

Figure 3. The 70.6-MHz ^{11}B nmr spectrum of $(\text{Ph}_4\text{As})_2\{(\text{B}_9\text{H}_9\text{S})\text{Pd}[\text{C}_2\text{S}_2(\text{CN})_2]\}$ in acetone solution.

conspicuous feature of this spectrum is the very low-field resonance at -39.4 ppm. A similar low-field resonance (-74.5 ppm) was reported recently for the unique apex boron atom in $\text{B}_9\text{H}_9\text{S}$.¹⁰ By analogy to this and other results on phosphacarboranes,¹¹ the -39.4 -ppm peak in the palladium complex may be due to the unique boron atom which is in an antipodal (transoid) relationship to the sulfur atom in the proposed structure (Figure 4). The ^1H nmr spectrum of $[\text{Ph}_4\text{As}]_2\{(\text{B}_9\text{H}_9\text{S})\text{Pd}[\text{C}_2\text{S}_2(\text{CN})_2]\}$ contains peaks in the aromatic region due to the cation but no high-field signals attributable to B-H-B or Pd-H-B protons.

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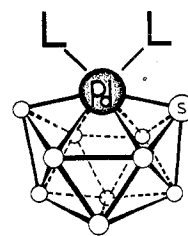


Figure 4. Proposed structure of $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{ligand})_2$ compounds.

In many cases 11-atom closo heteroatom-borane compounds readily undergo rearrangement to isomeric closo derivatives. Heating $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{PPh}_3)_2$ at reflux in mesitylene causes a color change from yellow to orange-brown. The purified product has the correct elemental analysis for $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{PPh}_3)_2$ but a distinctly different melting point, infrared spectrum, and ^{11}B nmr spectrum. This information suggests that a polyhedral rearrangement has occurred. Further structural studies are in progress to confirm this finding.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-33267X.

Registry No. 6- $\text{PhB}_{10}\text{H}_{13}$, 38998-69-5; 6- $\text{PhB}_{10}\text{H}_{11}(\text{PPh}_3)_2$, 52628-73-6; $(\text{Ph}_3\text{PCH}_3)_2[(\text{B}_9\text{H}_{11}\text{S})_2\text{Pd}]$, 52760-66-4; $(\text{Ph}_3\text{PCH}_3)_2[(\text{B}_9\text{H}_{11}\text{S})_2\text{Ni}]$, 52760-67-5; $\text{B}_9\text{H}_{11}\text{S}\cdot\text{C}_6\text{H}_6\text{O}$, 52628-75-8; $\text{B}_9\text{H}_{11}\text{S}\cdot\text{PPh}_3$, 52628-76-9; $(\text{C}_2\text{H}_5)_4\text{N}^+\text{HOB}_9\text{H}_{11}\text{S}^-$, 52760-68-6; $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{PPh}_3)_2$ (yellow isomer), 52628-77-0; $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{PPh}_3)_2$ (orange-brown isomer), 52555-13-2; $(\text{B}_9\text{H}_9\text{S})\text{Pd}(\text{C}_{10}\text{H}_8\text{N}_2)$, 52628-78-1; $(\text{Ph}_4\text{As})_2(\text{B}_9\text{H}_9\text{S})\text{Pd}[\text{C}_2\text{S}_2(\text{CN})_2]$, 52628-80-5; $(\text{B}_9\text{H}_9\text{S})\text{Pt}(\text{PPh}_3)_2$, 52628-81-6; 6- $\text{PhCH}_2\text{B}_{10}\text{H}_{13}$, 52628-82-7; $\text{B}_9\text{H}_{11}\text{S}\cdot\text{DMF}$, 52628-83-8; $\text{C}_5\text{B}_9\text{H}_{14}$, 52555-14-3; $\text{C}_5\text{B}_9\text{H}_{13}\text{S}$, 52555-12-1; $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, 13965-03-2; phenanthroline, 66-71-7.

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Substituent Effects on the Redox Behavior of a Series of Chromium-Phenanthroline Complexes

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The formal redox potentials of the couples $\text{CrL}_3^{3+}-\text{CrL}_3^{2+}$ and $\text{CrL}_3^{2+}-\text{CrL}_3^+$, where L is 1,10-phenanthroline or substituted 1,10-phenanthroline, were evaluated using dc and ac polarography and cyclic voltammetry. The results indicate that the degree of metal-ligand interaction in these complexes increases markedly as the oxidation state of the central metal atom decreases and/or the electron-acceptor ability of the ligand increases. The effect of the ligand substituents is especially great for the Cr(I) oxidation state. A chemical reaction coupled to the $\text{CrL}_3^{3+}-\text{CrL}_3^{2+}$ electron transfer was observed and measured for several of the complexes. The interference of the coupled chemical reaction on the measured redox potentials could be eliminated using ac polarography and cyclic voltammetry.

