oxidation of *cis*-$Cr(CO)_2(DPM)_2$.[3]

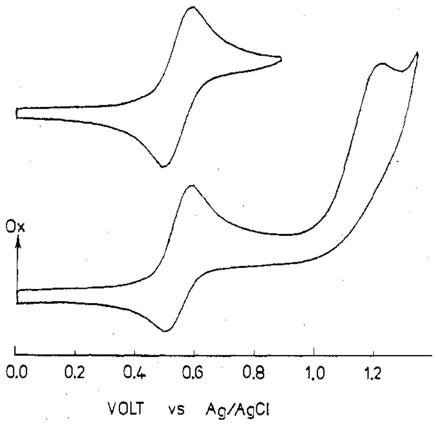

Figure 3. Cyclic voltammogram at Pt of $Cr(CO)_2DAM$ in acetone (scan rate 500 mV/s).

Pulse voltammograms of $Cr(CO)_2DAM$ indicate that the limiting current of the first two oxidation waves is the same, so it appears that $Cr(CO)_2DAM$ undergoes two one-electron oxidations. Electrode process 2 shows no chemical reversibility even at −78 °C.

Electrode process 1 corresponds to the reversible removal of an electron from $Cr(CO)_2DAM$:

$$Cr(CO)_2DAM \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Cr(CO)_2DAM]^+ \qquad (3)$$

i.e., $[Cr(CO)_2DAM]^+$ appears stable on the electrochemical time scale. The second electrode process can be summarized as

$$[Cr(CO)_2DAM]^+ \xrightarrow{-e^-} [Cr(CO)_2DAM]^{2+} \xrightarrow{fast} \text{products} \qquad (4)$$

The $[Cr(CO)_2DAM]^{2+}$ cation possesses no inherent stability even at −78 °C which is surprising since cations such as $[Cr(CO)_2(L\text{-}L)_2]^{2+}$ (L-L = DPM, DPE) are stable at low temperatures on the electrochemical time scale.[1,2] The dichloromethane results were similar to those in acetone, except that no electrode processes other than those described by eq 3 and 4 were observed.

(ii) Acetonitrile. Figure 4a shows a cyclic voltammogram of $Cr(CO)_2DAM$ at 20 °C. At this temperature, a well-defined irreversible oxidation wave is observed at 0.59 V. A broad irreversible wave is also observed at 1.82 V. A comparison of the limiting current for the first oxidation process with *cis*-$Cr(CO)_2(DPM)_2$ showed that it was a one-electron step. Hence the $[Cr(CO)_2DAM]^+$ cation appears unstable in acetonitrile at room temperature in complete contrast to results in acetone and dichloromethane.

At lower temperatures, however, the first electrode process becomes more reversible and is completely reversible at −43 °C (see Figure 4b), just above the freezing point of acetonitrile (0.1 M Et_4NClO_4). The second process is also seen at −43 °C but is more drawn out at low temperatures than in acetone at 20 °C. These facts can be understood as follows: In acetonitrile at 20 °C, the first oxidation wave corresponds to equations of the type

$$Cr(CO)_2DAM \rightleftharpoons [Cr(CO)_2DAM]^+ + e^- \qquad (5a)$$

$$[Cr(CO)_2DAM]^+ + 4CH_3CN \rightarrow [Cr(CO)_2(CH_3CN)_4]^+ + DAM \qquad (5b)$$

that is, $[Cr(CO)_2DAM]^+$ has no inherent stability in acetonitrile and forms a solvated complex which in turn could also readily decompose or rearrange. The new complex(es) formed at the electrode either do not contain DAM or are in equi-

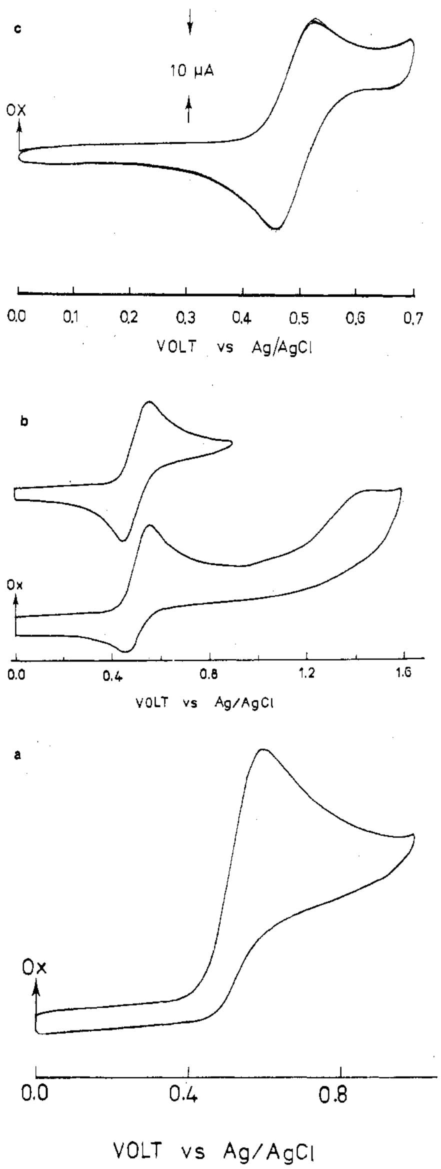

Figure 4. Cyclic voltammograms of $\mathrm{Cr(CO)_2DAM}$ in acetonitrile: (a) at Pt, 20 °C, scan rate 500 mV/s; (b) at Pt, −43 °C, scan rate 500 mV/s; (c) at Hg, 20 °C, scan rate 500 mV/s.

librium with DAM which itself is then subsequently oxidized at 1.82 V. No Cr(I) → Cr(II) wave is therefore observed, as in acetone and dichloromethane. As the temperature is lowered, the decomposition pathway is quenched and $[\mathrm{Cr(CO)_2DAM}]^+$ becomes more stable and the Cr(I) to Cr(II) oxidation wave appears. The more coordinating acetonitrile solvent appears to rapidly attack the cationic species in contrast to the less coordinating acetone and dichloromethane species. Further proof of these processes is presented later.

