

82544-42-1; [Re(CNCMe₃)₆Cl](PF₆)₂, 82544-44-3; [Re-(CNCMe₃)₆Br](PF₆)₂, 82544-46-5; [Re(CNCMe₃)₆I](PF₆)₂, 82544-48-7; [Re(CNCMe₃)₄(PPh₃)₂]PF₆, 80006-29-7; [Re-(CNC₆H₁₁)₄(PPh₃)₂]PF₆, 80006-27-5; [Re(CNCMe₃)₄(PEtPh₂)₂]PF₆, 80006-33-3; Re₂(O₂CCH₃)₄Cl₂, 14126-96-6; (*n*-Bu₄N)₂Re₂Cl₈,

14023-10-0; Re₂Cl₆(PEtPh₂)₂, 55661-10-4; Re₂Cl₄(P-*n*-Pr₃)₄, 52359-07-6; Re₂Cl₄(PEt₃)₄, 52359-06-5; ReH₇(PPh₃)₂, 12103-40-1; ReH₅(PPh₃)₂, 12104-75-5; ReH₃(PPh₃)₂C₆H₁₁NH₂, 25702-61-8; (*n*-Bu₄N)₂Re₂Br₈, 14049-60-6; Re₂Cl₆(dppe)₂, 53139-98-3; ReH₇(PEtPh₂)₂, 12101-53-0.

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Inductive, Steric, and Environmental Effects in the Nonaqueous Electrochemistry of Hexakis(aryl isocyanide)chromium Complexes

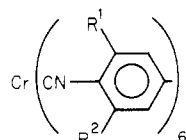
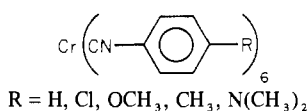
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Received January 22, 1982

The electrochemical behavior of a series of hexakis(aryl isocyanide)chromium(I) complexes has been studied by cyclic voltammetry. The inductive effects of para substituents on $E^{\circ'}$ for the (0 ↔ 1+), (1+ ↔ 2+), and (2+ ↔ 3+) couples have been found to give linear correlations with the Hammett σ_p parameter. Solvent and supporting-electrolyte effects have also been investigated and are discussed in terms of donor/acceptor theory and ion-pairing effects, respectively. The introduction of bulky ortho substituents on the aryl isocyanide ring was found to dramatically influence both the $E^{\circ'}$ _{3+/2+} and the substitutional lability of the Cr(CNR)₆³⁺ complexes. These effects are attributed to significant weakening of the Cr^{III}-C bonds in the ortho-substituted complexes relative to the para-substituted complexes due to steric interactions among the ortho substituents.

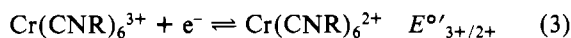
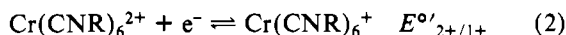
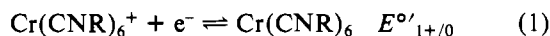
Introduction

The photochemistry and electrochemistry of hexakis(aryl and alkyl isocyanide)metal complexes have been an area of increasing interest in recent years, with contributions arising from several groups.¹⁻¹⁰ Our intended utilization of these compounds Cr(CNR)₆ in photoelectrochemical systems re-



R¹, R² = H, CH₃; CH₃, CH₃; CH(CH₃)₂, CH(CH₃)₂

quired that we carefully characterize their electrochemical behavior. Previous studies^{5,6,8,10} had shown that these compounds undergo a series of three reversible one-electron-transfer reactions at solid electrodes:



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- (2) K. R. Mann, Ph.D. Thesis, California Institute of Technology, 1976.
- (3) K. R. Mann, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **99**, 306 (1977).
- (4) H. B. Gray, K. R. Mann, N. S. Lewis, J. A. Thich, and R. M. Richman, *Adv. Chem. Ser.*, No. **168**, 44 (1978).
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- (11) W. S. Mialki, T. E. Wood, and R. A. Walton, *J. Am. Chem. Soc.*, **102**, 7105 (1980).

However, junction potential effects and solvent/electrolyte effects had not been extensively investigated. Additionally, we wished to assess the effect of ortho ring substituents on the $E^{\circ'}$ values of the complexes, because their photochemical³ and spectroscopic² behaviors differ markedly from those exhibited by para-substituted complexes.

This paper reports the results of electrochemical studies which show that inductive, environmental, and steric effects are all important in influencing not only the formal potentials for the processes described in eq 1-3 but also the substitutional lability of the complexes.