In recent years there have been a number of reports concerning the complexes of chromium(II) with the chelating imine ligands 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine. Farina and Wilkins² have reported the spectrum of $\text{Cr}(\text{terpy})_2^{2+}$, and Herzog and Aul³ have reported the preparation and magnetic moments of $\text{Cr}(\text{terpy})_2\text{I}_2$. Lutz⁴ has detailed the preparation, magnetic properties, and spectra of several bis(terpyridine)chromium(II) complexes. We have previously reported the dc and ac polarographic behavior of $\text{Cr}(\text{terpy})_2^{2+}$.⁵ A number of studies of the dc and

ac polarography of $\text{Cr}(\text{bipy})_3^{2+}$ have been reported.⁶⁻¹⁰

The preparation and properties of tris(phenanthroline)-chromium(II) complexes have been reported by several authors.¹¹⁻¹⁶ More recently, La Mar and Van Hecke¹⁷⁻²² have

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Table I. Abbreviations for Ligands and Analytical Data for $\text{CrL}_3(\text{ClO}_4)_3$ Complexes

Ligand	Abbrevn	Complex	% found			% calcd		
			C	H	N	C	H	N
2,2',2''-Terpyridine	terpy							
2,2'-Bipyridine	bipy							
1,10-Phenanthroline	phen	$\text{Cr}(\text{phen})_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$	46.3	2.9	8.8	46.6	3.0	9.1
5-Methyl-1,10-phenanthroline	5-Me(phen)	$\text{Cr}(5\text{-Me}(\text{phen}))_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$	48.3	3.1	8.7	48.2	3.5	8.3
5,6-Dimethyl-1,10-phenanthroline	5,6-Me ₂ phen	$\text{Cr}(5,6\text{-Me}_2\text{phen})_3(\text{ClO}_4)_3$	51.6	4.9	8.4	51.7	3.7	8.6
4,7-Dimethyl-1,10-phenanthroline	4,7-Me ₂ phen	$\text{Cr}(4,7\text{-Me}_2\text{phen})_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	51.0	3.8	8.5	50.8	3.8	8.5
3,4,7,8-Tetramethyl-1,10-phenanthroline	Me ₄ phen							
5-Phenyl-1,10-phenanthroline	5-Ph(phen)	$\text{Cr}(5\text{-Ph}(\text{phen}))_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	55.8	3.1	7.0	57.0	3.3	7.4
5-Chloro-1,10-phenanthroline	5-Cl(phen)	$\text{Cr}(5\text{-Cl}(\text{phen}))_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	41.0	1.8	7.9	42.6	2.3	8.3
5-Bromo-1,10-phenanthroline	5-Br(phen)	$\text{Cr}(5\text{-Br}(\text{phen}))_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	36.8	1.7	7.0	36.6	1.8	7.1

reported the nuclear magnetic resonance behavior of $\text{Cr}(\text{phen})_3^{2+}$ and a number of complexes of chromium(II) with methyl-substituted phenanthrolines. Soignet and Hargis²³ have reported the electrochemistry of $\text{Cr}(\text{phen})_3^{3+}$ and $\text{Cr}(\text{phen})_3^{2+}$ and the corresponding bis-phenanthroline complexes under conditions where equilibria involving the tris and bis complexes become a determining factor in the electrochemistry.

This paper deals with a study of a series of chromium(II) and chromium(III) complexes with various substituted phenanthroline ligands. These complexes were chosen because phenanthrolines with a wide range of substituents in positions well removed from the coordination sites are available and because at least three oxidation states—Cr(III), Cr(II), and Cr(I)—are accessible and stable in aqueous solution. The relationship among the formal redox potential, ligand structure, and oxidation state of the central metal atom was investigated.

Experimental Section

Chemicals. All ligands were obtained from the G. Frederick Smith Chemical Co. and were used as received. Table I gives a list of the ligands and the abbreviations used in the text. Tetramethylammonium chloride (TMAC) of polarographic grade was obtained from Southwestern Analytical Chemicals Co. High-purity nitrogen was washed with acidic chromous chloride solution and alcoholic KOH solution before use.

The solutions of the chromium(II) complexes were prepared *in situ* by the addition of chromous chloride to a deaerated solution of the ligand in 0.1 M TMAC in 50% ethanol-water. The chromous chloride solutions which were used to make the complex solutions were prepared and analyzed by methods described previously.⁵ The solutions were prepared with at least a 10-fold excess of ligand over metal and at a pH value which varied between 5 and 6.5 depending upon the ligand. The pH was kept at least one unit higher than the pK_a value of the ligand. The presence of only the tris(ligand)chromium(II) species was confirmed for the phenanthroline and bipyridine complexes by comparison with known spectra.^{2,5,24,25} For these and all other complexes the presence of smaller amounts of the lower complexes (approximately 1–2%) could be detected by the appearance of a second oxidation wave in the dc polarograms at potentials at

least several hundred millivolts cathodic of the wave of the tris-ligand complex. This behavior has been observed previously and confirmed for the bipyridine complexes of Cr(II).^{6,10} At the pH values employed, significant concentrations of the lower complexes did not appear until the ligand-to-metal ratio was very near the stoichiometric value of 3:1.

The tris(ligand)chromium(III) perchlorate complexes were prepared by a procedure previously described.⁵ Analytical data are given in Table I. In addition to the compounds listed in the table, the complex of 3,4,7,8-tetramethylphenanthroline was prepared; however, both the ligand and the complex were extremely insoluble in most of the solvents used and the complex decomposed in those solvents in which the ligand dissolved. As a result this complex gave a poor analysis, apparently due to contamination by unreacted ligand. The complex prepared without washing or recrystallization did give satisfactory polarograms with no reduction waves present which could be ascribed to lower complexes, although elemental analyses were again unsatisfactory.