B. Electrochemistry at Mercury Electrodes. At the dropping mercury electrode, one reversible oxidation wave is seen in all three solvents, including acetonitrile. Figure 4c shows a cyclic voltammogram at mercury in acetonitrile and, unlike the situation at Pt at 20 °C, reversibility is observed. This rather surprising result in acetonitrile indicates that bridging or mercury compound formation at the electrode surface must be considerable. Further comment on this point will be made at a later stage.

C. Controlled Potential Electrolysis. (i) 20 °C at Platinum. Exhaustive controlled potential electrolysis at platinum under argon at 0.8 V in all solvents gave a very pale green solution and an *n* value of 2.0 ± 0.1. A comparison of polarograms of the electrolysis solution before and after oxidation indicated that 1 mol of DAM was released (Figure 5). No carbonyl bands appeared in the infrared spectrum of this solution. The reduction region of the polarogram of the oxidized solution was very similar to that of an equimolar solution of $\mathrm{Cr(ClO_4)_3{\cdot}6H_2O}$. A sharp single-line ESR signal ($g = 1.97$) in acetone consistent with that of Cr(III)[17] was also obtained from the oxidized solution; however, this signal is much narrower than that for $\mathrm{Cr(H_2O)_6}^{3+}$ in acetone and the nature of the signal was time dependent.

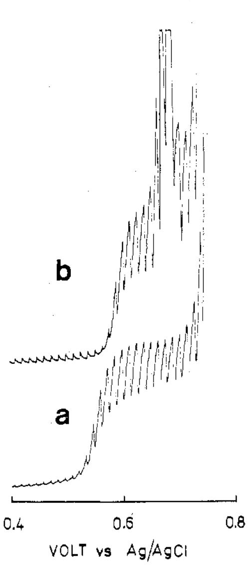

Figure 5. Polarograms of 10^{-3} M $\mathrm{Cr(CO)_2DAM}$ (a) before and (b) after controlled potential electrolysis at Pt in acetone at 0.8 V. One mole of DAM is lost on oxidation.

This information, together with the electrochemical results, is consistent with the overall oxidation mechanism of eq 6

$$\mathrm{Cr(CO)_2DAM} \xrightarrow{-2e^-} \mathrm{Cr(II)} \xrightarrow{\text{solvent,etc.}} \mathrm{Cr(III)} \qquad (6)$$

occurring via the $[\mathrm{Cr(CO)_2DAM}]^+$ intermediate. Under carbon monoxide, the same products were obtained.

(ii) 20 °C at Mercury. At a mercury pool electrode, exhaustive controlled potential electrolysis of $\mathrm{Cr(CO)_2DAM}$ in all solvents ultimately gave a pale green solution which exhibited the same characteristics as the solution obtained by oxidation at platinum, but an *n* value of 3.0 ± 0.1 was obtained instead of 2.0. During the course of the electrolysis, however, a red solution was obtained. A polarographic study of this solution indicated a reduction wave with $E_{1/2}$ almost identical with that for the oxidation wave of $\mathrm{Cr(CO)_2DAM}$. This is in agreement with the reversibility observed for the oxidation of $\mathrm{Cr(CO)_2DAM}$ under the conditions of cyclic voltammetry at a hanging drop mercury electrode in all solvents, including acetonitrile. If the electrolysis was interrupted at this point, the reduction wave slowly decreased in height and waves corresponding to the presence of DAM and the oxidation of $\mathrm{Cr(CO)_2DAM}$ began to grow. After exhaustive electrolysis, no oxidation waves are observed and a reduction wave with $E_{1/2} = 0.59$ V was present. This corresponded to the formation of the mercury–DAM complex described earlier.

It is apparent from the above that the mercury itself is involved in complex formation. This can be verified as follows: on addition of mercurous or mercuric nitrate to a solution of $\mathrm{Cr(CO)_2DAM}$ in any of the three solvents, a red coloration was observed, as previously noted in controlled potential electrolysis experiments. The red coloration was visible in all solvents for a considerable period of time under argon but does decompose slowly at 20 °C. Unfortunately the solid complex

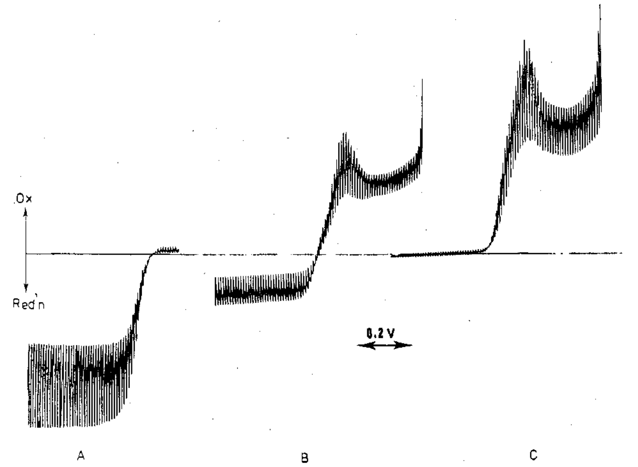

Figure 6. Curve A shows a polarogram of $[Cr(CO)_2DAM]^+$ at −40 °C in acetone, produced by controlled potential electrolysis at Pt at −78 °C. As the temperature increases, the limiting current of this wave decreases and an oxidative component grows until no reduction component remains at −5 °C (curve C). Initial potential 0.0 V in each case.

