$(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-33-5; $[diarsW(CO)_4SnCl_3]$-$[SnCl_5OH_2]$, 53849-35-7; $[(H^3)As_2Mo(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-37-9; $[(H^3)As_2W(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-39-1; diphos$Mo(CO)_4$, 15444-66-3; $SnCl_4$, 7646-78-8.

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Electrochemical Investigation of the Dichlorobis(1,10-phenanthroline)chromium(III) Complex Ion

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In a recent paper describing the results of an electrochemical investigation of tris(1,10-phenanthroline)chromium(III) ion, we reported briefly on the electrochemical behavior of a bis complex that was prepared *in situ via* the catalytic elimination of a phenanthroline molecule.[1] From that brief study it appeared that the reduced complex was not behaving in a straightforward manner and that oxidation of the reduced complex produced a substance quite different from the starting material. Similar behavior was noted in a complemental study of the tris-[2] and bis(2,2'-bipyridine)chromium(III)[3] systems.

This study was initiated to determine if the behavior of the bis(1,10-phenanthroline) complex would parallel that of its 2,2'-bipyridine analog and to clarify further the somewhat unusual behavior of the chromium(II) complex.[1,3] This study, like those previous, is based on the polarographic and cyclic voltammetric behavior of the bis system at various stages of reduction, where the reductions were performed by controlled-potential electrolysis at a mercury cathode.

Experimental Section

Apparatus. The electrochemical apparatus and electrolysis cell used were the same as described in previous studies.[2]

Solutions. Except where otherwise stated, solutions were about 10^{-3} M in the complex and 10^{-1} M in potassium chloride as the supporting electrolyte. All solutions contained 0.01% Triton X-100 as a maximum suppressor. Stock solutions were stable for at least 1 month as indicated by periodic comparisons of their ultraviolet and visible absorption spectra.

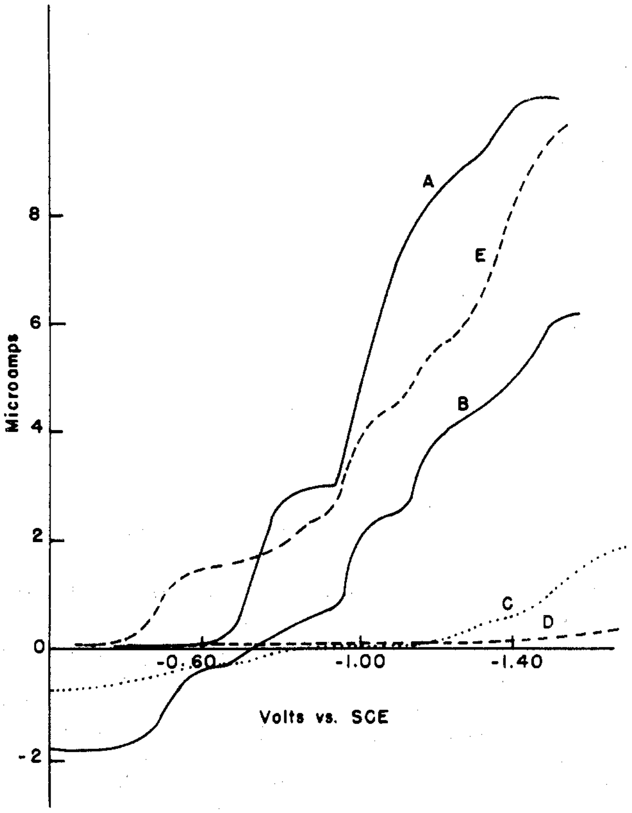

Figure 1. Polarograms of 1.34×10^{-3} M $[Cr(phen)_2Cl_2]^+$ and of products of successive coulometric reductions in 0.1 M KCl at pH 4.3 and 26°: (A) unreduced complex; (B) complex reduced one electron/molecule at -0.78 V ($n = 1$); (C) complex reduced a second electron/molecule at -1.06 V ($n = 2$); (D) complex reduced a third electron/molecule at -1.30 V ($n = 3$); (E) complex reduced a total of three electrons/molecule and rapidly oxidized with oxygen gas.

Dichlorobis(1,10-phenanthroline)chromium(III) Chloride Dihydrate. This cis[4] complex was prepared according to the method of Burstall and Nyholm[5] except that 1,10-phenanthroline was substituted for 2,2'-bipyridine. After recrystallization from hot water, the solid product was suspended in chloroform to remove any unreacted 1,10-phenanthroline.