Solutions of the Cr(III) complexes were prepared by dissolving a weighed amount of the complex in 0.1 M TMAC in 50% ethanol-water. Whenever possible a 10-fold excess of ligand was also present.

Ligand pK_a values were determined by the standard addition method;^{26,27} the ionic strength was maintained constant at 0.1 M with KCl, and the temperature at $25 \pm 1^\circ$.

Apparatus. All electrochemical instrumentation was assembled from Philbrick Research solid-state operational amplifiers and other standard electronic components. A Princeton Applied Research Model 121 lock-in amplifier was used for the phase-selective ac polarographic measurements. In most cases, permanent records were obtained with a Moseley Model 7001A X-Y recorder. Rapid-scan cyclic voltammograms were obtained with a Tektronix Model 564 storage oscilloscope fitted with a Beattie-Coleman Oscillotron camera with a Polaroid back. A Beckman Zeromatic pH meter was used to obtain pH values. Absorption spectra were taken with Beckman Model DB and Cary Model 14 recording spectrophotometers. A conventional thermostated polarographic H cell was used for all measurements and a saturated potassium chloride calomel electrode was used as the reference electrode. Where it was appropriate, the temperature was maintained at $25.0 \pm 0.1^\circ$. Other runs were maintained at $25 \pm 1^\circ$. An IBM APL/360 computer program was used in reducing the ac polarographic data.

Results and Discussion

Dc Polarography. The dc polarographic data on the various complexes are presented in Table II. In general, each complex showed two dc polarographic waves. The chromium(II) complexes showed an oxidation wave (wave I) and, at more cathodic potentials, a reduction wave (wave III). Wave III was obscured by the ligand reduction in many of the complexes. The polarographic behavior is typified by that of $\text{Cr}(\text{phen})_3^{2+}$ in 0.1 M TMAC and 50% ethanol-water at pH 5.8 (see Figure 1). The chromium(III) complexes showed a reduction wave (wave II) at the same potential as wave I. A second reduction wave was observed at the same half-wave potential as wave III above. The diffusion currents of the two waves observed for a given complex were the same, and the ratio of diffusion current to concentration for wave I was the same for all of the complexes studied. The diffusion

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Table II. Dc and Ac Polarographic Data^c for CrL₃²⁺ and CrL₃³⁺ Complexes

Ligand	$E_{1/2}$, V vs. sce		Log plot slope, mV			pH	E_p , V vs. sce			ΔE_p , ^d mV	
	Wave I or II	Wave III	Wave I or II	Wave III	$10^{-3}i_d/C$, $\mu\text{A}/\text{mM}$		Wave I	Wave II	Wave III	Wave I	Wave III
terpy ^a	-0.280(I)	-0.690	60(I)	60	1.63(I) ^b	6.0	-0.280	-0.280	-0.690	100	100
	-0.285(II)		62(II)								
phen	-0.355(I)		60(I)		1.51(I) ^b	5.8	-0.355	-0.360	-0.875	100	100
	-0.360		60(II)								
5-Me(phen)	-0.360(I)		60(I)		1.21(I)	5.8	-0.360	-0.365	-0.875	100	100
	-0.360(II)		65(II)								
5,6-Me ₂ phen	-0.375(I)		60(I)		1.17(I)	6.2	-0.375	-0.380	-0.885	100	100
	-0.370(II)		65(II)								
4,7-Me ₂ phen	-0.485(I)		60(I)		1.22(I)	6.6	-0.495	-0.510	-1.000	100	100
	-0.510(II)		60(II)								
Me ₄ phen	-0.535(I)		60(I)		1.02(I)	6.2	-0.530	-0.540	-1.040	100	100
	-0.545(II)		60(II)								
5-Ph(phen)	-0.290(I)	-0.785	65(I)	63	1.24(I)	6.0	-0.290	-0.290	-0.790	110	100
	-0.290(II)		55(II)								
5-Cl(phen)	-0.250(I)	-0.725	65(I)	70	1.22(I)	5.5	-0.235	-0.240	-0.725	110	100
	-0.230(II)		60(II)								
5-Br(phen)	-0.240(I)	-0.725	65(I)	80	1.14(I)	5.2	-0.235	-0.235	-0.725	110	100
	-0.230(II)		55(II)								

^a Data taken from ref 1. ^b Terpyridine and phenanthroline complexes were measured with a capillary different from the others, so the values are not directly comparable. ^c All data taken at an applied ac frequency of 20 Hz (125 radians/sec). ^d Half-peak width in millivolts.