could not be isolated. In view of all the above information the reaction may be represented as

$$2Cr(CO)_2DAM + 2Hg \rightleftharpoons 2[HgCr(CO)_2DAM]^+ + 2e^- \quad (7)$$

$$2[HgCr(CO)_2DAM]^+ \overset{K}{\rightleftharpoons} [Hg(Cr(CO)_2DAM)_2]^{2+} + Hg \quad (8)$$

$$[Hg(Cr(CO)_2DAM)_2]^{2+} \rightarrow Cr(CO)_2DAM + Cr(II) + DAM + Hg + 2CO \quad (9)$$

The red intermediate is probably the mercury complex $[Hg(Cr(CO)_2DAM)_2]^{2+}$ although the possibility of it being $[HgCr(CO)_2DAM]^+$ or a derivative such as $[Hg_2(Cr(CO)_2DAM)_2]^{2+}$ or ClO_4–Hg–$Cr(CO)_2DAM$ cannot be ruled out. Chromium carbonyl complexes containing Cr–Hg–Cr bonds have been reported previously.[18] More definitive evidence for this kind of complex is obtained in the $Mo(CO)_2DAM$ section.

At mercury, because of the proximity of oxidation potentials for $Cr(CO)_2DAM$ and mercury in the presence of DAM, a further one-electron step occurs as per eq 1 and 2, accounting for the $n = 3.0$ value obtained under coulometric conditions.

(iii) −78 °C at Pt in Acetone. Controlled potential oxidation at platinum in acetone (0.2 M t-Bu_4NClO_4) at −78 °C gave a yellow-brown solution and an n value of 1.0 ± 0.1. The product was completely stable at this temperature. As the solution is warmed to −40 °C and monitored polarographically, only a reduction wave with $E_{1/2} = 0.58$ V was observed. This corresponds to

$$[Cr(CO)_2DAM]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Cr(CO)_2DAM \quad (10)$$

At around −35 °C, the limiting current of the reduction wave began to decrease and an oxidative component began to grow, until eventually no reduction component remained at −5 °C (see Figure 6). The solution was pale yellow at this stage and the oxidative component of the polarogram was shown to be an equimolar mixture of $Cr(CO)_2DAM$ and DAM, and pulse voltammograms at Pt showed that half the initial concentration of $Cr(CO)_2DAM$ was regenerated.

Clearly, the reason for the instability of the cation in acetone (and dichloromethane) is established by this experiment as being due to disproportionation, as has been previously shown for $Cr(CO)_5X$.[19] The mechanism for oxidation is now established in more detail to be

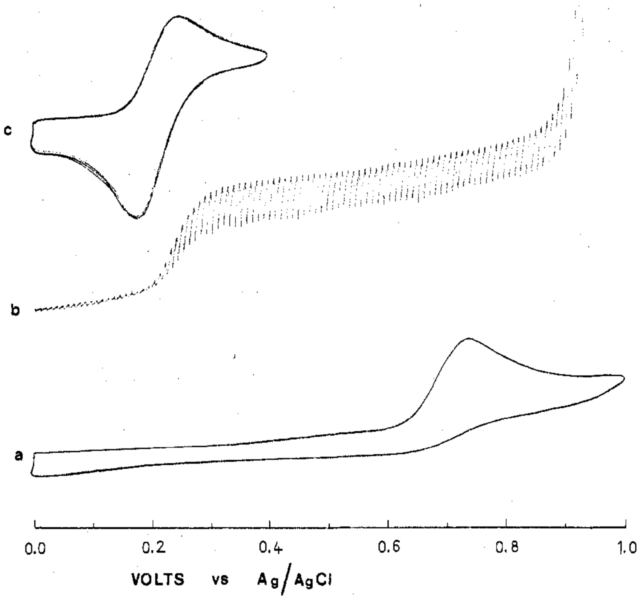

Figure 7. (a) Cyclic voltammogram at platinum for the oxidation of $Mo(CO)_2DAM$ in acetone. Scan rate 500 mV/s. (b) Polarogram of $Mo(CO)_2DAM$ in acetone. (c) Cyclic voltammogram at mercury of $Mo(CO)_2DAM$ in acetone. Scan rate 500 mV/s.

$$2Cr(CO)_2DAM \rightleftharpoons 2[Cr(CO)_2DAM]^+ + 2e^- \quad (11)$$

$$2[Cr(CO)_2DAM]^+ \rightarrow Cr(CO)_2DAM + [Cr(CO)_2DAM]^{2+} \quad (12)$$

$$[Cr(CO)_2DAM]^{2+} \rightarrow \text{products (CO, DAM, Cr(III), etc.)} \quad (13)$$

In acetonitrile, substitution of the 17-electron cation can occur, presumably at a faster rate than disproportionation.