Anal. Calcd for $[Cr(C_{12}H_8N_2)_2Cl_2]Cl \cdot 2H_2O$: C, 51.95; H, 3.61; N, 10.10; total Cl, 19.18. Found: C, 51.20; H, 3.45, N, 9.79; total Cl, 18.97.

Procedures. The general procedures used have been described previously.[3]

Results and Discussion

Polarograms of the solution initially containing $[Cr(phen)_2Cl_2]^+$ taken at various stages of the coulometric electrolysis are shown in Figure 1. The polarogram of the unreduced complex (Figure 1A) contains two major waves with $E_{1/2}$ values of -0.73 and -1.02 V *vs.* the sce. The second wave, whose diffusion current is about twice that of the first wave, probably consists of two closely spaced waves. Curtis has reported a similar polarogram for this complex.[6]

A cyclic voltammogram of a solution of the unreduced bis complex, taken over a voltage range of -0.20 to -0.85 V and at a scan rate of 0.1 V/sec, contained a single cathodic wave (1) at -0.80 V on the first cathodic sweep. On the reverse anodic sweep, two anodic waves were observed, one at -0.68 V (2) and the other at -0.43 V (3). On the second and all subsequent scans, a second cathodic wave (4) appeared at -0.54 V. The ratio of peak currents between waves 3 and 1 was affected only slightly by temperature but significantly by pH (see Figure 2). This behavior was remarkably similar to that observed for the $[Cr(bipy)_2Cl_2]^+$ complex[3] and is typical

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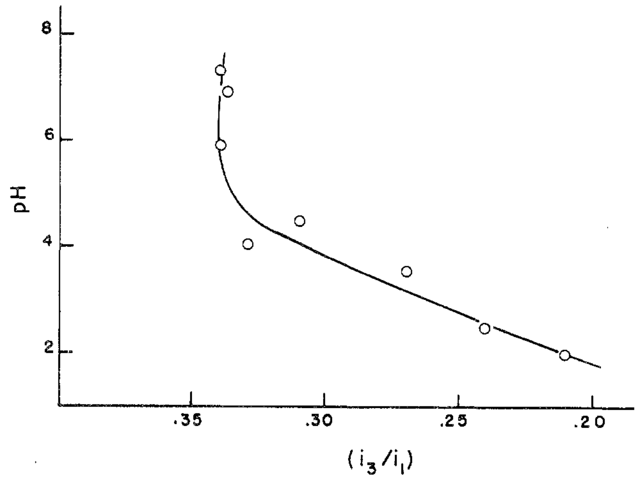

Figure 2. Ratio of anodic current of wave 3 to cathodic current of wave 1 for a solution of $[Cr(phen)_2Cl_2]^+$ as a function of pH. Scan rate was 0.1 V/sec.

behavior for a system in which the initial electron-transfer reaction process (reduction) is followed by a fast chemical reaction producing a new species capable of being oxidized in the potential range under study. In the $[Cr(bipy)_2Cl_2]^+$ study it was concluded[3] that the new species being produced after the reduction was $[Cr(bipy)_3]^{2+}$. Since the positions of cyclic voltammetric waves 3 and 4 are similar to those of waves observed in a cyclic voltammetric study of $[Cr(phen)_3]^{3+}$, which have been shown to be associated with the $[Cr(phen)_3]^{3+}$–$[Cr(phen)_3]^{2+}$ couple,[1] it is reasonable to conclude that the mechanism parallels that found for the $[Cr(bipy)_2Cl_2]^+$ system.[3] The mechanism, then, is as given in eq 1–4. The symbol ↔ represents a polarographically reversible reaction at the potential indicated.

$$[Cr(phen)_2Cl_2]^+ + e^- \longleftrightarrow [Cr(phen)_2Cl_2]^0 \quad E_{1/2} = -0.73\ V \tag{1}$$

$$[Cr(phen)_2Cl_2]^0 + 2H_2O \overset{fast}{\rightleftharpoons} [Cr(phen)(H_2O)_2Cl_2]^0 + phen \tag{2}$$

$$[Cr(phen)_2Cl_2]^0 + phen \overset{fast}{\rightleftharpoons} [Cr(phen)_3]^{2+} + 2Cl^- \tag{3}$$

$$[Cr(phen)_3]^{2+} \longleftrightarrow [Cr(phen)_3]^{3+} + e^- \quad E_{1/2} = -0.49\ V \tag{4}$$

