Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville 3052, Victoria, Australia

Electrochemical Reduction of Seven-Coordinate, Substituted Molybdenum(II) and Tungsten(II) Halocarbonyls

A. M. BOND,* R. COLTON, and J. J. JACKOWSKI

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Electrochemical reduction of $M(CO)_3(YPh_3)_2X_2$ (M = Mo, W; Y = P, As, Sb; X = Cl, Br, I) in dichloromethane and acetone results in a two-electron irreversible reduction at mercury and platinum electrodes. Data can only be interpreted by assuming that the seven-coordinate oxidation state II complexes are kinetically labile. Cyclic voltammetry at mercury indicates that loss of a halide ion occurs on reduction and thus provides information about the reduction pathway. Controlled-potential electrolysis in the presence of carbon monoxide produces $[M(CO)_5X]^-$ anions. The overall reaction for this reduction can be written as $M(CO)_3(YPh_3)_2X_2 + 2CO + 2e^- \rightarrow [M(CO)_5X]^- + 2YPh_3 + X^-$. However, $[Mo(CO)_5X]^-$ anions are unstable and generally decompose to non-carbonyl-containing species, whereas $[W(CO)_5X]^-$ anions can be isolated as stable tetraethylammonium salts. In the presence of argon, pentacarbonyl halide anions are also produced, but in lower concentration, as the result of a disproportionation or dissociation reaction. No oxidation state I complexes are observed on the electrochemical time scale as intermediates in the reduction.

Introduction

Chemical oxidation of molybdenum and tungsten carbonyls in zero oxidation state has been reported on numerous occasions.[1-15] Where a carbonyl-containing product has been well characterized, a diamagnetic oxidation state II species has usually been reported. Frequently, the oxidized species has been a monomeric seven-coordinate complex (e.g., $M(CO)_3L_2X_2$) or a dimer (e.g., $[M(CO)_4X_2]_2$, still seven-coordinate), although monomeric six-coordinate species are also found in oxidation state II.[8,16-18] In the particular case of $M(CO)_2(P–P)_2$ (M = Mo, W; P–P = bidentate phosphorus ligand), chemical oxidation with some reagents leads to the isolation of a formal oxidation state I species $[M(CO)_2(P–P)_2]^+$.[7,10,11,15] However, stable paramagnetic oxidation state I species have not been commonly reported. Electrochemical oxidation of zero-valent carbonyl complexes confirms the chemical results. With $M(CO)_6$[19] and $[M(CO)_5X]^-$[20] no stable oxidation state I species are isolated, in contrast to electrochemical oxidation of $M(CO)_2(P–P)_2$,[12,15,21] which confirms the existence of a stable $[M(CO)_2(P–P)_2]^+$ cation.

While the electrochemical and chemical oxidation studies of molybdenum and tungsten zero-valent carbonyls are fairly widespread, the reduction of oxidation state II species does not appear to have been investigated. Seven-coordinate neutral complexes of the kind $M(CO)_3L_2X_2$ (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$; X = Cl, Br, I) have been reported.[8,16-18] However, little is known about their solution chemistry, although some substitution reactions have been documented.[22] Reduction of such complexes should prove very interesting from several viewpoints. For example, products are likely to be six-coordinate, and structural considerations should determine whether the leaving group is CO, L, or X. Electrochemical studies of these complexes should therefore yield substantial information on the reduction pathways as well as provide considerable data on the chemistry of the substituted-carbonyl systems in the different oxidation states.

Experimental Section

Chemicals and Reagents. Molybdenum and tungsten hexacarbonyls (Pressure) were dried over phosphorus pentoxide for several days prior to reaction. A. R. grade bromine and iodine were not purified further, but chlorine gas was passed through a concentrated sulfuric acid trap before use. Triphenylphosphine, triphenylarsine, and triphenylantimony (Strem) were used without further purification. All solvents used were of A.R. grade purity.

Preparation of the Complexes. The complexes $[M(CO)_4X_2]_2$ and $M(CO)_3(YPh_3)_2X_2$ were generally prepared as described in the literature,[8,16-18] except for X = Br where the literature methods[17,18] were modified in the following fashion to give a considerably improved yield of about 30%. A 1-g amount of molybdenum or tungsten hexacarbonyl was suspended in 10 cm^3 of dry dichloromethane at −78 °C under a very slow stream of nitrogen. On addition of 5 (Pasteur pipet) drops of bromine and warming slightly, a reaction took place with the evolution of carbon monoxide. The reaction mixture was shaken continuously and then cooled again. Small amounts of bromine were added, the above procedure being repeated each time, until all the hexacarbonyl appeared to have reacted. The solvent was removed by a strong stream of nitrogen. The powdered, impure tetracarbonyl was added to 2 g of YPh_3 dissloved in dry acetone (20 cm^3). Carbon monoxide was immediately evolved, and after a few minutes yellow crystals began separating out of solution. The volume of solution was reduced under vacuum with the final portion being decanted. The impure tricarbonyl was purified on a cellulose column using dichloromethane and subsequently recrystallized with *n*-hexane.

All complexes were stored under vacuum as decomposition occurs slowly in the atmosphere. Only very small yields of $[Mo(CO)_4I_2]_2$ were obtained, and consequently no molybdenum iodide derivatives could be prepared.

Electrochemical Instrumentation. Polarograms and voltammograms were recorded at 25 ± 1 °C on either a PAR Model 170 electrochemistry system or a PAR Model 174A polarographic analyzer. For studies in dichloromethane, 0.07 M tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte and Ag/AgCl (saturated Et_4NCl, dichloromethane) was used as the reference electrode. In acetone, 0.10 M TEAP was used as the supporting electrolyte and Ag/AgCl (saturated LiCl, acetone) as the reference electrode. A three-electrode system employing positive feed-back circuitry was used on all occasions with platinum wire as the auxiliary electrode. The reference electrode was separated from the test solution by a salt bridge containing the supporting electrolyte. The working electrode was either 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 174/51 linear sweep accessory module. Solutions were degassed with argon or carbon monoxide for 10 min prior to recording a polarogram or voltammogram.

Controlled-potential electrolysis experiments were performed at mercury pool and platinum gauze electrodes using a PAR Model 173 potentiostat in conjunction with a Model 9600 coulometry cell system and a 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 reference electrodes were the same as those for the polarography and voltammetry analyses. The test solution was stirred during the course of the experiment, and a stream of argon or carbon monoxide was passed over the solution at all times. All controlled-potential reductions were performed at −1.60 V in both solvents, and the platinum electrode was cleaned in 6 M nitric acid before each use.