Electrochemical Oxidation of $Mo(CO)_2DAM$

A. Electrochemistry at Platinum. A cyclic voltammogram of the oxidation of $Mo(CO)_2DAM$ in acetone at 20 °C is shown in Figure 7a. At a scan rate of 500 mV/s, a well-defined oxidation wave is observed at 0.74 V. No other oxidation waves occur up to the solvent limit and no reduction waves occur on the reverse scan under all conditions examined. The limiting current magnitude per unit concentration of the oxidation wave for a 10^{-3} M solution of $Mo(CO)_2DAM$ in acetone, under conditions of normal pulse voltammetry, was equal to that for an equimolar solution of $Cr(CO)_2DAM$ and therefore the oxidation process involves a one-electron step. Similar voltammetric data were obtained in dichloromethane and acetonitrile, except that in acetonitrile, because of the extended potential range available, an additional oxidation wave is observed at 1.82 V. This wave corresponds to the oxidation of free DAM.

Controlled potential oxidation at 0.8 V at platinum in acetone, dichloromethane, and acetonitrile gave an n value of 1.0 ± 0.1. The infrared spectrum of the resultant dark green solution contained no carbonyl absorptions. A comparison of polarograms of the electrolysis solution before and after oxidation indicated that 1 mol of DAM was released.

These electrochemical results are consistent with the electrode process at platinum being

$$Mo(CO)_2DAM \overset{-e^-}{\rightleftharpoons} [Mo(CO)_2DAM]^+ \xrightarrow{\text{very fast}} \text{products} \quad (14)$$

where the products include CO, generated DAM, and unknown Mo species. Even on the electrochemical time scale, $[Mo(CO)_2DAM]^+$ is extremely unstable and decomposes rapidly in each of the three solvents. This is in complete contrast to $[Cr(CO)_2DAM]^+$ which was stable on the electrochemical time scale in acetone and dichloromethane at 20 °C and in acetonitrile at −43 °C. This again reflects the greater kinetic stability of chromium as compared with molybdenum in their oxidation state I carbonyl complexes as has been noted on other occasions.[1] The different n value obtained under coulometric conditions at platinum ($n = 1$ for $Mo(CO)_2DAM$ and $n = 2$ for $Cr(CO)_2DAM$) suggests that, with molybdenum, reactions to release free DAM occur faster than disproportionation which occurs for $[Cr(CO)_2DAM]^+$ in acetone and dichloromethane.

B. Electrochemistry at Mercury Electrodes. A polarogram of the oxidation of $Mo(CO)_2DAM$ in acetone at 20 °C is shown in Figure 7b. Only one oxidation wave is observed with $E_{1/2} = 0.24$ V. A comparison of the limiting current per unit concentration of this wave with that for an equimolar solution of $Cr(CO)_2DAM$ indicated that, at mercury, $Mo(CO)_2DAM$ is oxidized in an overall one-electron step.

A cyclic voltammogram of $Mo(CO)_2DAM$ in acetone at 20 °C is shown in Figure 7c. On the first anodic scan an oxidation wave is observed with $E_p = 0.25$ V. On the reverse scan, a reduction wave occurred at $E_p = 0.18$ V. These two waves form a chemically reversible couple with $E_{1/2} = 0.23$ V. This is in complete contrast to the irreversible electrode process at platinum. The vastly different oxidation potentials and behavior at mercury and platinum electrodes for this complex imply that different mechanisms occur at the different electrodes. At mercury, analogous equations to those proposed for chromium (eq 7 and 8) are consistent with the observed data.

To verify the nature of the electrode process, we monitored the chemical reaction of $Mo(CO)_2DAM$ with $Hg(ClO_4)_2 \cdot 3H_2O$ polarographically. A freshly prepared 6.38×10^{-2} M solution of $Hg(ClO_4)_2 \cdot 3H_2O$ in acetone was added via a 0.1-mL Eppendorf pipet to a solution containing 5.1×10^{-5} mol of $Mo(CO)_2DAM$ in acetone (0.1 M Et_4NClO_4). The initial oxidation wave at $E_{1/2} = 0.24$ V had completely disappeared after the addition of 0.4 mL (i.e., 2.55×10^{-5} mol) of the mercuric perchlorate solution. At this point, only a reduction wave, with $E_{1/2}$ and limiting current values identical with those of the initial oxidation wave, was observed. Hence 2 mol of $Mo(CO)_2DAM$ reacts with 1 mol of Hg^{2+} in an overall one-electron oxidation. This reaction is the same as that found for $Cr(CO)_2DAM$; however, the cation $[Hg(Mo(CO)_2DAM)_2]^{2+}$ is considerably more stable—i.e., the decomposition step (eq 9) is insignificant.

For a characterization of the solvent-independent nature of the electrode process, controlled potential oxidation of $Mo(CO)_2DAM$ was performed at a mercury pool electrode at 0.4 V in acetone, dichloromethane, and acetonitrile. In each case an n value of 1.0 ± 0.1 was obtained which is consistent with polarographic data. A polarogram of the resultant yellow-green solution showed only a reduction wave. The $E_{1/2}$ of this wave and its limiting current were identical with those observed for the initial oxidation wave. After the oxidized solution had been concentrated under vacuum, the infrared spectrum showed three carbonyl absorptions at 1920, 1956, and 1970 cm^{-1} (see Figure 8). A product, with an identical infrared spectrum, was also obtained from the reaction of $Mo(CO)_2DAM$ and $Hg(ClO_4)_2 \cdot 3H_2O$ (2:1). *Attempts to isolate and characterize this material in the solid state led to a yellow solid which exploded violently on drying under vacuum.* The use of perchlorate salts or perchloric acid in the presence of organic materials has been known to result in explosions.[20-22] The explosive nature of the yellow solid suggested that it was a perchlorate salt; however, endeavors to further handle the solid mixture were discontinued due to its detonating properties. Attempts to use other mercuric salts, e.g., $Hg(NO_3)_2$ were not successful, since these were only slightly soluble in acetone or acetonitrile. Despite this inability to obtain the product from oxidation of $Mo(CO)_2DAM$ with Hg^{2+}, the chemical and electrochemical data demonstrate that it is a mercury complex incorporating 2 mol of $Mo(CO)_2DAM$/mol of mercury.