Experimental Section

All electrochemical measurements were performed *in the dark* at 20 ± 2 °C with a PAR Model 170 electrochemistry system. A three-electrode configuration was used, employing a platinum flag or platinum disk working electrode, a platinum spiral auxiliary electrode, and a AgCl/Ag reference electrode. The reference electrode (1.0 M KCl, saturated with AgCl) was connected to the working electrode compartment via a salt bridge terminating in a modified Luggin capillary. The salt bridge contained 0.5 M supporting electrolyte. The electrolysis solution was 0.1 M in supporting electrolyte and generally 0.5 mM in complex. Methylene chloride, acetonitrile (UV grade), and propylene carbonate were used directly as received from Burdick and Jackson without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium hexafluorophosphate (TBAH) (electrometric grade, Southwestern Analytical Chemicals, Inc.) were used as supporting electrolytes without further recrystallization.

Ferrocene was used as an internal reference system to correct for the junction potential.¹²⁻¹⁴ This correction employed an $E^{\circ'}$ value for FeCp₂^{+/0}/FeCp₂ of 0.400 V vs. NHE,¹⁴ which was assumed to be independent of the medium. All potentials reported here are reported vs. corrected AgCl/Ag(aq). Ferrocene appeared at varying potentials, depending on the solvent/supporting electrolyte system used: CH₃CN/TBAH, $E^{\circ'}$ _{FeCp₂^{+/0}/FeCp₂} = 0.41 V; CH₃CN/TBAP, $E^{\circ'}$ = 0.43 V; CH₂Cl₂/TBAH, $E^{\circ'}$ = 0.48 V; CH₂Cl₂/TBAP, $E^{\circ'}$ = 0.49 V; propylene carbonate/TBAP, $E^{\circ'}$ = 0.39 V. No *iR* compensation was used in any of the electrochemical studies.¹²

- (12) R. R. Gagne, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.*, **19**, 2854 (1980).
- (13) Strictly, this method of correcting for the junction potential is correct only if no differences in the solvation energies between FeCp₂⁺ and FeCp₂ are present in each solvent.
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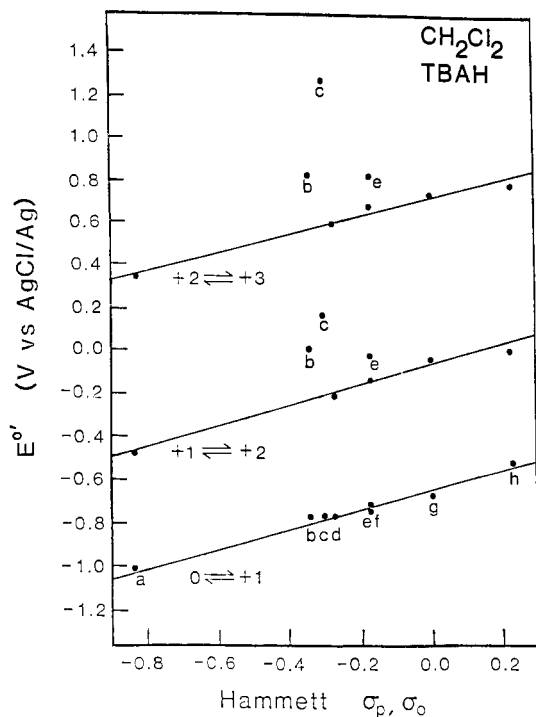


Figure 1. Dependence of $E^{\circ'}$, $E^{\circ'}$, and $E^{\circ'}$ on σ_p and σ_o for $\text{Cr}(\text{CNR})_6$ complexes in CH_2Cl_2 containing 0.1 M TBAH. Linear regression lines were calculated only from data for para-substituted complexes: (a) = 4-N(CH₃)₂; (b) = 2,6-dimethyl; (c) = 2,6-diisopropyl; (d) = 4-OCH₃; (e) = 2-CH₃; (f) = 4-CH₃; (g) = H; (h) = 4-Cl. Regression parameters are as follows. $E^{\circ'}$: slope = 0.44, intercept = -0.65, $R = 0.995$. $E^{\circ'}$: slope = 0.46, intercept = -0.08, $R = 0.991$. $E^{\circ'}$: slope = 0.42, intercept = 0.71, $R = 0.987$.

All solutions were deoxygenated with purified argon presaturated with solvent. The solutions of complex were then prepared after dehydrating the solvent/supporting electrolyte by adding 80–200 mesh activity 1 alumina (Fisher Scientific) with vigorous stirring, directly to the working-electrode compartment.