Isolation of Electrolysis Products. In dichloromethane the electrolysis products were isolated by washing the test solution several times with water to remove tetraethylammonium perchlorate. The dichloromethane was then removed under vacuum and the impure product recrystallized from dichloromethane/*n*-hexane.

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Table I. IR Data (Carbonyl Region) for $M(CO)_3(YPh_3)_2X_2$ and Related Complexes in Dichloromethane under Argon and Carbon Monoxide

Complex	Wavenumber, cm^{-1}	
	Argon	Carbon monoxide
$Mo(CO)_3(PPh_3)_2Cl_2$	1958 1880	2029 1958 1918
$Mo(CO)_2(PPh_3)_2Cl_2$	1958 1880	2029 1958 1918
$Mo(CO)_3(PPh_3)_2Br_2$	1960 1881	2024 1960 1920
$W(CO)_3(PPh_3)_2Cl_2$	2018 1940 1906	2018 1940 1906
$W(CO)_3(PPh_3)_2Br_2$	1941 1878	2022 1941 1907
$W(CO)_2(PPh_3)_2Br_2$	1941 1878	2022 1941 1907
$W(CO)_3(PPh_3)_2I_2$	2013 1940 1910	2013 1940 1910
$Mo(CO)_3(AsPh_3)_2Cl_2$	2024 1963 1919	2024 1963 1919
$Mo(CO)_3(AsPh_3)_2Br_2$	2026 1962 1924	2026 1962 1924
$W(CO)_3(AsPh_3)_2Cl_2$	2020 1942 1910	2020 1942 1910
$W(CO)_3(AsPh_3)_2Br_2$	2020 1945 1915	2080 2005 1923
$W(CO)_3(AsPh_3)_2I_2$	2014 1941 1914	2074 2008 1948
$Mo(CO)_3(SbPh_3)_2Cl_2$[a]	2030 1962 1924	2030 1962 1924
$Mo(CO)_3(SbPh_3)_2Br_2$[a]	2023 1959 1919	2023 1959 1919
$W(CO)_3(SbPh_3)_2Cl_2$[b]	2014 1937 1908	2014 1937 1908
$W(CO)_3(SbPh_3)_2Br_2$[b]	2018 1948 1913	2080 2005 1923
$W(CO)_3(SbPh_3)_2I_2$	2011 1943 1913	2074 2008 1948

[a] Decomposition catalyzed by tetraethylammonium perchlorate. [b] Slow decomposition occurs in the presence of tetraethylammonium perchlorate.

In acetone the solvent was removed under vacuum, the solid remaining redissolved in dichloromethane, and the product isolated as described above.

Other Instrumentation and Experimental Details. Infrared spectra of the carbonyl region were recorded on a Unicam SP 1200 grating infrared spectrophotometer. Conductivity data was obtained with a Phillips PR 9500 conductivity meter. All analyses were carried out by the Australian Microanalytical Service, Melbourne.

Results and Discussion

A. Electrochemistry in Dichloromethane. Reduction of $Mo(CO)_3(PPh_3)_2X_2$ and $Mo(CO)_2(PPh_3)_2X_2$ (X = Cl, Br). In dichloromethane (0.07 M Et_4NClO_4) the yellow complexes $Mo(CO)_3(PPh_3)_2X_2$ readily form blue complexes of the type $Mo(CO)_2(PPh_3)_2X_2$ when argon is bubbled through the solution, as is undertaken when removing oxygen prior to recording a voltammogram or polarogram. The loss of CO is reversible,[16,17] and on bubbling CO through the solution the yellow tricarbonyl is re-formed (IR monitoring; see Table I). Thus, under argon the electrochemistry reported is actually that for the blue dicarbonyl complex rather than that for the prepared tricarbonyl complex. This was confirmed conclusively by synthesizing $Mo(CO)_2(PPh_3)_2X_2$ and showing that its electrochemistry and infrared spectrum (Table I) are identical with those of the tricarbonyl complex under argon. Thus, equilibrium 1 can be used to study the electrochemistry of both

$$Mo(CO)_3(PPh_3)_2X_2 \underset{CO}{\overset{Argon}{\rightleftharpoons}} Mo(CO)_2(PPh_3)_2X_2 \qquad (1)$$

the dicarbonyl and tricarbonyl complexes.

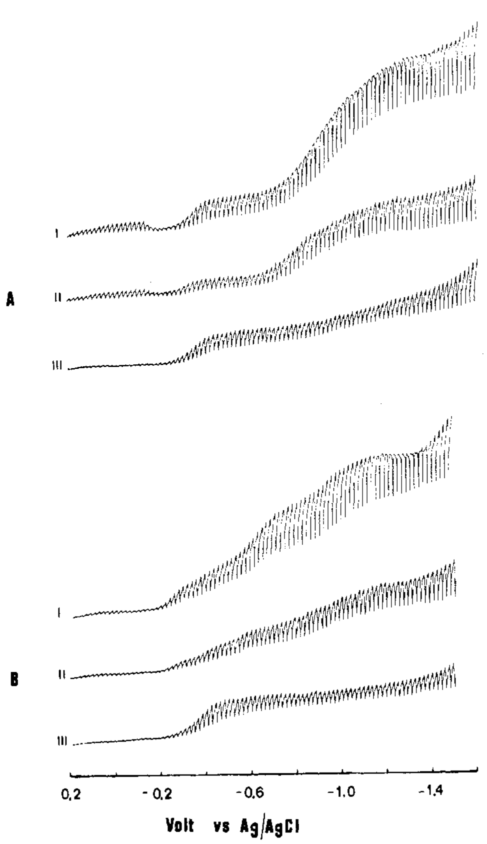

Figure 1. Polarograms (dc) of $Mo(CO)_3(PPh_3)_2Cl_2$ under (A) carbon monoxide and (B) argon at concentrations of (I) 5 × 10^{-3} M, (II) 2.5 × 10^{-3} M, and (III) 1.25 × 10^{-3} M in dichloromethane; drop time 1 s.