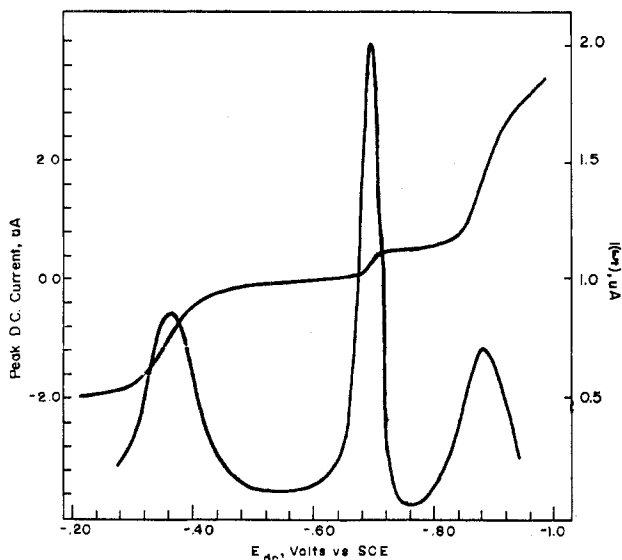


Figure 1. Dc and ac polarograms of Cr(phen)₃²⁺ in 0.1 M TMAC and 50% ethanol-water at pH 5.8.

currents of waves I and II were found to be linear functions of the square root of the column height. Dc log plots for waves I and II gave slopes which were in the range of 60 ± 5 mV expected for a reversible one-electron change.

Table II also gives dc polarographic data for wave III for those complexes where the ligand reduction did not interfere. Wave III was visible on all polarograms, but the slope of the wave was often so steep as to preclude its use (again see Figure 1). The few data presented for wave III are consistent with a reversible, one-electron change between Cr(II) and Cr(I) but are not conclusive. In both the Cr(II) and Cr(III) complexes a small prewave occurs at potentials 100–150 mV anodic of wave III. The prewave was not studied in great detail, but its behavior and appearance, particularly with ac polarography, were consistent with the interpretation given previously for the prewave observed for Cr(terpy)₂²⁺; *i.e.*, the prewave is primarily due to an adsorption process involving the depolarizer itself.⁵

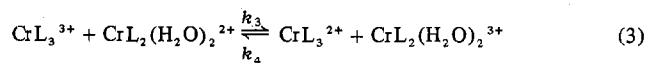
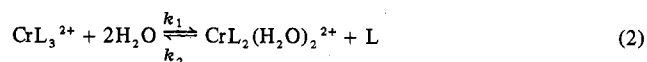
Cyclic Voltammetry. Cyclic voltammograms of the Cr(II) complexes always show the presence of two electrode processes. The more anodic of these is an oxidation and can be

identified by comparing the potential of the anodic and cathodic peaks with the half-wave potential of wave I of the corresponding dc polarograms. The more cathodic process is a reduction and occurs at a potential identical with that of wave III.

The peaks which appear at the potential of wave I are apparently due to the reversible electron transfer between the Cr(III) and Cr(II) complexes. These peaks generally show the splitting indicative of a reversible, one-electron process (60 ± 5 mV at scan rates in the range of 0.1–0.05 V/sec); the value of the potential at 86% of the peak height agrees within ±10 mV of the dc $E_{1/2}$ value for wave I. The ratio of the peak currents, i_c/i_a , which should be 1.0 for all scan rates used, is observed to decrease with decreasing scan rate below about 0.1 V/sec (the lowest scan rate employed was 0.005 V/sec) for the complexes of phen, 5-Me(phen), 5-Cl(phen), and 5-Br(phen) and was less than 1.0 even at a scan rate of 0.1 V/sec for the complexes 5-Br(phen) and 5-Cl(phen). The complexes of 5,6-Me₂phen, 4,7-Me₂phen, and Me₄(phen) did not show this behavior; the ratio i_c/i_a was 1.0 at all scan rates employed.

A possible cause for the observed cyclic voltammetric behavior could be the occurrence of a slow chemical reaction following the electrode process which removes the electrode reaction product, in this case, CrL₃³⁺, before it can be reduced on the reverse sweep.²⁸

A reaction mechanism which would account for this behavior has been proposed for the tris(bipyridine)chromium(III) complex.^{6,29} In general terms this mechanism is



Evidence that a mechanism of this type is operative for the chromium phenanthroline complexes was obtained from polarographic and spectrophotometric measurements. In

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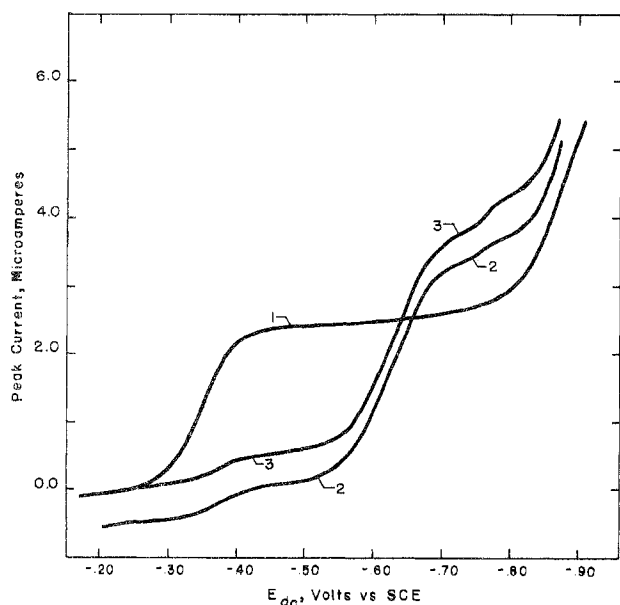


Figure 2. Polarograms of $\text{Cr}(\text{phen})_3^{3+}$ in 0.1 M TMAC and 50% ethanol-water in excess ligand showing the effect on the polarographic behavior.