The hexakis(aryl isocyanide)chromium complexes studied were synthesized by standard methods.^{6,8,15} The complexes were characterized by using IR, NMR, and cyclic voltammetry. These techniques yielded results in good agreement with published data.^{1,3,6,8,15} Chromium(I) complexes (as PF_6^- salts) were generally used due to their solubility in both acetonitrile and methylene chloride and their photochemical inactivity. The exception was for the *p*-(dimethylamino)phenyl isocyanide ligand where the Cr(0) complex was used. It should be noted that reproducible electrochemical results were obtained with this complex *only* if the solid was stored under nitrogen in the dark. This complex undergoes very rapid oxidation with subsequent decomposition when dissolved in organic solvents containing O₂. Passivation of the electrode occurred when the potential was scanned to potentials anodic of $E^{\circ'}$. Cyclic voltammetric experiments on this complex were carried out with extreme care to avoid these complications.

The previously unreported complex $[\text{Cr}(2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NC})_6]\text{PF}_6$ was prepared by a standard method.⁶

$[\text{Cr}(2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3)_6]\text{PF}_6$ was obtained as a bright yellow powder from acetone/hexane in 72% yield. Anal. Calcd: C, 65.91; H, 5.53; N, 8.54. Found: C, 65.67; H, 5.70; N, 8.42. IR: $\nu_{\text{C}\equiv\text{N}}$ 2051 cm^{-1} . Mp: 144 °C dec.

Results and Discussion

Behavior of Para-Substituted Complexes. The $E^{\circ'}$ values (Table I) for the electrode reaction (1) for all of the complexes studied correlate well (see Figures 1–4) with the Hammett σ_p and σ_o parameters for substituted benzoic acids.^{8,16–19}

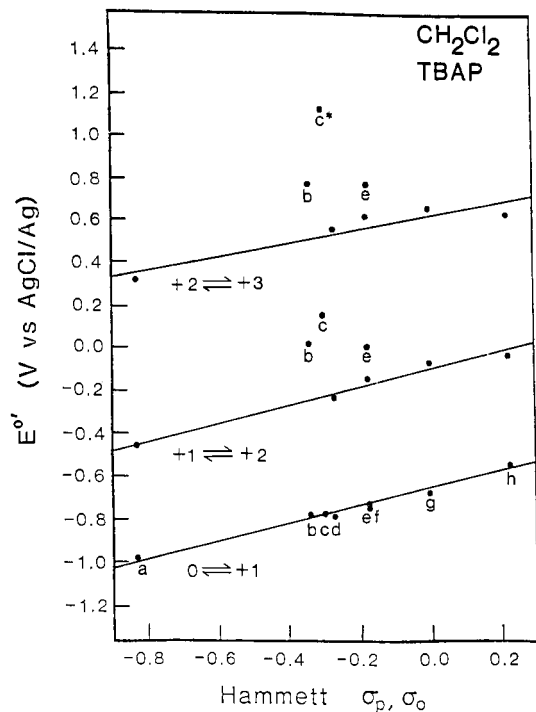


Figure 2. Dependence of $E^{\circ'}$, $E^{\circ'}$, and $E^{\circ'}$ on σ_p and σ_o for $\text{Cr}(\text{CNR})_6$ complexes in CH_2Cl_2 containing 0.1 M TBAP. Linear regression lines were calculated only from data for para-substituted complexes. See Figure 1 for complex identification code. For the point marked with an asterisk the potential reported is the peak potential for oxidation of $\text{Cr}(\text{CNR})_6^{2+}$ (see text). Regression parameters are as follows. $E^{\circ'}$: slope = 0.41, intercept = -0.66, $R = 0.990$. $E^{\circ'}$: slope = 0.41, intercept = -0.11, $R = 0.986$. $E^{\circ'}$: slope = 0.30, intercept = 0.62, $R = 0.917$.

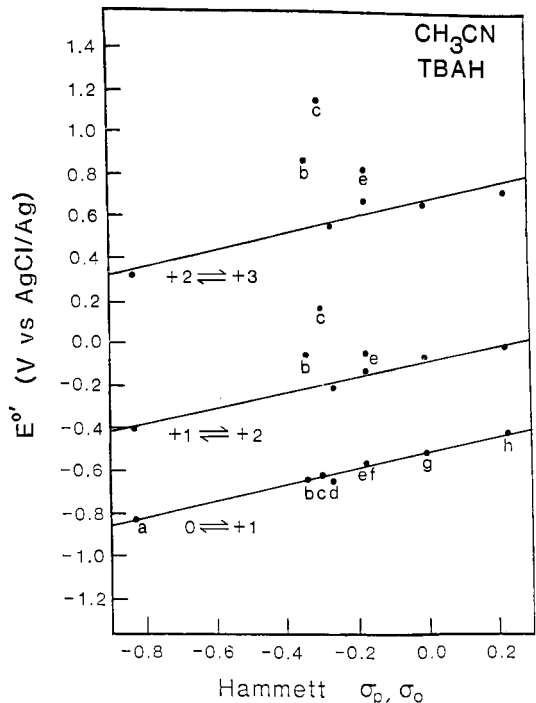


Figure 3. Dependence of $E^{\circ'}$, $E^{\circ'}$, and $E^{\circ'}$ on σ_p and σ_o for $\text{Cr}(\text{CNR})_6$ complexes in CH_3CN containing 0.1 M TBAH. Linear regression lines were calculated only from data for para-substituted complexes. See Figure 1 for complex identification code. Regression parameters are as follows. $E^{\circ'}$: slope = 0.37, intercept = -0.53, $R = 0.994$. $E^{\circ'}$: slope = 0.36, intercept = -0.10, $R = 0.997$. $E^{\circ'}$: slope = 0.37, intercept = 0.64, $R = 0.990$.