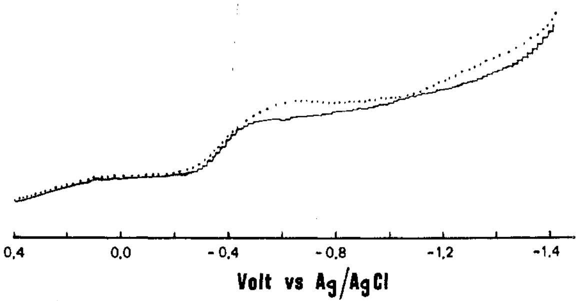

Figure 2. A current-sampled dc polarogram of 1.25 × 10^{-3} M $Mo(CO)_3(PPh_3)_2Cl_2$ in dichloromethane under argon (dotted line) and carbon monoxide (full line). Drop time 1 s.

Figure 1 shows a series of polarograms at various concentrations in CH_2Cl_2 for the chloro dicarbonyl/tricarbonyl system under argon and carbon monoxide. At high concentrations the two complexes give considerably different behavior, and obviously strong adsorption is present as the number of waves and their $E_{1/2}$ values are very concentration dependent. At high concentrations the i–t curves are also consistent with adsorption. As the concentration decreases the behavior of the two species becomes more and more similar until ultimately the electrode process is simplified to one wave with an $E_{1/2}$ value of about −0.38 V for concentrations less than 10^{-3} M (see Figure 2). The limiting current in the presence of CO is slightly less than that in the presence of argon at low concentrations, and the $E_{1/2}$ value is slightly less negative. The bromo system ($E_{1/2}$ = −0.49 V at 10^{-3} M) shows similar behavior in dichloromethane. Electrochemical data for these complexes are contained in Table II. At the low concentrations, when only one wave was found, the limiting current was close to diffusion controlled, and the limiting current magnitude per unit concentration was twice that for the known one-electron reduction of *trans*-$Mo(CO)_2(dpe)_2^+$,[12]

$$trans\text{-}Mo(CO)_2(dpe)_2^+ + e^- \rightleftharpoons trans\text{-}Mo(CO)_2(dpe)_2 \qquad (2)$$

where dpe = bis(diphenylphosphino)ethane (eq 2), and the one-electron oxidation of mercury in the presence of triphenylphosphine[23] (eq 3). An overall two-electron reduction

$$2PPh_3 + Hg \rightleftharpoons Hg(PPh_3)_2^{2+} + 2e^- \qquad (3)$$

step at a dropping mercury electrode would therefore seem to be occurring with complications due to both adsorption and kinetic control.

Figure 3A shows cyclic voltammograms of the bromo complex recorded by synchronizing the sweep to commence 1 s after the mercury drop growth commences. The results

Table II. Electrochemical Data for the $M(CO)_3(YPh_3)_2X_2$ Complexes[a]

	Dichloromethane (0.07 M TEAP)				Acetone (0.1 M TEAP)				
	Mercury		Platinum		Mercury		Platinum		
Complex	Argon	CO	Argon	CO	Argon	CO	Argon	CO	Comments
$Mo(CO)_3(PPh_3)_2Cl_2$	−0.66 −1.16[b] −1.47[b]	−1.10[b]	−1.19	−1.17	−0.59	−0.58	−0.63	−0.67	Polarography and voltammetry show that the number of waves and their position depend markedly on concentration at DME and that strong adsorption occurs. Main waves only are quoted. At Pt, position and shape of wave are strongly dependent on electrode history
$Mo(CO)_3(PPh_3)_2Br_2$	−1.11	−0.93	−1.23	−1.19	−0.95	−0.91	−1.21	−1.24	
$W(CO)_3(PPh_3)_2Cl_2$	−1.59	−1.51	−1.46	−1.44	−1.11	−1.25	−1.46	−1.44	
$W(CO)_3(PPh_3)_2Br_2$	−1.27	−1.23	−1.18	−1.14	−1.08	−1.10	−1.38	−1.36	
$W(CO)_3(PPh_3)_2I_2$	−0.89	−1.00	−1.14	−1.10	−0.85	−0.93	−1.35	−1.32	
$Mo(CO)_3(AsPh_3)_2Cl_2$	−0.47 −0.82 −1.40	−0.49 −0.84 −1.44	−1.30[b]	−1.33	−0.63 −0.90[b]	−0.62 −0.95[b]	−0.67	−0.55	As for PPh_3 complexes although adsorption is not quite as marked
$Mo(CO)_3(AsPh_3)_2Br_2$	−1.06	−1.04	−1.12	−1.12	−1.03[b]	−1.03[b]	−1.12	−1.38	
$W(CO)_3(AsPh_3)_2Cl_2$	−0.90 −1.24 −1.47	−0.90 −1.24 −1.46	−1.34	−1.33	−1.22	−1.27	−1.46	−1.55	
$W(CO)_3(AsPh_3)_2Br_2$	−1.20	−1.20	−1.57	−1.54	−1.10[b]	−1.09	−1.31	−1.35	
$W(CO)_3(AsPh_3)_2I_2$	−0.98	−0.96	−1.16	−1.18	−0.98[b]	−0.96 −1.20	−1.14	−1.22	
$Mo(CO)_3(SbPh_3)_2Cl_2$	−0.73 −1.13 −1.54	−0.68 −1.13 −1.40	−1.18	−1.18	cft[c]	−0.91	cft[c]	−1.12	The molybdenum–triphenylstibine complexes are unstable, particularly in acetone under argon, and they decompose to non-carbonyl-containing species. Decomposition of all chlorides is catalyzed by presence of TEAP. Less adsorption than for PPh_3 and $AsPh_3$ complexes
$Mo(CO)_3(SbPh_3)_2Br_2$	−0.85	−0.84	−0.99	−0.99	cft[c]	−1.05 −1.39	cft[c]	−1.04 −1.44	
$W(CO)_3(SbPh_3)_2Cl_2$	−1.16 −1.30	−1.14 −1.32	−1.24	−1.24	−1.07	−1.27	−1.32[b]	−1.55[b]	
$W(CO)_3(SbPh_3)_2Br_2$	−0.96	−1.08	−1.10	−1.12	−0.98	−1.09	−1.15	−1.33	
$W(CO)_3(SbPh_3)_2I_2$	−0.98	−0.89	−1.35	−1.35	−0.89	−0.92	−1.15	−1.22	

[a] Peak potentials (volts; vs. Ag/AgCl) for voltammetric reduction of complexes at mercury and platinum electrodes; scan rate 1 V/s at mercury, 0.5 V/s at platinum. Temperature 25 ± 1 °C. Dichloromethane 2.5×10^{-3} M: saturated solutions were used in acetone; N.B. tetraethylammonium perchlorate (TEAP). [b] Broad. [c] cft, changes as a function of time.

are again concentration and scan-rate dependent, but in the presence of both CO and argon the bromide ion is seen to be released after the reduction step, and no evidence could be found for the loss of triphenylphosphine. Figure 3B shows a cyclic voltammogram at platinum for the same complex, and one well-defined reduction step is observed. In the presence of CO the peak potentials are slightly less negative than under argon, but there is no evidence that distinctly different electrode processes occur, despite the fact that different complexes are present in the bulk solution under the different conditions. The same was true in the polarograms, so any description of the electrochemistry must incorporate the equilibrium given by eq 1.