Figure 8. Infrared spectrum (carbonyl region) of a solution of $Mo(CO)_2DAM$ in dichloromethane before (top) and after (bottom) controlled potential oxidation at a mercury pool electrode.

Several group 6 carbonyl complexes containing metal–Hg–metal bonds are known. The complexes $[(\pi\text{-}C_5H_5)M(CO)_3]_2Hg$ (M = Cr, Mo, W)[18] and their derivatives $[(\pi\text{-}C_5H_5)M(CO)_2L]_2Hg$ (M = Mo, W; L = $P(OMe)_3$, $P(OPh)_3$, PPh_3)[23] have been reported. These latter complexes have four carbonyl bands in their infrared spectrum and are substituted similarly to $Mo(CO)_2DAM$. In view of these facts, the product obtained from both the chemical reaction of $Mo(CO)_2DAM$ with Hg^{2+} and the electrochemical oxidation at mercury electrodes appears to be $[DAM(CO)_2Mo\text{–}Hg\text{–}Mo(CO)_2DAM]^{2+}$.

The difference between the oxidation of $Cr(CO)_2DAM$ and $Mo(CO)_2DAM$ at mercury and the large potential difference between data obtained at mercury and platinum for Mo-

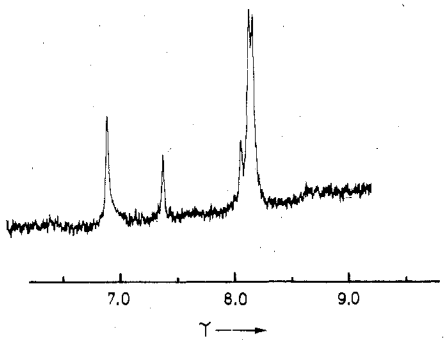

Figure 9. ^1H NMR of $[Cr(CO)_2(NO)DAM(CH_3CN)_2]^+$ in CD_2Cl_2 showing the presence of two coordinated acetonitrile groups at τ 8.14 and 8.18 and a monodentate DAM at τ 6.90.

$(CO)_2DAM$ can now be understood in terms of the magnitude of the equilibrium constant following charge transfer. That is the value of K in eq 8 determines the position of the wave.

Chemical Oxidation

From the electrochemical data it seems clear that chemical oxidation in the absence of coordinating ligands is unlikely to lead to stable carbonyl complexes. Thus, two classes of chemical oxidation reactions were considered: the first class included potentially coordinating groups which could provide stable complexes, and the second class consisted of simple noncoordinating oxidants which should parallel the electrochemical behavior.

A. $Cr(CO)_2DAM$. (i) $NOPF_6$. Addition of solid $NOPF_6$ to $Cr(CO)_2DAM$ (1:1) in acetonitrile produced a red solution from which a pale orange solid was obtained on addition of water. The solid complex was air stable and showed three strong infrared absorptions at 1712, 1973, and 2068 cm^{-1} in solution along with two very weak absorptions at 2282 and 2308 cm^{-1} which are only observed in a solid-state (KBr disk) spectrum. The absorption at 1712 cm^{-1} is indicative of a coordinated NO group. The shift in the terminal CO frequencies to higher wavenumbers is consistent with oxidation of the chromium atom.[12] The two very weak absorptions are attributed to two coordinated acetonitrile groups. Coordination of acetonitrile in group 6 metal carbonyl complexes has been well documented.[8,24]

The complex was diamagnetic and the ^1H NMR spectrum indicated that the phenyl group, previously π bonded to the chromium, is no longer coordinated. Instead, a singlet is observed at τ 6.90 and two resonances occur at τ 8.14 and 8.18 (see Figure 9). Small resonances were also observed at τ 7.38 and 8.06. During the NMR experiment, these latter resonances began to grow at the expense of the former resonances until only the latter remained. At this point, no nitrosyl or carbonyl groups could be observed in the infrared spectrum.

These results can be interpreted in the following manner. The resonance at τ 6.90 is consistent with a monodentate DAM group.[14] Since no π-bonded phenyl proton resonances were observed, oxidation by $NOPF_6$ causes the π-bonded phenyl group to break away from the chromium but the other end of the DAM molecule remains coordinated through the arsenic atom. The two resonances at τ 8.14 and 8.18 are attributed to two coordinated acetonitrile groups in different environments,[8] consistent with the two very weak absorptions observed in the infrared. The disappearance of these resonances is a result of slow decomposition to noncoordinated DAM (τ 7.38) and acetonitrile (τ 8.06).

The analytical data were consistent with the formula $[Cr(CO)_2(NO)DAM(CH_3CN)_2]PF_6$, an 18-electron system, in agreement with the infrared and NMR data. Conductivity data (66 Ω^{-1} cm^2 mol^{-1}) confirmed the complex was a 1:1 electrolyte.[3] The probable structure of this complex is shown in Figure 10. All data are consistent with this being regarded as a Cr(I) complex with coordinated NO. Thus the mechanism of formation is

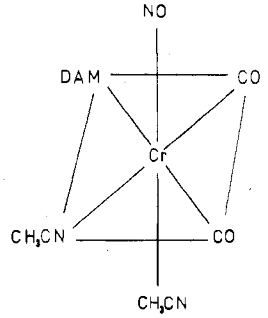

Figure 10. Probable structure of $[Cr(CO)_2(NO)DAM(CH_3CN)_2]^+$.