Deviations between our results and those of a previous study⁸ can be attributed to differences in junction potentials and the

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Table I. $E^{\circ'}$ Values (V) for $\text{Cr}(\text{CNR})_6$ Complexes in Various Media^a

ligand	couple	CH_2Cl_2		CH_3CN		propylene carbonate TBAH
		TBAH	TBAP	TBAH	TBAP	
4-(dimethylamino)phenyl isocyanide	1+/0	-1.01	-0.98	-0.83	-0.83	
	2+/1+	-0.47	-0.46	-0.40	-0.41	
	3+/2+	+0.35	+0.32	+0.32	+0.29	
4-methoxyphenyl isocyanide	1+/0	-0.78	-0.79	-0.65	-0.66	-0.62
	2+/1+	-0.21	-0.23	-0.21	-0.23	-0.21
	3+/2+	+0.59	+0.56	+0.55	+0.51	+0.59 ^b
2,6-dimethylphenyl isocyanide	1+/0	-0.78	-0.78	-0.64	-0.63	
	2+/1+	+0.01	+0.01	-0.06	-0.07	
	3+/2+	+0.82	+0.77 ^c	+0.86 ^c	+0.82 ^c	
2,6-diisopropylphenyl isocyanide	1+/0	-0.78	-0.78	-0.62	-0.61	
	2+/1+	+0.16	+0.15	+0.17	+0.18	
	3+/2+	+1.27	+1.12 ^d	+1.14 ^c	+1.14 ^c	
4-methylphenyl isocyanide	1+/0	-0.74	-0.75	-0.57	-0.59	
	2+/1+	-0.13	-0.15	-0.13	-0.16	
	3+/2+	+0.67	+0.61	+0.67	+0.59	
2-methylphenyl isocyanide	1+/0	-0.72	-0.73	-0.57	-0.58	-0.55
	2+/1+	-0.02	-0.00	-0.06	-0.07	-0.07
	3+/2+	+0.82	+0.76 ^c	+0.81 ^c	+0.75 ^c	+0.72 ^b
phenyl isocyanide	1+/0	-0.67	-0.67	-0.53	-0.53	-0.50
	2+/1+	-0.05	-0.08	-0.09	-0.09	-0.09
	3+/2+	+0.73	+0.64	+0.65	+0.66	+0.68 ^b
4-chlorophenyl isocyanide	1+/0	-0.53	-0.54	-0.44	-0.43	
	2+/1+	0.00	-0.05	-0.03	-0.03	
	3+/2+	+0.77	+0.62	+0.71	+0.69	

^a As determined from cyclic voltammetry. In general ΔE_p was less than 100 mV at a sweep rate of 50 mV s⁻¹, indicating a high degree of electrochemical reversibility. All values were reported vs. AgCl/Ag (corrected as per text). ^b All 3+/2+ couples studied in propylene carbonate were quasi-reversible with a ΔE_p of ca. 200 mV at a sweep rate of 50 mV s⁻¹. ^c For these cases, the $E^{\circ'}$ values are an estimate, since there was evidence for a significant extent of reaction of the Cr(III) complex at 50 mV s⁻¹. ^d For this case, the Cr(III) complex is completely unstable on the cyclic voltammetric time scale, so that no cathodic wave attributable to the reduction of the Cr(III) complex was observed. The value reported here is the wave due to oxidation of the Cr(II) complex to the Cr(III) form.

difficulties associated with handling the *p*-(dimethylamino)-phenyl isocyanide complex. Considering these possible sources of error, our ρ values for $E^{\circ'_{1+0}}$ vs. the Hammett σ_p parameter are in reasonable agreement with the previously published work, and the differences do not affect the chemical interpretation of ρ for the (0 \leftrightarrow 1+) process.

We have also extended the study of $E^{\circ'}$ vs. Hammett σ_p or σ_o to the (1+ \leftrightarrow 2+) and (2+ \leftrightarrow 3+) couples in eq 2 and 3. The plots of $E^{\circ'_{2+/1+}}$ vs. Hammett σ_p give a good fit to a least-squares line as do the $E^{\circ'_{3+/2+}}$ vs. Hammett σ_p plots, although the correlation coefficients are not as large as they are for eq 1. In contrast, the $E^{\circ'}$ values for the *ortho*-substituted complexes show large systematic deviations from their expected positions on the plots for eq 2 and 3. We defer a discussion of these deviations to a later section of this paper.