Controlled-potential electrolysis of $Mo(CO)_3(PPh_3)_2Cl_2$ at −1.6 V at both mercury pool and platinum electrodes gave an n value of 2.0 under both argon and carbon monoxide for the number of electrons transferred during reduction. It was shown polarographically that, after exhaustive electrolysis, under carbon monoxide and allowing the solution to stand, 2.0 ± 0.1 mol of chloride were released by comparison with a standard solution of $t\text{-}Bu_4NCl$. No free triphenylphosphine could be detected. Both chloride and triphenylphosphine give extremely well-defined polarographic waves in CH_2Cl_2 which can be used for quantitative determination of these species. Solution infrared monitoring of the products showed the result depicted in Figure 4a. The electrolysis products were isolated and refluxed in dichloromethane. The infrared spectrum was simplified to that shown in Figure 4b, and this was identical to an authentic sample of *trans*-$Mo(CO)_4(PPh_3)_2$.[24] In situ monitoring of the infrared spectrum during the course of electrolysis under carbon monoxide showed that another species, having an infrared spectrum (Table III) identical with that for an authentic sample of $[Mo(CO)_5Cl]^-$,[25] was formed as an intermediate (see other complexes for further proof of identity). On the removal of CO, however, the infrared spectrum gradually changed with time and proved that $[Mo(CO)_5Cl]^-$ slowly reacted with the triphenylphosphine present to give the same spectrum shown in Figure 4a. Under carbon monoxide the electrolysis gave a clear yellow solution, consistent with only $[M(CO)_5Cl]^-$ being obtained, whereas under argon a green solution was obtained, obviously containing a mixture of $Mo(CO)_4(PPh_3)_2$ and non-carbonyl-containing species. From this observation it is clear that a disproportionation or dissociation occurs in the absence of CO. Furthermore, half the concentration of $Mo(CO)_4(PPh_3)_2$ is obtained, compared with the experiment under carbon monoxide.

Table III. IR Data (Carbonyl Region) for $[M(CO)_5X]^-$ Species Produced by Controlled-Potential Electrolysis of $M(CO)_3(YPh_3)_2X_2$ Complexes in Dichloromethane and Acetone[a]

	Wavenumber, cm^{-1}	
Complex	Dichloromethane	Acetone
$[Mo(CO)_5Cl]^-$	1920 (s) 1840 (w)	1922 (s)
$[Mo(CO)_5Br]^-$	1922 (s) 1840 (w)	1924 (s)
$[W(CO)_5Cl]^-$	1912 (s) 1842 (w)	1914 (s)
$[W(CO)_5Br]^{-}$[b]	1912 (s) 1844 (w)	1915 (s)
$[W(CO)_5I]^-$	1913 (s) 1848 (w)	1915 (s)

[a] Data obtained can be compared with that contained in ref 25. [b] An additional very weak band at 2053 cm^{-1} is observed in concentrated solutions of $W(CO)_5Br^-$ in dichloromethane.

In accordance with the above, the electrochemistry under carbon monoxide is consistent with equations of the type 4–7.

$$Mo(CO)_3(PPh_3)_2Cl_2 \underset{\text{Fast}}{\overset{\text{Fast}}{\rightleftharpoons}} Mo(CO)_2(PPh_3)_2Cl_2 + CO \tag{4}$$

$$Mo(CO)_2(PPh_3)_2Cl_2 + e^- \rightleftharpoons [Mo(CO)_2(PPh_3)_2Cl_2]^- \tag{5}$$

$$[Mo(CO)_2(PPh_3)_2Cl_2]^- + Mo(CO)_3(PPh_3)_2Cl_2 \xrightarrow{\text{Fast}} Mo(CO)_3(PPh_3)_2Cl + Mo(CO)_2(PPh_3)_2Cl_2 + Cl^- \tag{6}$$

$$Mo(CO)_3(PPh_3)_2Cl + e^- \rightleftharpoons [Mo(CO)_3(PPh_3)_2Cl]^- \tag{7}$$

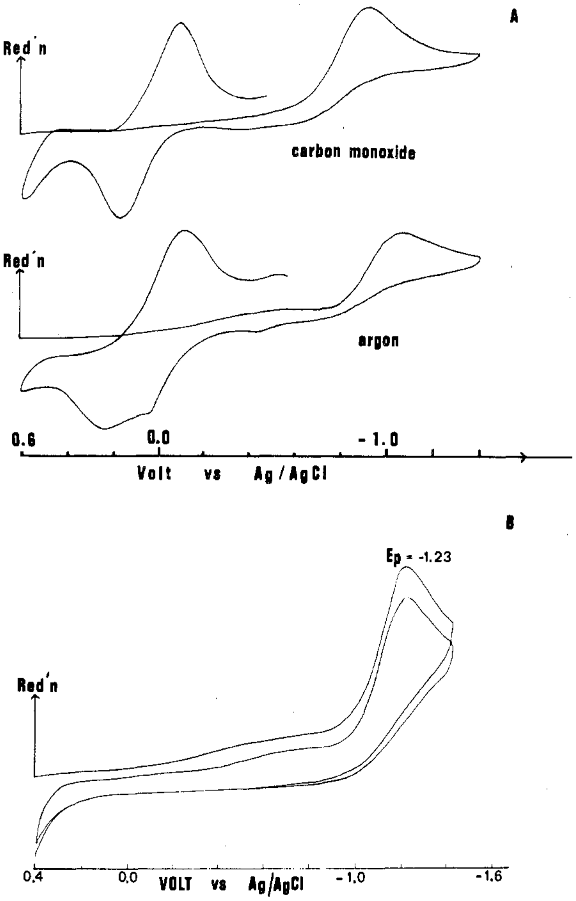

Figure 3. (A) Cyclic voltammograms at DME of $Mo(CO)_3(PPh_3)_2Br_2$ under carbon monoxide and argon in dichloromethane; scan rate 1 V/s. (B) Cyclic voltammogram at platinum of $Mo(CO)_3(PPh_3)_2Br_2$ under carbon monoxide in dichloromethane; scan rate 500 mV/s.