Figure 2, curve 1 is a polarogram of $\text{Cr}(\text{phen})_3^{3+}$ in 0.1 M TMAC and 50% ethanol-water in the presence of excess ligand. Sufficient chromium chloride was added to make this solution about 0.1 mM in $\text{Cr}(\text{phen})_3^{2+}$. After 5 min a polarogram of this solution (Figure 2, curve 2) showed a wave due to the oxidation of $\text{Cr}(\text{phen})_3^{2+}$ at -0.36 V vs. sce and a new wave at -0.62 V vs. sce. The latter wave had a diffusion current of $2.42 \mu\text{A}$. The solution was next oxidized in air and a polarogram run to confirm that the oxidation of the $\text{Cr}(\text{phen})_3^{2+}$ did not produce any appreciable amount of the dissociation product of $\text{Cr}(\text{phen})_3^{3+}$. The polarogram of the oxidized solution (Figure 2, curve 3) again showed a reduction wave at -0.36 V vs. sce and one at -0.62 V vs. sce with a diffusion current of $2.50 \mu\text{A}$. A spectrum of this last solution showed an absorption band at 510 nm, identical with that reported for $\text{Cr}(\text{phen})_2(\text{OH})_2^+$.³⁰ This spectrum is distinctly different from that of $\text{Cr}(\text{phen})_3^{3+}$, which shows only a poorly defined shoulder in the region 420–430 nm.³¹ Upon acidification to pH 2, the band shifted to 500 nm, most likely due to the formation of $\text{Cr}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}$.

From the reaction mechanism given in eq 1–3, Baker and DevMehta⁶ have shown that, by applying the steady-state approximation for $[\text{CrL}_2(\text{H}_2\text{O})_2^{2+}]$, the concentration of $\text{Cr}(\text{phen})_3^{3+}$ in the presence of $\text{Cr}(\text{phen})_3^{2+}$ should decrease linearly with time and with a slope of $k_1 [\text{CrL}_3^{2+}]$. The predicted behavior was observed; however, some curvature was evident in the region where $[\text{Cr}(\text{phen})_3^{3+}]$ is very low. This is true of both our measurements and those of Baker and DevMehta⁶ which suggests that the approximation used is no longer valid in this part of the curve.

The value of k_1 was calculated from a derived equation which relates the diffusion current to t and $[\text{Cr}(\text{phen})_3^{3+}]$. A plot was also made of $\Delta i_d/\Delta t$ for $\text{Cr}(\text{phen})_3^{3+}$ vs. i_d for $\text{Cr}(\text{phen})_3^{3+}$, and k_1 was calculated from the slope. The first method yielded a value of $0.033 \pm 0.006 \text{ sec}^{-1}$ and the second gave $0.032 \pm 0.001 \text{ sec}^{-1}$ at 25° and pH 5.8.

Nicholson and Shain²⁸ have described a method for evalua-

Table III.^{a,b} Cyclic Voltammetric Data for Complexes Which Showed a Measurable Following Reaction

Complex	Scan rate, V/sec	i_c/i_a	τ , sec	$k_f\tau$	k_f , sec^{-1}
$\text{Cr}(\text{phen})_3^{2+}$	6.6×10^{-3}	0.67	32.0	0.460	0.014
	1.6×10^{-2}	0.77	11.8	0.275	0.023
	3.0×10^{-2}	0.90	6.3	0.115	0.018
	4.9×10^{-2}	0.93	4.5	0.072	0.016
	6.5×10^{-2}	0.94	2.9	0.060	0.021
				Av	0.018
$\text{Cr}(5\text{-Me}(\text{phen}))_3^{2+}$	1.9×10^{-2}	0.84	10.9	0.183	0.017
	3.7×10^{-2}	0.90	5.4	0.100	0.019
	5.7×10^{-2}	0.91	3.5	0.100	0.028
	8.0×10^{-2}	0.94	2.3	0.057	0.025
				Av	0.022
$\text{Cr}(5\text{-Cl}(\text{phen}))_3^{2+}$	1.8×10^{-2}	0.49	6.7	1.03	0.15
	3.0×10^{-2}	0.62	4.4	0.57	0.13
	3.7×10^{-2}	0.64	3.5	0.54	0.15
	5.3×10^{-2}	0.70	2.5	0.41	0.16
	7.1×10^{-2}	0.72	1.8	0.36	0.20
				Av	0.16
$\text{Cr}(5\text{-Br}(\text{phen}))_3^{2+}$	3.4×10^{-2}	0.47	5.6	1.17	0.21
	4.7×10^{-2}	0.56	4.2	0.76	0.18
	6.0×10^{-2}	0.52	3.6	0.90	0.25
	6.5×10^{-2}	0.63	2.4	0.56	0.23
					Av

^a pH values for each complex are the same as those given in Table II. ^b Temperature $25 \pm 1^\circ$.