The slight decrease in the correlation of $E^{\circ'}$ with the Hammett σ_p parameter in the couples that involve the 2+ and 3+ formal oxidation states may be ascribed to an increase in the importance of media effects, because solvation and ion-pairing effects are expected to increase with increasing charge on the complex. To further investigate these media effects on $E^{\circ'}$, we have examined the consequences of varying the solvent and electrolyte. The results of these studies for the entire series of complexes are presented in Table I and Figures 1-4.

Effect of Solvent. The concept of donor/acceptor theory has previously^{7,20-26} been found useful in describing the effect

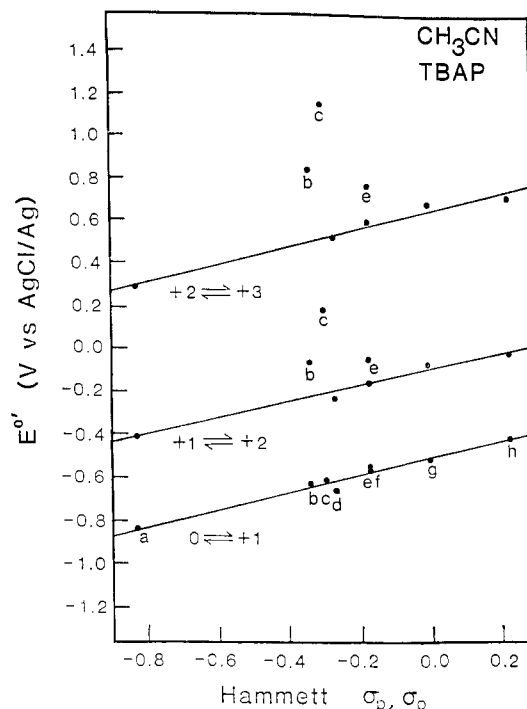


Figure 4. Dependence of $E^{\circ'_{1+0}}$, $E^{\circ'_{2+/1+}}$, and $E^{\circ'_{3+/2+}}$ on σ_p and σ_o for $\text{Cr}(\text{CNR})_6$ complexes in CH_3CN containing 0.1 M TBAP. Linear regression lines were calculated only from data for para-substituted complexes. See Figure 1 for complex identification code. Regression parameters are as follows. $E^{\circ'_{1+0}}$: slope = 0.38, intercept = -0.53, $R = 0.993$. $E^{\circ'_{2+/1+}}$: slope = 0.37, intercept = -0.11, $R = 0.994$. $E^{\circ'_{3+/2+}}$: slope = 0.40, intercept = 0.63, $R = 0.985$.

of the solvent on the redox behavior of metal complexes in solution. Briefly, donor/acceptor theory relates the ability of

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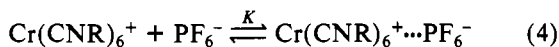
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a solvent to function as a Lewis acid or base toward a given solute. Neither $E^{\circ'}_{1+/0}$ nor $E^{\circ'}_{2+/1+}$ shows consistent trends that can be attributed to a donor/acceptor interaction with the solvent. However, changes in $E^{\circ'}_{3+/2+}$ for a complex with a given para substituent *do* appear to correlate with the donor properties of the solvent. The data suggest that as the donating properties of the substituted aryl isocyanide ligands increase, the additional stabilization afforded the higher oxidation state complex by a donating solvent such as acetonitrile (DN = 14.1) is decreased relative to the poor donor solvent methylene chloride (DN = 0). Conversely, as electron density is withdrawn from the already electron-deficient Cr(III) core (as in the 4-Cl-substituted case), stabilization of the higher oxidation state by acetonitrile becomes appreciable, shifting the $E^{\circ'}$ values cathodically.