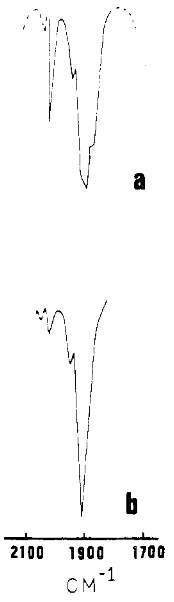

Figure 4. Infrared spectrum (carbonyl region) (a) in dichloromethane of the product of reduction of $Mo(CO)_3(PPh_3)_2Cl_2$ and (b) after refluxing the reduction product in dichloromethane, the infrared spectrum (a) simplifies to that for *trans*-$Mo(CO)_4(PPh_3)_2$.

These are postulated to occur at the electrode surface. In solution, in the presence of CO

$$[Mo(CO)_3(PPh_3)_2Cl]^- + 2CO \xrightarrow{\text{Slow}} [Mo(CO)_5Cl]^- + 2PPh_3 \qquad (8)$$

An almost unlimited number of steps can be postulated to give the overall equation under CO (eq 9). $[Mo(CO)_5Cl]^-$

$$Mo(CO)_3(PPh_3)_2Cl_2 + 2CO + 2e^- \rightarrow [Mo(CO)_5Cl]^- + 2PPh_3 + Cl^- \qquad (9)$$

is known to be unstable,[25] and on removal of CO reaction 10

$$[Mo(CO)_5Cl]^- + 2PPh_3 \xrightarrow{\text{Slow}} Mo(CO)_4(PPh_3)_2 + CO + Cl^- \qquad (10)$$

is observed to occur.

In the presence of argon rather than carbon monoxide, reaction 8 cannot occur, and the species $[Mo(CO)_3(PPh_3)_2Cl]^-$ could dissociate, as does $Mo(CO)_3(PPh_3)_3$[26] to give $Mo(CO)_4(PPh_3)_2$ directly, plus a non-carbonyl-containing species, or alternately via the $[Mo(CO)_5Cl]^-$ pathway, which seems more likely based on results for other complexes considered subsequently. In either case a reduced concentration of $Mo(CO)_4(PPh_3)_2$ is expected compared with undertaking the electrolysis in the presence of CO. Reactions of the kind presented in eq 4–10 have also been proposed to explain the electrochemical reduction of other transition-metal carbonyl complexes.[27] Controlled-potential electrolysis of the bromo system was similar to that of the chloro system except that $[Mo(CO)_5Br]^-$ was the only complex seen (IR evidence); i.e., reaction 10 does not occur. Instead, $[Mo(CO)_5Br]^-$ decomposes without substitution by PPh_3 to give a non-carbonyl-containing product.

Reduction of $W(CO)_3(PPh_3)_2X_2$ (X = Cl, Br, I). The electrochemistry of $W(CO)_3(PPh_3)_2X_2$ in dichloromethane (0.07 M Et_4NClO_4) was similar to that for the analogous molybdenum bromide complexes in the sense that on controlled-potential electrolysis at −1.6 V under carbon monoxide $[W(CO)_5X]^-$ was the sole product of a two-electron reduction at both platinum and mercury electrodes. Under argon half the concentration of $[W(CO)_5X]^-$ was obtained compared with the carbon monoxide reduction, and a green rather than yellow solution resulted, which is consistent with the presence of a non-carbonyl-containing complex in addition to $[W(CO)_5X]^-$. In contrast to $[Mo(CO)_5Cl]^-$, no reaction with the released PPh_3 occurs, and $[W(CO)_5X]^-$ is the final product. $[W(CO)_5X]^-$ is known to be far more stable[25] than $[Mo(CO)_5Cl]^-$ and is not substituted readily by triphenylphosphine.

This result for all tungsten systems strongly suggests that, for the reduction of $Mo(CO)_3(PPh_3)_2X_2$, the $Mo(CO)_4(PPh_3)_2$ species isolated under argon does indeed arise from a slow substitution reaction with $[Mo(CO)_5Cl]^-$, as was inferred from data obtained under carbon monoxide where $[Mo(CO)_5Cl]^-$ was detected as an intermediate.

Polarographic monitoring of the species present under carbon monoxide revealed that triphenylphosphine can be partially replaced in the $W(CO)_3(PPh_3)_2Br_2$ and $W(CO)_3(PPh_3)_2I_2$ complexes, but not for the chloro complex. Under argon the dicarbonyl species was formed in significant concentrations for the bromo complex only. Thus, the solution chemistry exhibits some differences compared with the molybdenum complexes where only a dicarbonyl/tricarbonyl equilibrium need be invoked. Table I contains the relevant infrared data under argon and carbon monoxide, and it can be seen that, for $W(CO)_3(PPh_3)_2X_2$ (X = Br, I), under carbon monoxide, a shift is observed in the position of the CO stretches but the number of stretches remains at three. It was also noted that, on addition of $[W(CO)_4Br_2]_2$ and $[W(CO)_4I_2]_2$ to dichloromethane (0.07 M Et_4NClO_4), evolution of CO occurred, the decomposition being strongly catalayzed by tetraethylammonium perchlorate. The infrared spectrum of the species in solution after loss of CO was very similar to that of $W(CO)_3(PPh_3)_2X_2$ under CO. Apparently a series of complexes, containing between three and four carbonyl ligands per metal atom, exists in solution, but the exact nature could not be ascertained. However, all the complexes appear to be in rapid equilibrium since the overall electrochemical response is the