ting the rate of a first-order or pseudo-first-order chemical reaction following an electron transfer from the ratio of anodic and cathodic peak currents in cyclic voltammetry. To do this, two experimental parameters must be evaluated. One is the ratio of the peak currents (i_c/i_a) for the case where the electrode reaction is an oxidation, and the other is τ , the time elapsed from the point where the potential scan was equal to the dc half-wave potential value to where the potential scan was reversed. Nicholson and Shain tabulated the values of i_c/i_a for several values of $k_f\tau$, where k_f is the rate constant for the following reaction. For the reaction under study in this paper, standard kinetic measurements show that the effective rate of the following reaction for both $\text{Cr}(\text{bipy})_3^{2+}$ ⁶ and $\text{Cr}(\text{phen})_3^{2+}$ (the present work), i.e., k_f as measured by cyclic voltammetry, should be equal to k_1 , the rate of dissociation of the complex CrL_3^{2+} .

Table III shows the cyclic voltammetric results for those complexes which gave evidence for a following reaction along with the calculated values of k_f . The value of k_f for $\text{Cr}(\text{phen})_3^{2+}$ is in excellent agreement with the value obtained by standard kinetic measurements and with the value of 0.015 sec^{-1} recently reported by Hargis and Soignet²³ at 25° . The results also indicate that the value of k_f increases markedly as the electron-acceptor ability (as indicated by the Hammett σ value) of the substituent increases. This effect has been noted previously for a similar series of iron(II) complexes with substituted phenanthrolines by Brandt and Gullstrom.³²

The complexes of 5,6-Me₂phen, 4,7-Me₂phen, and 3,4,7,8-Me₄phen exhibited cyclic voltammetric behavior characteristic of an uncomplicated, reversible electron transfer at the lowest scan rates employed. The addition of CrL_3^{2+} to solutions of CrL_3^{3+} , where L is one of the above three ligands, produces a result similar to that shown in Figure 2, except that the potentials of all the observed waves are of course moved to more cathodic values. Apparently, the rate of the following reaction for these three complexes is so slow that it does not take place to any appreciable extent during the

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course of the cyclic voltammetry measurement even with an applied scan rate as low as 5 mV/sec.

Ac Polarography. In Figure 1 is also displayed a low-frequency phase-selective ac polarogram of $\text{Cr}(\text{phen})_3^{2+}$ which illustrates the typical ac polarographic behavior of the complexes studied. Three waves are observed, the first two corresponding to the observed dc waves and the third to the dc prewave mentioned earlier. Table II shows the ac polarographic data for the various Cr(II) complexes.

From Table II it is apparent that the peak potentials of the ac waves are in good agreement with the corresponding dc half-wave potentials. The half-peak widths are generally slightly larger than the accepted one-electron value of $93 \pm 3 \text{ mV}^{33}$ indicating that the electrode processes may be slightly quasireversible under ac polarographic conditions.

A theoretical treatment of the ac polarographic behavior of systems with first-order or pseudo-first-order reactions coupled to the electrode reaction has been given by Smith.³⁴ The general equations are involved, but in the case which is relevant here, *i.e.*, that of a very slow following reaction, it has been shown that the ac equations are identical with those obtained for a diffusion-controlled, quasireversible charge-transfer process provided no assumption is made regarding the value of the standard heterogeneous rate constant. The equation, of course, will reduce to that for a reversible process if $k_{s,h}$ is sufficiently large, or if ω , the angular frequency of the applied alternating potential, is small.

Experimentally it is found for all of the complexes that a plot of $\cot \phi$ vs. $\omega^{1/2}$ (where ϕ is the phase angle between the applied alternating potential and the faradaic alternating current) at low frequencies is linear. This is taken as satisfactory evidence that the process is indeed quasireversible at low frequencies (implying that the rate of the coupled reaction is so slow that it does not interfere with the ac process even at low frequencies). A nonlinear "humped" region is expected in such plots if the coupled reaction makes a significant contribution to the overall ac process.

The linear increase of $\cot \phi$ with increasing $\omega^{1/2}$ is characteristic of a quasireversible electrode reaction. Plots were also made of the peak faradaic ac current vs. $\omega^{1/2}$. These plots show the peak ac current increasing linearly with frequency at low frequencies but reaching a limiting value at higher frequencies; such behavior is also characteristic of quasireversible electrode processes.

The standard heterogeneous rate constant $k_{s,h}$ may be calculated from the slope of a plot of $\cot \phi$ vs. $\omega^{1/2}$. Assuming values of 0.5 for the values of α and β , the charge-transfer coefficients for the forward and reverse electrode reactions, respectively, and using a value of $1.8\omega^{-6} \text{ cm}^2/\text{sec}$ for the diffusion coefficient (determined from dc polarography using the Ilkovic equation), the values of $k_{s,h}$ calculated for the various complexes were all between 2 and $4 \times 10^{-2} \text{ cm}^2/\text{sec}$, for both wave I and wave III.