Effect of the Electrolyte. We have also observed shifts in the $E^{\circ'}$ values of the studied complexes with changes in supporting anion (ClO_4^- , PF_6^-). Previous work investigating the effects of ion pairing on reversible couples has involved studies of anionic complexes such as $\text{Mn}(\text{acac})_3^-$ ²³ and $\text{Fe}(\text{CN})_6^{3-}$ ^{21,22,24} or of electroactive organic molecules such as 1,2-naphthoquinone.²⁷ These studies have shown that the formation of ion pairs is a strong function of the dielectric constant of the solvent, while donor/acceptor interactions between the ions and the solvent play a much smaller role. In solvents with high dielectric constants, ion pairing is minimized, while in low dielectric solvents, ion pairing becomes more important.^{21,23,25,26} Because the solvents used here differ appreciably in dielectric constant (acetonitrile ($\epsilon = 37.5$) and methylene chloride ($\epsilon = 8.9$)), we expected to see substantial shifts in $E^{\circ'}$ for data obtained in the two solvents due to differences in the extent of ion pairing. These expectations were realized. In fact, we have observed as did previous workers^{8,9} a large (190 mV on the average) anodic shift in $E^{\circ'}_{1+/0}$ for *all* of the studied complexes between methylene chloride and acetonitrile regardless of the nature of the anion (ClO_4^- or PF_6^-). This shift was previously attributed to solvent interactions, junction potential, and substituent effects.^{8,9} Because we have corrected our data for these effects,¹²⁻¹⁴ we believe the 190-mV shift to be primarily due to differences in the extent of ion pairing. The uncharged complexes would obviously not be ion paired in solution, so that any solvent/solute interactions (i.e., solvent stabilization of the uncharged species) would have to be large. Small effects might be expected from solvent/solute interactions, but the 190-mV shift in the case of PF_6^- corresponds to a ratio of the K 's of approximately 1.6×10^3 ($\Delta G = -4.3$ kcal) for reaction 4 in CH_3CN vs. CH_2Cl_2 . This is too large of an effect to be



attributed only to solvation. If donor/acceptor theory is used, the better donating solvent, acetonitrile, should stabilize $\text{Cr}(\text{CNR})_6^+$ to a greater extent than methylene chloride, a poor donor. This would shift $E^{\circ'}_{1+/0}$ to more cathodic potentials in acetonitrile. However, the shift is observed in the opposite direction. For resolution of this question, data for $E^{\circ'}_{1+/0}$ for several of the complexes were also obtained in propylene carbonate ($\epsilon = 69.0$). An additional anodic shift of approximately 45 mV relative to the acetonitrile data was observed in this solvent. Data from the three solvents, taken together, clearly show that ion pairing decreases with an increase in dielectric constant and is quite significant for the 1+ oxidation state. If it is assumed that the complexes in the 1+ oxidation state are completely dissociated in propylene carbonate and the ion pairing of the 1+ oxidation state is described by the

stoichiometry of eq 4, the ~ 235 -mV shift from propylene carbonate to methylene chloride corresponds to a value of K of $9.6 \times 10^3 \text{ M}^{-1}$ ($\Delta G = -5.4$ kcal/mol). This result is consistent with previous measurements of ion-pairing constants for univalent ions in solvents of similar dielectric constant.^{28,29}

Smaller shifts were observed with change in the dielectric constant of the solvent for $E^{\circ'}_{2+/1+}$. The observation of smaller shifts here is consistent with the interpretation that *both* the Cr(I) and the Cr(II) complexes are ion paired to a significant but similar extent.

Although shifts in $E^{\circ'}$ caused by differences in the extent of ion pairing with different anions were not observed in the analogous system $\text{Mn}(\text{CNR})_6^{2+}/\text{Mn}(\text{CNR})_6^+$, our methylene chloride data clearly show that a change in the anion from PF_6^- to ClO_4^- causes a cathodic shift in $E^{\circ'}$ (ion pairing is greater for ClO_4^-). This shift is most apparent in $E^{\circ'}_{3+/2+}$ for the complexes with electron-withdrawing substituents. The well-documented ability of ClO_4^- to function as a much stronger ligand than PF_6^- in the coordination sphere of metal ions³⁰⁻³⁵ is consistent with this observation, which may indicate the presence of a more specific interaction of the ClO_4^- anion with $\text{Cr}(\text{CNR})_6^{3+}$ than that implied by the ion-pairing formalism.

Behavior of Complexes with Ortho Substituents. Thermodynamic Effects. Although the correlations between $E^{\circ'}$ and the Hammett σ parameter are good for the para-substituted complexes we have studied, some dramatic anomalies in the correlation are apparent for complexes that contain ortho substituents. From a thermodynamic viewpoint, the source of these anomalies may be best understood by examining the data obtained for the ortho-substituted complexes in the medium of least interaction ($\text{CH}_2\text{Cl}_2/\text{TBAH}$). The data obtained in the other media show similar effects but are complicated by the occurrence of substitution reactions (*vide infra*).