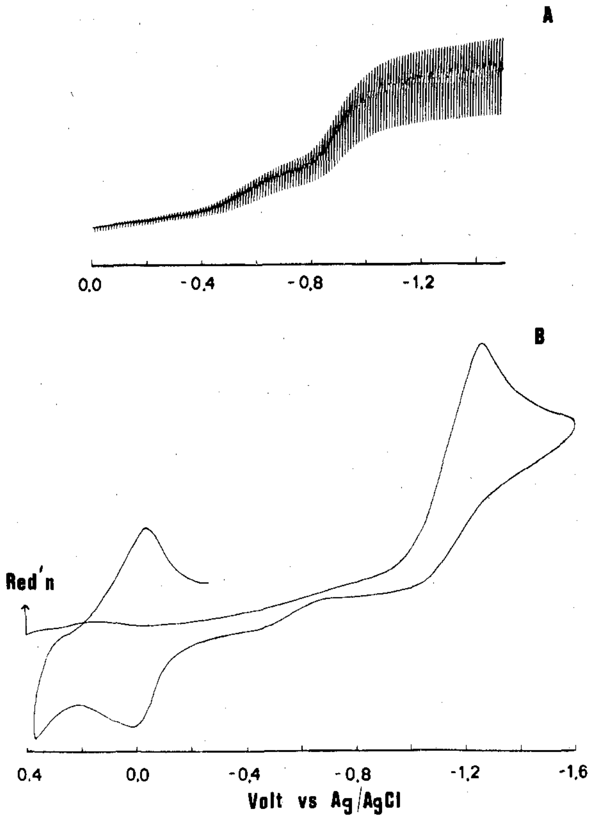

Figure 5. (A) Plarogram for reduction of 4 × 10^{-3} M $W(CO)_3(SbPh_3)_2Br_2$ in acetone; drop time 0.5 s. (B) Cyclic voltammogram at DME of $W(CO)_3(AsPh_3)_2Cl_2$ under carbon monoxide in acetone; scan rate = 1 V/s.

same as for complexes only exhibiting dicarbonyl/tricarbonyl equilibrium. An extended version of eq 4 would therefore need to be included in the overall reaction scheme for the $W(CO)_3(PPh_3)_2X_2$ complexes.

Reduction of $M(CO)_3(YPh_3)_2X_2$ (M = Mo, W; Y = As, Sb; X = Cl and Br for Mo and Cl, Br, and I for W). Tables I–III contain infrared and electrochemical data for this series of complexes. In all cases the product seen after a two-electron reduction is $[M(CO)_5X]^-$. Reduction of $W(CO)_3(SbPh_3)_2Br_2$ at −1.6 V gave $[W(CO)_5Br]^-$, which was isolated as a tetraethylammonium salt and characterized by elemental analysis, infrared, and conductivity. Anal. Calcd for $[W(CO)_5Br]^-$: C, 29.2; H, 4.7; N, 2.7; Br, 15.0. Found: C, 30.7; H, 3.7; N, 2.6; Br, 14.8. The conductivity data was consistent with a 1:1 electrolyte in 60:40 acetone/dichloromethane.[15] Its electrochemical behavior was identical with that for an authentic sample of $[W(CO)_5Br]^-$.[20]

Unlike the situation for $Mo(CO)_3(PPh_3)_2Cl_2$ where $Mo(CO)_4(PPh_3)_2$ is isolated as the end product, $[Mo(CO)_5X]^-$ gradually decomposes rather than reacts with uncoordinated YPh_3. Under carbon monoxide some YPh_3 is displaced in the analogous fashion to that described above for $W(CO)_3(PPh_3)_2I_2$. Addition of X^- to complexes of the type being considered is known to produce $[M(CO)_4X_3]^-$ and related species,[22] so it is clear that the YPh_3 groups are not strongly coordinated.

B. Electrochemistry in Acetone. In view of the results in dichloromethane and the observation that the YPh_3 groups are only weakly coordinated, electrochemical investigations were undertaken in acetone. This solvent was chosen because it is a medium used frequently in the synthesis of these complexes (see Experimental Section). Furthermore, relative to dichloromethane, acetone is a potentially coordinating ligand, and some differences in behavior could be anticipated.

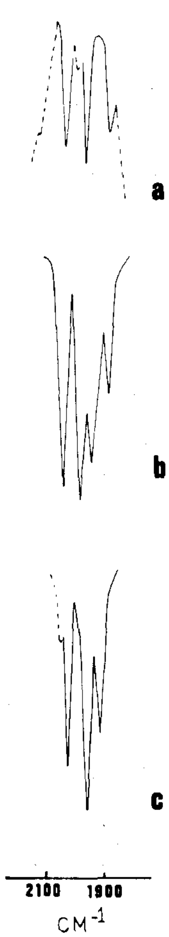

Figure 6. Infrared spectrum (carbonyl region): (a) $Mo(CO)_3(SbPh_3)_2Cl_2$ in acetone; (b) a mixture of tricarbonyl products in dichloroethane obtained on reaction of $[Mo(CO)_4Cl_2]_2$ and $SbPh_3$ in acetone (on addition of $SbPh_3$ the spectrum converts to that shown in c); (c) $Mo(CO)_3(SbPh_3)_2Cl_2$ in dichloromethane.

Electrochemical and infrared data in acetone are summarized in Tables II and IV, and some representative electrochemical curves are shown in Figure 5. Infrared data indicate that the nature of the tricarbonyl species in acetone is different from that in dichloromethane. Figure 6 shows that, in the synthesis of $Mo(CO)_3(SbPh_3)_2Cl_2$ from acetone, an additional infrared band is seen in CH_2Cl_2 for the isolated solid if insufficient $SbPh_3$ is added. This additional infrared band corresponds closely to that found for the complex in acetone, and addition of further $SbPh_3$ converts the infrared spectrum to that seen for pure $Mo(CO)_3(SbPh_3)_2Cl_2$ in CH_2Cl_2. Similar observations can be made by infrared monitoring of other systems.

Polarograms for many of the complexes indicate the partial replacement of YPh_3 after degassing with CO; i.e., growth of the oxidation wave for YPh_3 is observed. The extent of this replacement of YPh_3 is greater in acetone than in dichloromethane. No wave for free halide was observed under argon or carbon monoxide, thereby excluding the presence of complexes such as $[M(CO)_4(YPh_3)_2X]^+X^-$.

Solution infrared spectra of these tricarbonyls under argon and carbon monoxide are compared in Figure 7. Under CO the infrared spectrum is similar to that of its parent dimer after decomposition (involving loss of CO) in solution.