The data obtained by ac polarography on wave III are particularly significant, since in many cases the dc waves of the complexes were obscured by the ligand reduction (see Figure 1); however, since ac polarograms of the ligand by itself show only a slight inflection in the background current because the ligand reduction is irreversible, the reduction of the complex is well defined and unobscured. The half-peak width and the $k_{s,h}$ values calculated for wave III indicate that this wave is due to a reversible, one-electron reduction and that the

effect of the concurrent ligand electrode process is insignificant. This reasoning is supported by considering those complexes for which both dc and ac data are available for wave III and by results previously reported on the complexes of Cr(II) and Cr(III) with terpyridine⁵ and bipyridine.^{7,8,35} It seems reasonable to conclude, then, that wave III is the result of a one-electron reversible change between the Cr(II) and Cr(I) complexes of the ligand studied.

Since the dc polarographic data in Table II demonstrate the reversibility of the Cr(III)-Cr(II) couple for the complexes of terpyridine, phenanthroline, 5-methylphenanthroline, 5,6-dimethylphenanthroline, and 5-phenylphenanthroline and the ac polarographic measurements support this conclusion, the measured $E_{1/2}$ values can thus be taken as good measures of the formal potentials for the chromium(III)-chromium(II) ligand couples studied.

For the complexes of 5-bromophenanthroline and 5-chlorophenanthroline, the measured $E_{1/2}$ value for the Cr(II)-Cr(III) oxidation is significantly more negative than the Cr(III)-Cr(II) reduction half-wave potential. This behavior is characteristic of an electrode reaction with a slow reaction following the electron transfer.³⁶ It has already been noted that the cyclic voltammetry of the Cr(II) complexes of these two ligands indicates that the rate of the following chemical reaction is higher for them than for any of the other complexes. The observed dc behavior would seem to bear out this conclusion, since these two are the only complexes for which behavior characteristic of a following chemical reaction is observed in the dc polarography. The coupled reaction is evidently too slow to influence the dc polarographic behavior of the other complexes studied. In addition, it can be seen that for the 5-Br(phen) and 5-Cl(phen) complexes the ac peak potentials for the oxidation and reduction processes agree better than the dc $E_{1/2}$ values and lie between the dc $E_{1/2}$ values. This is the expected result if the coupled reaction is too slow to affect the ac process. It seems reasonable, then, to use the low-frequency ac peak potentials as being the most reliable measures of the correct formal potential values.

The complexes with 4,7-dimethylphenanthroline and 3,4,7,8-tetramethylphenanthroline also show significant differences between the $E_{1/2}$ values for oxidation and reduction in the Cr(III)-Cr(II) couple, but the relative positions of the two waves are now those expected for a slightly irreversible electrode process. No evidence is given by any of the other electrochemical methods which can account for this behavior. In particular, the peak splitting in cyclic voltammetry is the value expected for a reversible, one-electron process, *i.e.*, 60 mV, and the $k_{s,h}$ values calculated from ac polarography do not differ significantly from those calculated for the Cr(III)-Cr(II) in the other complexes. In any case, the separation of the waves is not great, and the formal potential of the Cr(III)-Cr(II) couple for each complex may be taken as the average of the oxidation and reduction potentials without introducing an error of more than $\pm 10 \text{ mV}$.

Table IV summarizes the formal redox potentials of the Cr(III)-Cr(II) and Cr(II)-Cr(I) couples with the various ligands studied, determined according to the criteria given above. The formal potential becomes more positive as ligand acidity increases, but the dependence is not linear. The significance of ligand $\text{p}K_a$ vs. formal potential has been discussed by Tomkinson and Williams³⁷ for a series of substitut-

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Table IV. Formal Redox Potentials for the CrL_3^{n+} - $\text{CrL}_3^{(n-1)+}$ Couples

L	pK value	E^f , V vs. sce		ΔE^f , ^a V vs. sce	
		Cr(III)- Cr(II)	Cr(II)- Cr(I)	Cr(III)- Cr(II)	Cr(II)- Cr(I)
Me ₄ phen	5.71 ± 0.02	-0.535	-1.040	-0.175	-0.165
4,7-Me ₂ phen	5.61 ± 0.01	-0.500	-1.000	-0.140	-0.125
5,6-Me ₂ phen	5.13 ± 0.03	0.375	-0.885	-0.015	-0.010
5-Me(phen)	4.78 ± 0.06	-0.360	-0.875	0	0
phen	4.55 ± 0.04	-0.360	-0.875	0	0
5-Ph(phen)	4.24 ± 0.02	-0.290	-0.790	+0.070	+0.085
terpy		-0.280	-0.690	+0.080	+0.185
5-Cl(phen)	3.73 ± 0.04	-0.235	-0.725	+0.125	+0.150
5-Br(phen)	3.71 ± 0.05	-0.235	-0.725	+0.125	+0.150

$$^a \Delta E^f = E^f_{\text{CrL}_3^{n+}-\text{CrL}_3^{(n-1)+}} - E^f_{\text{Cr(phen)}_3^{n+}-\text{Cr(phen)}_3^{(n-1)+}}$$

ed phenanthroline complexes with the Fe(III)-Fe(II) couple. They also found a nonlinear relationship between E^f and pK_a and ascribed this to the fact that the formal potential, because of its dependence on the formation constants, reflects changes in both π - and σ -electron density, whereas the pK_a reflects principally changes in σ -electron density.