This mechanism satisfactorily accounts for the polarographic and cyclic voltammetric data obtained. As in the $[Cr(bipy)_2Cl_2]^+$ study, a number of experiments were performed to test the validity of the mechanism, namely, measurement of the amount of phenanthroline liberated on reduction, controlled-potential reduction in the presence of excess phenanthroline, and slow and rapid oxidations of chromium(II) solutions. These experiments have been described in a study of the corresponding chromium–bipyridine system and the results for this study were in all cases exactly parallel to those previously reported for that system.[3]

It should be emphasized that slow oxidation of a reduced solution, even in the presence of excess phenanthroline, where the oxidized and unoxidized portions are intimately mixed (*e.g.*, bubbling air through the solution) results in formation of $[Cr(phen)_2(H_2O)_2]^{3+}$ almost exclusively. This is the result of a fast electron-transfer reaction between the oxidized (tris) species and the reduced (bis) species. Reaction 5 occurs even

$$[Cr(phen)_2(H_2O)_2]^{2+} + [Cr(phen)_3]^{3+} \rightarrow [Cr(phen)_2(H_2O)_2]^{3+} + [Cr(phen)_3]^{2+} \tag{5}$$

in the presence of excess 1,10-phenanthroline where only a small equilibrium amount of the bis(diaquo)chromium(II) complex exists. This phenomenon has important connotations in attempting to synthesize the tris complex.[6]

Two further successive one-electron reductions were performed at −1.06 and −1.30 V but no further unusual behavior was noted. Polarograms of the solutions after each reduction are shown in Figure 1. The reduction at −1.06 V produced a black precipitate suspended in a clear liquid. Very little electroactive material was dissolved as evidenced by the small polarographic response (Figure 1C). Addition of the third electron at −1.30 V took nearly six times as long as that of either of the first two electrons, probably because of the insolubility of the two-electron-reduced species. The result of the final reduction was again a black suspension showing very little polarographic activity (Figure 1D). The final reduced solution could be rapidly oxidized to produce the tris complex in the same manner as the one-electron reduced solution.

Registry No. *cis*-$[Cr(phen)_2Cl_2]^+$, 27803-06-1.

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Action of Lewis Acids upon Base–Pentaborane(9) Adducts

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A recent doctoral dissertation, exploring the behavior of HCl, B_2H_6, BF_3, and CH_3OH toward the adducts $B_5H_9{\cdot}2(CH_3)_3N$, $B_5H_9{\cdot}2(CH_3)_3P$, and $B_5H_9{\cdot}(CH_3)_2NC_2H_4N(CH_3)_2$ (the basic ligands of which are hereinafter designated as TMA, TMP, and TMED, respectively) showed a variety of chemical consequences which would correlate with different structures for these adducts.[1]

For example, only the action of HCl upon the adduct $B_5H_9{\cdot}2TMA$ led to appreciable yields of B_6H_{10}, and a more thorough study of this reaction finally led to better than 25% yields of this hexaborane. Thus it could be argued that either a different adduct structure or a Lewis acid very different from HCl would fail to produce an intermediate required for the formation of B_6H_{10}. A more general result was the persistent formation of useful yields of HBF_2 from the BF_3 reactions; also $TMA{\cdot}B_3H_7$ and $TMED{\cdot}B_4H_8$ with BF_3 gave as much as 0.2 HBF_2/mol.

In general, it seems that the formation of a base adduct of a polyborane leads to enhanced boron–base character. Thus either HCl or BF_3 may insert at an electron-dense B–B bond, presumably forming BHB or BBB three-center bonds, with interesting consequences. No doubt diborane can attack in the same manner; indeed, Onak, *et al.*, indicated that its absorption by $B_5H_9{\cdot}2TMA$ is the first step toward the liberation of B_5H_9.[2] Accordingly, it is interesting that their $^{10}B_2H_6$ reaction led to B_5H_9 having a ^{10}B content (43.5%) only 6.3% less than expected (49.8%) for its formation from $^{10}B_2H_6$ and a B_3H_x fragment. The difference may relate to some more direct action of $^{10}BH_3$ to remove TMA.

Exploratory Experiments. A summary of typical results is given by Table I. For such experiments, each of the three