From these results it seems perfectly clear that acetone itself can be used to occupy coordination positions in these seven-coordinate systems and that equilibria of type 11, and others

$$M(CO)_3(YPh_3)_2X_2 + Me_2CO \rightleftarrows M(CO)_3(YPh_3)X_2(Me_2CO) + YPh_3 \quad (11)$$

Table IV. IR Data (Carbonyl Region) for Saturated Solutions of $M(CO)_3(YPh_3)_2X_2$ in Acetone (0.1 M Et_4NClO_4) under Argon and Carbon Monoxide

	Wavenumber, cm^{-1}	
Complex	Argon	Carbon monoxide
$Mo(CO)_3(PPh_3)_2Cl_2$[a]	2028, 1965, 1880	2028, 1965, 1880
$Mo(CO)_3(PPh_3)_2Br_2$[a]	2022, 1962, 1882	2022, 1962, 1882
$W(CO)_3(PPh_3)_2Cl_2$	Too insoluble	Too insoluble
$W(CO)_3(PPh_3)_2Br_2$[a]	2015, 1939, 1868	2015, 1939, 1868
$W(CO)_3(PPh_3)_2I_2$	2007, 1940, 1878	2060, 1994, 1920
$Mo(CO)_3(AsPh_3)_2Cl_2$	2028, 1960, 1868	2028, 1960, 1868
$Mo(CO)_3(AsPh_3)_2Br_2$	2025, 1962, 1880	2076, 2018,[b] 1955, 1923, 1876
$W(CO)_3(AsPh_3)_2Cl_2$	2020, 1942, 1864	2088, 2006, 1912
$W(CO)_3(AsPh_3)_2Br_2$	2020, 1945, 1870	2080, 2008, 1920
$W(CO)_3(AsPh_3)_2I_2$	2012, 1940, 1876	2060, 1993, 1918
$Mo(CO)_3(SbPh_3)_2Cl_2$	2028, 1960, 1868	2028, 1960, 1868
$Mo(CO)_3(SbPh_3)_2Br_2$	2024, 1960, 1872	2076, 2020,[b] 1955, 1923, 1872
$W(CO)_3(SbPh_3)_2Cl_2$	2008, 1938, 1896[c] 2016, 1936, 1854[d]	2086, 2006, 1910
$W(CO)_3(SbPh_3)_2Br_2$	2013, 1938, 1880	2078, 2007, 1917
$W(CO)_3(SbPh_3)_2I_2$	2006, 1940, 1870	2060, 1994, 1920

[a] The dicarbonyls were too insoluble to obtain their infrared spectrum, but electrochemical and synthetic evidence indicate that under argon they are present. [b] Broad. [c] Spectrum obtained initially. [d] Spectrum obtained on standing.

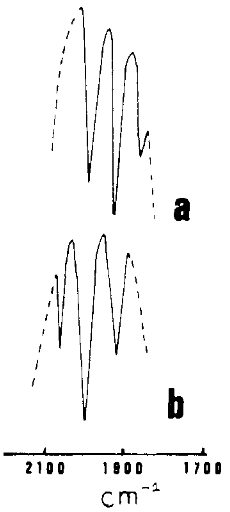

Figure 7. Infrared spectrum (carbonyl region) of $W(CO)_3(SbPh_3)_2Br_2$ in acetone (a) under argon and (b) under carbon monoxide. Broken line = solvent.

involving replacement of YPh_3 by CO or halide, must be important for this system.

Electrochemical reduction in acetone produces the same pattern of behavior and identical products with that found in dichloromethane, despite the difference in solution chemistry. Figure 8 shows a polarogram of the reduced solution of $Mo(CO)_3(PPh_3)_2Br_2$ under argon. After decomposition of $[Mo(CO)_5Br]^-$, 2 mol of bromide and 2 mol of triphenylphosphine are released.

Hence, regardless of the nature of the predominant species in solution, electrochemical reduction again produces $[M(CO)_5X]^-$ as the product, reflecting that the YPh_3 groups are not strongly bound.

C. Oxidation of the Complexes. $M(CO)_3(YPh_3)_2X_2$ complexes give oxidation waves at platinum and mercury electrodes in both acetone and dichloromethane. For $AsPh_3$ and $SbPh_3$ complexes, waves occur at essentially the same potentials as for the free ligand. The phosphorus complexes are oxidized at more positive potentials than free triphenylphosphine. At mercury the electrode itself is oxidized in the presence of free YPh_3 to produce $Hg(YPh_3)_2^{2+}$.[23] At platinum $O{=}PPh_3$ is the product with triphenylphosphine,[27] whereas triphenylarsine and triphenylantimony produce other oxy species.[28,29] The same products are obtained with the complexes as for the free ligand along with other non-carbonyl-containing species. While the oxidation processes are extremely complex, they undoubtedly again reflect the labile nature of the seven-coordinate system and the fact that PPh_3 is more strongly coordinated than $AsPh_3$ or $SbPh_3$. Clearly, reactions of type 12 are consistent with the electrochemical

$$M(CO)_3(YPh_3)_2X_2 + \text{solvent} \rightleftharpoons M(CO)_3(YPh_3)(\text{solvent}) + YPh_3 \quad (12)$$

oxidation pathway.

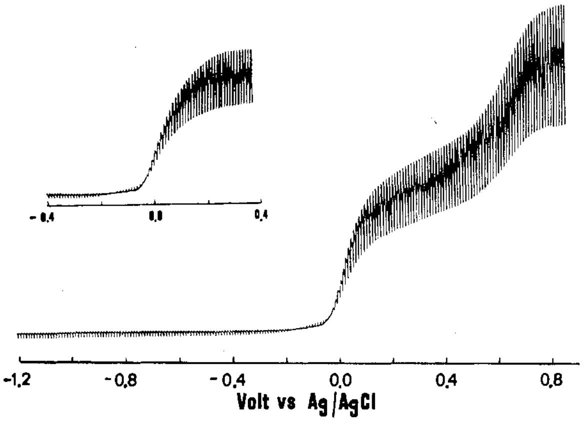

Figure 8. A polarogram of a reduced solution of 2 × 10^{-3} M $Mo(CO)_3(PPh_3)_2Br_2$ under argon in acetone. The inset shows a polarogram of a 4 × 10^{-3} M solution of t-Bu_4NBr in acetone.

Conclusions

From the above electrochemical data it is apparent that the seven-coordinate complexes $M(CO)_3(YPh_3)_2X_2$ represent a kinetically labile system in solution. In addition to loss of CO to give dicarbonyl species, the YPh_3 group may be replaced by CO, X, or solvent, with $SbPh_3$ being more easily replaced than PPh_3. No evidence of oxidation state I intermediates could be seen on reduction of the complexes, and $[M(CO)_5X]^-$ is the only carbonyl-containing species identified as the product of controlled-potential electrolysis, except for the $Mo(CO)_3(PPh_3)_2Cl_2$ system where an additional reaction occurs after formation of $[Mo(CO)_5Cl]^-$ to give $Mo(CO)_4(PPh_3)_2$. In a previous study,[20] electrochemical oxidation occurred as a two-electron oxidation and showed no evidence for an oxidation state I intermediate.