The relationship between the standard reduction potential, E° , of a complex and its electron affinity, ϵ , may be considered^{38,39}

$$nFE^\circ = \epsilon + T\Delta S^\circ + \text{constant} \quad (4)$$

In complexes derived by substitution into the same ligand substrate the value of ΔS° for the different complexes can be considered the same, and

$$nF(E^\circ_1 - E^\circ_2) = \epsilon_1 - \epsilon_2 \quad (5)$$

The electron affinity is primarily a measure of the ability of the oxidized form of the complex to accept an electron and undergo the changes necessary to produce the reduced form, making it a function of the properties of both the oxidized and reduced forms of the complex. For a complex which undergoes a reversible electron transfer with retention of configuration, it is implicit that the added electron is accommodated without any major changes in the complex structure. The reduction potential of the couple is then determined by the energy required to effect the electron transfer and any changes in orbital energies necessary to accommodate the added electron. In the complexes discussed here, the second term will actually lower the energy required to effect reduction, since the reduced species is spin paired.^{4,15,17} If it can be assumed that the pairing energy of Cr(II) is nearly the same in all of these complexes, then the variations in the formal potential values should reflect the energy of the molecular orbital into which the added electron is placed (redox orbital).

Table IV gives the shift in formal potential produced by the various ligands for the Cr(III)-Cr(II) couple compared with the shift in formal potential produced by the same ligands for the Cr(II)-Cr(I) couple. Since there is no Cr(II)-Cr(I) aquo couple, the reference potential is now taken to be the E^f value for each couple with the unsubstituted phenanthroline ligand. The ligands which have substituents which would make them poorer electron acceptors have a

smaller effect on the potential shift of the Cr(II)-Cr(I) couple than on that of the Cr(III)-Cr(II) couple, while ligands with substituents which would make them better electron acceptors than phenanthroline have a greater effect on the potential shift of the Cr(II)-Cr(I) couple than on the Cr(III)-Cr(II) potential shift. The indication is that all of the ligands, even those which are poorer acceptors than phenanthroline, stabilize Cr(I) relative to Cr(II) better than they stabilize Cr(II) relative to Cr(III). It seems that the most likely reason for this would be increasing metal-ligand interaction which becomes more extensive as the electron-acceptor ability of the ligand increases and/or the oxidation state of the central metal atom decreases. This interaction decreases the energy of the redox orbital and increases the electron affinity of the oxidized form of the couple.

Two theories have been advanced to explain the ability of such imine ligands to stabilize Cr(II): extensive electron delocalization by the ligands⁴⁰ and strong trigonal distortion.^{10,41}

La Mar and Van Hecke¹⁷ from proton contact shifts of Cr(II) complexes with methyl-substituted phenanthrolines first gave evidence in support of the presence of a strong trigonal distortion and relatively little electron delocalization. In a later study, however, they showed that their results could also be interpreted as favoring considerable metal-ligand electron delocalization.²¹ The present work cannot offer evidence which would provide a clear choice between these two points of view. It is evident, however, that whatever mechanism is operative in the Cr(II) complexes is present to an even greater extent in the Cr(I) complexes.

The wide range in formal potential found for both the Cr(III)-Cr(II) and Cr(II)-Cr(I) couples in the phenanthroline series indicates that considerable variation exists in the energy of the redox orbital in these complexes and that nmr studies such as those of La Mar and Van Hecke done on a series of complexes with a wider range of ligand structure would be helpful in resolving this problem. With the evidence available at the present time it does not seem likely that the substitution on the rigid phenanthroline ring system could produce changes in symmetry sufficient to cause the large variations observed in the formal potentials.

The comparison between phenanthroline and terpyridine is also interesting since terpyridine has a considerably more flexible structure than phenanthroline. In the Cr(III)-Cr(II) couple the redox potential of the terpy complex falls in the region expected on the basis of the ligand pK , but in the Cr(II)-Cr(I) couple an anomalously large positive shift is observed in the formal potential. This may be a reflection of a greater distortion in the terpyridine complexes of Cr(II) and Cr(I); however, there are insufficient data currently available to test this conclusion.

Registry No. Cr(phen)₃(ClO₄)₃, 51194-76-4; Cr(5-Me(phen))₃(ClO₄)₃, 51194-71-9; Cr(5,6-Me₂phen)₃(ClO₄)₃, 51261-68-8; Cr(4,7-Me₂phen)₃(ClO₄)₃, 51194-73-1; Cr(5-Ph(phen))₃(ClO₄)₃, 51194-61-7; Cr(5-Cl(phen))₃(ClO₄)₃, 51194-63-9; Cr(5-Br(phen))₃(ClO₄)₃, 51194-65-1; Cr(Me₄phen)₃³⁺, 51194-74-2; Cr(phen)₃²⁺, 47836-39-5; Cr(5-Me(phen))₃²⁺, 51194-66-2; Cr(5,6-Me₂phen)₃²⁺, 51261-69-9; Cr(4,7-Me₂phen)₃²⁺, 32698-30-9; Cr(Me₄phen)₃²⁺, 51194-75-3; Cr(5-Ph(phen))₃²⁺, 51194-67-3; Cr(5-Clphen)₃²⁺, 51194-68-4; Cr(5-Brphen)₃²⁺, 51194-69-5.

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