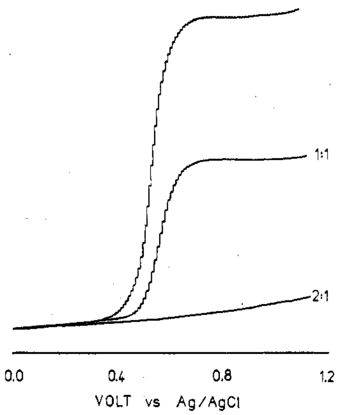

Figure 11. Reaction of $AgClO_4$ and $Cr(CO)_2DAM$ in acetone monitored by pulse voltammetry at Pt. At equal concentrations half the $Cr(CO)_2DAM$ remains. Scan rate 20 mV/s, duration between pulses 0.5 s.

$$Cr(CO)_2DAM + NO^+ \rightarrow [Cr(CO)_2DAM]^+ + NO \quad (15a)$$

$$Cr(CO)_2DAM + NO + 2CH_3CN \rightarrow [Cr(CO)_2(NO)DAM(CH_3CN)_2]^+ \quad (15b)$$

Thus a new mode of $NOPF_6$ oxidation has been found and, unlike the case of other π-bonded systems, rupture of the coordinated arene group occurs. Acetonitrile appears able to displace the π-bonded phenyl group in the cation $[Cr(CO)_2DAM]^+$. The irreversible electrochemical behavior in acetonitrile at platinum is therefore probably due to the reaction

$$[Cr(CO)_2DAM]^+ + 3CH_3CN \rightarrow [Cr(CO)_2DAM(CH_3CN)_3]^+ \quad (16)$$

$$[Cr(CO)_2DAM(CH_3CN)_3]^+ + CH_3CN \rightleftarrows [Cr(CO)_2(CH_3CN)_4]^+ + DAM \quad (17)$$

On the controlled potential electrolysis time scale, disproportionation or further redox reactions can occur in addition to the substitution reaction. However, when coordination is by NO, a three-electron donor, a stable 18-electron configuration is obtained.

(ii) $AgClO_4$ and Iodine. Oxidation of $Cr(CO)_2DAM$ with $AgClO_4$ (1:2) in acetonitrile, acetone, and dichloromethane led to the loss of all carbonyl groups from the complex. The reaction was monitored by pulse voltammetry at Pt. At the 1:1 end point, exactly half the original concentration of $Cr(CO)_2DAM$ remained (see Figure 11).

Oxidation of $Cr(CO)_2DAM$ with I_2 (1:1) in each solvent again led to the loss of all carbonyl groups to give a solution

Table III. Comparison of the Infrared Data (cm^{-1}) for the Complexes $[M(CO)_2(NO)DAM(CH_3CN)_2]^+$ (M = Cr, Mo) and Their Related Complexes[a]

	CH_2Cl_2		KBr disk
	CO	NO	C≡N
$[Cr(CO)_2(NO)DAM(CH_3CN)_2]^+$	2068, 1973	1712	2308, 2282
$Cr(CO)_2DAM$	1896, 1849		
$[Mo(CO)_2(NO)DAM(CH_3CN)_2]^+$	2040, 1961	1692	2300, 2275
$[Mo(CO)_2(NO)(CH_3CN)_3]^+$	2025, 1943	1645	
$Mo(CO)_2DAM$	1897, 1838		

[a] All carbonyl and nitrosyl stretches were strong whereas the nitrile stretches were very weak and were only observed in the solid-state infrared spectrum.

containing Cr(III) (identified by ESR). Clearly, these oxidation processes follow the electrochemical results and the $NOPF_6$ oxidation appears to be aided by the ability to form a stable 18-electron configuration via the three-electron NO donor.

B. $Mo(CO)_2DAM$. (i) $NOPF_6$. Addition of solid $NOPF_6$ to $Mo(CO)_2DAM$ (1:1) in dichloromethane (containing 10% acetonitrile) slowly produced a green solution from which a yellow precipitate was obtained on removal of the solvent under vacuum. This yellow solid was air stable and its infrared spectrum in CH_2Cl_2 showed three strong infrared absorptions at 1692, 1961, and 2040 cm^{-1}. In the solid state (KBr disk), however two other very weak absorptions at 2300 and 2275 cm^{-1} were also observed. These infrared data are similar to those obtained for the oxidation of $Cr(CO)_2DAM$ by $NOPF_6$ (see Table III). The analytical data were consistent with the formula $[Mo(CO)_2(NO)DAM(CH_3CN)_2]PF_6$, an 18-electron Mo(I) complex.

The ^1H NMR spectrum of $[Mo(CO)_2(NO)DAM(CH_3CN)_2]^+$ in $CDCl_3$ confirmed that the complex was diamagnetic and indicated a methylene resonance at τ 6.85 (consistent with a monodentate DAM ligand), and two resonances at τ 8.08 and 8.18 indicative of two coordinated acetonitrile ligands in different environments. Integration showed that the ratio of protons contributing to these three resonances was 2:3:3, as expected. Repeated NMR spectra showed that the complex decomposed in solution giving rise to increasing concentrations of uncoordinated DAM and acetonitrile. All data indicate that the molybdenum complex is isostructural with its chromium counterpart.