Anomalous behavior in $E^{\circ'}$ vs. σ_o correlations are *not* found for the interconversion of the Cr(0) and Cr(I) complexes. However, for $E^{\circ'}_{2+/1+}$ and $E^{\circ'}_{3+/2+}$ significant anodic shifts are found in excess of those predicted by only a consideration of the σ_o values for a given substituent. Moreover, the anodic shifts systematically increase as the number and size of the ortho substituents are increased, being most pronounced for the 3+ \leftrightarrow 2+ interconversion of the very bulky 2,6-diisopropylphenyl isocyanide ligand complex (Figure 2). For this case, the deviation is almost 690 mV anodic of that predicted by σ_o , corresponding to $\Delta G = 15.8$ kcal/mol. We feel that these deviations can only be attributed to steric effects, because we have systematically studied and accounted for inductive, solvent, and supporting-electrolyte effects (*vide supra*). The direction and magnitude of the shift suggest either that the divalent complex is greatly stabilized or that the trivalent complex is greatly destabilized by the presence of ortho ring substituents. We view the latter as the more reasonable explanation for this effect since the deviation of the $E^{\circ'}_{2+/1+}$ values are not as significant as those for $E^{\circ'}_{3+/2+}$ and are in the same direction, suggesting that the effect is due to destabilization of the higher oxidation state complex. We ascribe this anodic potential shift to unfavorable interligand steric

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Table II. Effects of Interligand Steric Interactions on Shifts in E° and $E^{\circ'}$

complex	process	$\Delta E^{\circ'}$, V	$\Delta G^{\circ'}$, kcal	$\Delta G^{\circ'}/$ group, kcal
2-methylphenyl isocyanide	2+/1+	0.14	3.2	0.53
	3+/2+	0.18	4.2	0.70
	total	0.32	7.4	1.23
2,6-dimethylphenyl isocyanide	2+/1+	0.25	5.7	0.47
	3+/2+	0.25	5.8	0.49
	total	0.50	11.5	0.96
2,6-diisopropylphenyl isocyanide	2+/1+	0.38	8.8	0.73
	3+/2+	0.69	15.8	1.30
	total	1.07	24.6	2.13

interactions present in those complexes containing ortho substituents. These interactions produce indirect electronic effects that destabilize the higher oxidation state species of the couples.

Consistent with this hypothesis, the 2,6-dimethyl-substituted ligand produces a substantially larger shift than that observed in the 2-methyl-substituted case. This shift is even larger in the complex containing the bulkier 2,6-diisopropyl ligand relative to the 2,6-dimethyl-substituted ligand. Further interpretations of these data at the molecular level must await comparisons of crystallographic data for a series of ortho- and para-substituted complexes in different oxidation states.

Although the magnitude of the shifts in $E^{\circ'}$ are very large (~ 1.0 V for the total destabilization of hexakis(2,6-diisopropylphenyl isocyanide)chromium(III) relative to the Cr(I) complex), the magnitude of the effect at the Cr atom per ortho substituent is relatively small (ca. 1.1 kcal/CH₃ and 2.0 kcal/isopropyl; see Table II).

Kinetic Effects. If significant weakening of the Cr-C bond via steric interactions among ortho substituents does occur, an increase in the relative substitutional lability of the ortho-substituted Cr(II) and Cr(III) complexes would be expected relative to their unhindered analogues. Indeed, there is evidence for enhanced ligand lability in *all* of the ortho-substituted Cr(III) complexes in media containing potential ligands (CH₃CN, ClO₄⁻). In *all* of the media we have studied and from previous studies^{5,6,8,10} three reversible one-electron waves are observed for the para-substituted complexes, suggesting them to be substitutionally inert in *all* oxidation states on the cyclic voltammetric time scale. However, the ortho-substituted complexes show similar behavior *only* in the least interacting medium (CH₂Cl₂/TBAP). In CH₂Cl₂/TBAH the oxidative peak height of the ortho-substituted complexes for the Cr(II) to Cr(III) interconversion corresponds to one electron per ion but the reduction peak height corresponds to less than one electron per ion. New reduction waves also appear cathodic of the corresponding reduction of the Cr-(CNR)₆ⁿ⁺ complex (see Figures 5-8 for the 2,6-diisopropyl-substituted complex). We ascribe this behavior to changes in the coordination sphere of the Cr(III) complexes because reversing the potential scan cathodic of $E^{\circ}_{3+/2+}$ results in the observation of no new peaks on the return scan. These coordination sphere changes may be of three types: addition of a seventh ligand, dissociation of a ligand to give a five-coordinate species, or substitution for one or more ligands by the anion or solvent to give six-coordinate species such as [Cr-(CNR)_{6-n}(ClO₄)_n]^{(m-n)+} or [Cr(CNR)_{6-n}(CH₃CN)_n]^{m+}.