In investigations where stable oxidation state I intermediates have been observed,[15] ESR data are consistent with considerable delocalization of the unpaired electron on the phosphorus ligand. It would thus seem that this may be a prerequisite for the isolation of stable 17-electron molybdenum and tungsten systems.

Registry No. $Mo(CO)_3(PPh_3)_2Cl_2$, 17250-39-4; $Mo(CO)_3(PPh_3)_2Br_2$, 17250-41-8; $W(CO)_3(PPh_3)_2Cl_2$, 18130-04-6; $W(CO)_3(PPh_3)_2Br_2$, 18130-07-9; $W(CO)_3(PPh_3)_2I_2$, 22533-57-9; $Mo(CO)_3(AsPh_3)_2Cl_2$, 17250-40-7; $Mo(CO)_3(AsPh_3)_2Br_2$, 17250-42-9; $W(CO)_3(AsPh_3)_2Cl_2$, 18130-05-7; $W(CO)_3(AsPh_3)_2Br_2$, 18130-08-0; $W(CO)_3(AsPh_3)_2I_2$, 22533-58-0; $Mo(CO)_3(SbPh_3)_2Cl_2$, 17250-44-1; $Mo(CO)_3(SbPh_3)_2Br_2$, 17250-43-0; $W(CO)_3(SbPh_3)_2Cl_2$, 18130-06-8; $W(CO)_3(SbPh_3)_2Br_2$, 18130-09-1; $W(CO)_3(SbPh_3)_2I_2$, 22547-53-1; $Mo(CO)_2(PPh_3)_2Cl_2$, 18973-52-9; $W(CO)_2(PPh_3)_2Br_2$, 18973-51-8; $[Mo(CO)_5Cl]^-$, 15079-15-9; $[Mo(CO)_5Br]^-$, 14911-73-0; $[W(CO)_5Cl]^-$, 14911-74-1; $[W(CO)_5Br]^-$, 15131-04-1; $[W(CO)_5I]^-$, 14911-58-1.

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Contribution from the Department of Chemistry,
The University of Texas at Arlington, Arlington, Texas 76019

Coenzyme B_{12} Model Studies: Thermodynamics and Kinetics of Axial Ligation of Substituted Alkyl(aquo)cobaloximes by Dimethoxyethylamine[1,2]

KENNETH L. BROWN* and ALLAN W. AWTREY

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The kinetics, equilibria, and thermodynamics of the axial ligation of a series of substituted alkyl(aquo)cobaloximes by dimethoxyethylamine (DEA) have been measured in aqueous solution, ionic strength 1.0 M, at 25.0 °C, and in some cases over the temperature range 5–45 °C. Equilibrium constants for proton dissociation of axial water are also reported for several previously unreported alkyl(aquo)cobaloximes. Free-energy correlations of the equilibrium constants for DEA ligation (K_f), the equilibrium constants for OH^- ligation (K_f^{OH}), and the enthalpy (ΔH_f) and entropy (ΔS_f) of DEA ligation with the Taft polar-substituent constant, σ^*, for the cobalt-bound alkyl groups are all distinctly nonlinear. These results are interpreted in terms of a mechanism for axial ligand substitution involving a preequilibrium dissociation of axial water to form a pentacoordinate alkylcobaloxime, followed by addition of the incoming ligand to this pentacoordinate species. Nonlinear least-squares analysis of these nonlinear free-energy correlations allows determination of the slope and intercept parameters for the hexacoordinate–pentacoordinate equilibrium constant (K_{cw}). Based on these considerations, the kinetics of these axial ligation reactions are interpreted in terms of an $\mathrm{S_N1_{lim}}$ mechanism, and the calculated values of K_{cw} allow estimation of the second-order rate constants for addition of the incoming ligand to the pentacoordinate intermediate (k_2). Free-energy correlations for k_2 for DEA and pyridine are linear, show the expected trans influence ($\rho^*_{k_2} = +1.17$ for DEA and $+1.13$ for pyridine), and lead to the conclusion that the transition state for these axial ligation reactions is "early", with bond formation only about 20% complete.

Introduction

In an earlier report,[3] one of us, as well as others, presented data supporting the hypothesis that the neutral alkyl(aquo)cobaloximes[4] exist in aqueous solution as an equilibrium mixture of two thermodynamically distinct forms: hexacoordinate alkyl(aquo)cobaloxime and a stable pentacoordinate species (or solvate, thereof) formed by loss of axially coordinated water:

$$\mathrm{RCo(D_2H_2)(HOH)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RCo(D_2H_2)} \qquad (1)$$

$$K_{cw} = [\mathrm{RCo(D_2H_2)}]/[\mathrm{RCo(D_2H_2)(HOH)}] = k_1/k_{-1} \qquad (2)$$

Support of this hypothesis came from temperature dependence of the electronic spectra of several representative alkyl(aquo)cobaloximes, analysis of the effects of electronic inductive abilities of the organic substituents on the electronic spectra of the alkyl(aquo)cobaloximes, and, most importantly, observation of nonlinear free-energy correlations for the substitution of axial ligands OH^- and pyridine for water in a series of substituted alkyl(aquo)cobaloximes.

The present paper reports our continued study of this system in which a series of extremely precise measurements of equilibrium 3 for displacement of axial water by a primary amine (DEA)[2] have been made in order to provide a set of

$$\mathrm{RCo(D_2H_2)(HOH)} + \mathrm{DEA} \underset{k_{\text{off}}}{\overset{k_{\text{on}}}{\rightleftarrows}} \mathrm{RCo(D_2H_2)(DEA)} \qquad (3)$$

binding data sufficiently numerous and of sufficient precision to allow a statistical test of the necessity of correlating the data with a nonlinear function of an electron-inductive parameter (σ^*)[5] for the cobalt-bound organic group. This set of data has also allowed a quantitative assessment of the importance of steric effects of the organic group on the equilibrium of eq 3. In addition, microcalorimetry, temperature-dependent equilibrium measurements, and kinetic measurements have been carried out in order to provide additional insight to the mechanism of this ligand-substitution process.

Substitution reactions of alkylcobaloximes and related organocobalt complexes have been extensively studied in recent years.[6–15] A few calorimetric measurements on the interaction of methylcobaloxime with several ligands[16] and for ligation reactions of aquocobalamin[17] have also been reported. Only in noncoordinating solvents has it been possible to obtain hard kinetic evidence for a purely dissociative (D or $\mathrm{S_N1_{lim}}$) mechanism.[11b,12b,14,15] Although several authors[10,15] feel that

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