On continual monitoring of infrared spectra of $[Mo(CO)_2(NO)DAM(CH_3CN)_2]^+$ in acetonitrile, a gradual shift in the frequencies of the carbonyl and nitrosyl absorptions was observed (see Table III). This change was much slower if the solution cell was removed from the infrared beam between the recordings of spectra. However, similar experiments in dichloromethane showed no changes to the original infrared spectrum. These results suggest the formation of a new species in acetonitrile. For a determination of the nature of this new species, the complex $[Mo(CO)_2(NO)DAM(CH_3CN)_2]PF_6$ was refluxed in acetonitrile for 1 h. The solvent was then removed under vacuum and the ^1H NMR spectrum of the residue in $CDCl_3$ indicated only free DAM, although resonances for coordinated acetonitrile still occurred. The infrared spectrum of the NMR solution showed three strong absorptions at 2025, 1943, and 1645 cm^{-1}. Hence, it appears that the monodentate DAM ligand in $[Mo(CO)_2(NO)DAM(CH_3CN)_2]^+$ is not strongly coordinated and can be readily replaced by acetonitrile to form $[Mo(CO)_2(NO)(CH_3CN)_3]^+$. This species could not be isolated as a solid suitable for analysis but spectroscopic evidence enables it to be fully characterized. The proposed structure for this species is octahedral with the acetonitrile groups being facial. This result provides further evidence for the irreversible electrochemical behavior in acetonitrile being due to substitution of DAM.

(ii) $AgClO_4$ and Iodine. Oxidation of $Mo(CO)_2DAM$ with $AgClO_4$ or iodine produced non-carbonyl-containing products in agreement with predictions based on electrochemical data.

Conclusions

The oxidation behavior of $Cr(CO)_2DAM$ is unusual compared with that of related π-bonded complexes. Except at low temperatures and in some solvents, the cation $[Cr(CO)_2DAM]^+$ does not have any stability on the synthetic time scale and disproportionates, a characteristic which seems to be related to the 17-electron configuration. The formally 16-electron chromium(II) carbonyl complex $[Cr(CO)_2DAM]^{2+}$ does not appear to have any stability on short time scale electrochemical experiments even at −78 °C in either coordinating or noncoordinating solvent. That is, it is even more reactive than its 17-electron counterpart. Clearly, the unusual structure associated with the π-bonded DAM system cannot be readily maintained in these electronic configurations. The electrochemical behavior of $Mo(CO)_2DAM$ at a platinum electrode is different from that of $Cr(CO)_2DAM$ in the sense that the cation $[Mo(CO)_2DAM]^+$ does not have any inherent stability, even at −78 °C, and decomposes rapidly in either coordinating or noncoordinating solvents. That is, the 17-electron molybdenum cation is even more reactive than its chromium analogue.

Oxidation is reversible at a mercury electrodes for both species although for $Mo(CO)_2DAM$, oxidation at mercury occurs almost 500 mV more negative than at platinum, whereas only a very small potential difference was observed for $Cr(CO)_2DAM$. For $Mo(CO)_2DAM$, the oxidation product has been characterized as the mercury cation $[DAM(CO)_2Mo{-}Hg{-}Mo(CO)_2DAM]^{2+}$ with both Mo atoms being seven-coordinate, and a similar less stable product is postulated for the chromium case.

Chemical oxidation of $M(CO)_2DAM$ with $NOPF_6$, although associated with the rupture of the π-bonded phenyl group, does lead to a stable 18-electron M(I) complex in the presence of coordinating solvents, because of the generation of the three-electron donor, NO.

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Registry No. $Cr(CO)_2DAM$, 34829-56-6; $Mo(CO)_2DAM$, 35768-63-9; $[Cr(CO)_2(NO)DAM(CH_3CN)_2]PF_6$, 69881-50-1; $[Mo(CO)_2(NO)DAM(CH_3CN)_2]PF_6$, 69881-52-3; DAM, 21892-63-7; $[Cr(CO)_2DAM]^+$, 69927-31-7; $[Mo(CO)_2(NO)(CH_3CN)_3]^+$, 69927-35-1; $[Mo(CO)_2DAM]^+$, 69927-30-6; $[DAM(CO)_2Mo\text{-}Hg\text{-}Mo(CO)_2DAM]^{2+}$, 69927-32-8.

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Competition Studies and Stereochemistry of Base Hydrolysis of (Dimethyl sulfoxide)- and (Trimethyl phosphate)amminebis(ethylenediamine)cobalt(III) Ions

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The preparation, properties, and base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3(Me_2SO)](ClO_4)_2(NO_3)$ (**1**) and $(+)_{589}$-$[Co(en)_2NH_3(TMP)](ClO_4)_3$ (**2**) (Me_2SO = dimethyl sulfoxide; TMP = trimethyl phosphate) are reported; $k_{OH}(\mathbf{1}) = 2.35 \times 10^2$ and $k_{OH}(\mathbf{2}) = 2.5 \times 10^3$ mol dm^{-3} s^{-1} in 1.0 mol dm^{-3} $NaClO_4$ at 25 °C. Base hydrolysis of **1** involves 100% Co–O bond breaking, and Cl_2 oxidation gives 100% optical retention in the $(+)_{589}$-$[Co(en)_2NH_3(OH_2)]^{3+}$ product. Base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ (X = Br, Me_2SO, TMP) gives 77% trans and 23% cis hydroxo products, but the retention in the cis ion varies with X (78% (Br^-), 83.5% (Me_2SO), 85% (TMP)); these ratios are independent of both the electrolyte (NaN_3, $NaClO_4$) and its concentration (0–2 mol dm^{-3}). The relative amounts of *cis*- and *trans*-$[Co(en)_2NH_3N_3]^{2+}$ formed in the presence of N_3^- are independent of N_3^- concentration (66% cis, 34% trans), but the retention in the cis azide also depends on X (73.5% (Br^-), 83% (Me_2SO), 85% (TMP)); marginally more (~3%) azide products are formed for X = Me_2SO and TMP than for X = Br. The results are interpreted in terms of an ion-pairing mechanism for base hydrolysis.

Recent studies on the mechanism of base hydrolysis of acidopentaaminecobalt(III) complexes support a limiting S_N1cB mechanism.[1-5] These studies embrace competition experiments[1-3] and the stereochemistry of the products,[3-5] and the conclusion concerning the mechanism was drawn from the fact that all results were independent of the nature of the leaving group. However, recent studies using three different $[Co(Metren)NH_3X]^{2+,3+}$ isomers suggest that the stereochemistry is not independent of leaving group (X = Cl^-, Br^-, NH_3),[6] and we report here some additional results on the competition products of base hydrolysis of three $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ complexes which also show a leaving group dependence.

The previous results on the base hydrolysis of the $(+)_{589}$-$[Co(en)_2NH_3X]^{2+}$ ions (X^- = Cl^-, Br^-, NO_3^-)[3] gave common stereochemistries and competition ratios for both the hydroxo and azido products (N_3^- present) with the former result agreeing with that obtained in the absence of N_3^-. This was interpreted in terms of the S_N1cB mechanism in which the five-coordinate intermediate (or intermediates) competed for various solvated leaving groups including water as depicted by Scheme I.

The present results extend these studies to include the neutral leaving groups Me_2SO (dimethyl sulfoxide) and TMP (trimethyl phosphate). The preparation and base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3(Me_2SO)](NO_3)(ClO_4)_2$ and $(+)_{589}$-$[Co(en)_2NH_3TMP](ClO_4)_3$ have not been reported previously, and the position of bond cleavage of the Me_2SO moiety is examined. Also, the stereochemistry of the Cl_2-induced oxidation of the Me_2SO complex is reported.

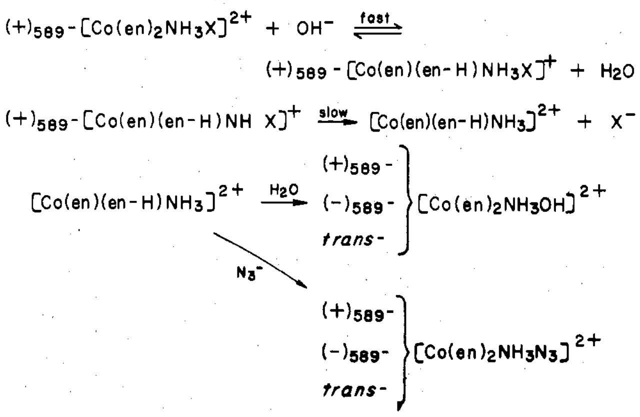
Experimental Section

$(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$ was prepared as described by Werner[7] $[\alpha]^{25}_{589}$ +135°. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Cl]Br_2$: N, 17.89; H, 4.89; C, 12.27. Found: N, 17.8; H, 4.9; C, 12.1.

***cis*-$[Co(en)_2NH_3Br]Br_2$** was prepared from *trans*-$[Co(en)_2Br_2]Br$ as follows. *trans*-$[Co(en)_2Br_2]Br$ (48 g) was ground to a paste with 15 cm^3 of H_2O and 15 cm^3 of MeOH; a few crystals of $Co(NO_3)_2 \cdot 6H_2O$ were added, followed closely by addition of NH_4OH (sp gr 0.88 g cm^{-3}) from a Pasteur pipet. On mixture the green starting complex rapidly changed to the mauve product. Additional $MeOH–H_2O$ (80:20) was added from time to time to keep the mixture workable, and after 1 h the product was extracted with MeOH and washed on a glass filter; yield 48 g. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br]Br_2$: N, 16.07; H, 4.39; C, 11.02. Found: N, 15.9; H, 4.5; C, 10.9. This material could be converted to the perchlorate salt by passing an aqueous solution through Dowex AG 1-X8 (ClO_4^-) exchange resin, concentration on a rotary evaporator, and addition of $NaClO_4$. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br](ClO_4)_2$: N, 14.75; H, 4.03; C, 10.11. Found: N, 14.7; H, 4.2; C, 10.1. This complex was resolved according to the method of Kauffman and Lindley.[8] The $(+)_{589}$-BCS diastereoisomer ($[\alpha]_{589}$ = +105°) was converted to the Cl^- salt by passing an aqueous solution through Dowex AG 1-X4 (Cl^-) exchange resin, concentrating it on a rotary evaporator, and adding concentrated HCl. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br]Cl_2$: N, 20.19; H, 5.52; C, 13.84. Found: N, 20.1; H, 5.4; C, 13.8. $[\alpha]^{25}$ was +125° (589 nm), −340° (436 nm), +68° (656 nm) for a 0.1% aqueous solution. For the $(-)_{589}$ salt, $[\alpha]^{25}_{589}$ was −125°.

$(+)_{589}$-$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$. To $(+)_{589}$-$[Co(en)_2NH_3Br]Cl_2$ (2.1 g) suspended in Me_2SO (20 cm^3) was added $AgClO_4$ (3.8 g, 3 equiv). On standing, the solution immediately

Scheme I



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