Although seven-coordinate chromium alkyl isocyanide complexes are known,¹¹ it seems unlikely that the complexes studied here could accommodate a seventh ligand. In addition to the reported instability of seven-coordinate *aryl* isocyanide chromium complexes,¹¹ the extreme steric interactions present in the ortho-substituted complexes would seem to preclude their binding a seventh ligand. Furthermore, the unhindered complexes would be expected to add a seventh ligand more

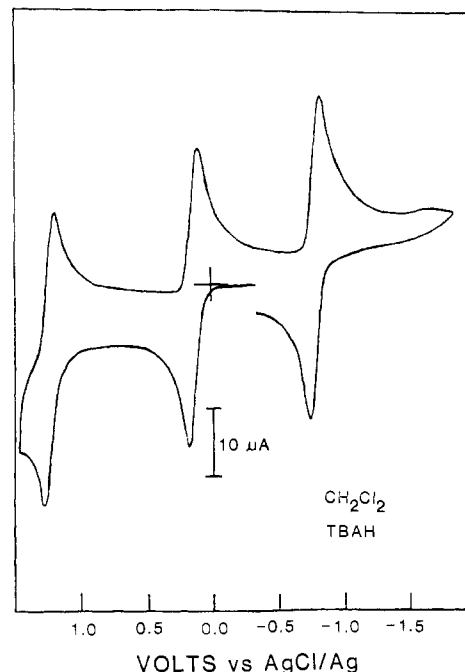


Figure 5. Cyclic voltammogram of 0.31 mM [Cr(2,6-(*i*-Pr)₂C₆H₃NC)₆]PF₆ recorded in 0.1 M TBAH/CH₂Cl₂ at 50 mV s⁻¹ (electrode area 0.26 cm²).

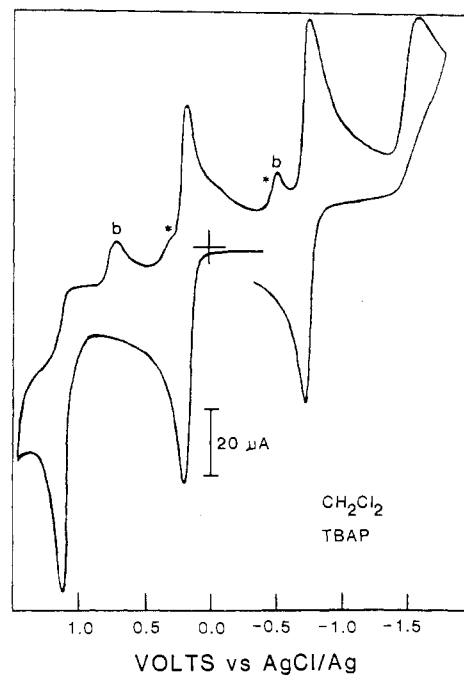


Figure 6. Cyclic voltammogram of 0.89 mM [Cr(2,6-(*i*-Pr)₂C₆H₃NC)₆]PF₆ recorded in 0.1 M TBAP/CH₂Cl₂ at 50 mV s⁻¹ (electrode area 0.26 cm²). Peaks labeled b are assigned to Cr-(CNR)_{6-n}(ClO₄)_n^{(m-n)+} complexes. The peaks labeled with asterisks are assigned to uncoordinated CNR by comparison to the voltammetry of authentic CNR. The cathodic processes occurring at 0.0 and -1.50 V cannot be assigned at this time.

readily compared to the hindered complexes. Even the 4-Cl-substituted isocyanide complex, which from electronic considerations would be expected to show the greatest tendency to bind a seventh ligand, does not.

We also view as unlikely from electronic considerations the generation of stable, five-coordinate complexes of the form Cr(CNR)₅ⁿ⁺ ($n = 0, 1, 2, 3$). Differences in the positions of the waves attributable to ligand substitution processes are observed, with medium (Figures 5-8 support this assertion),

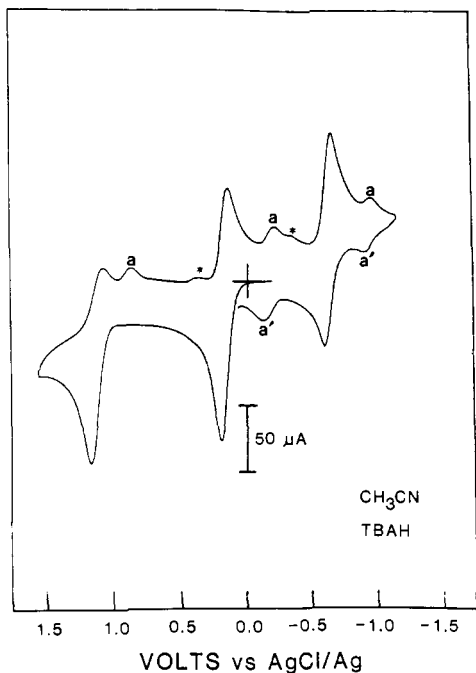


Figure 7. Cyclic voltammogram of 0.23 mM $[\text{Cr}(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{NC})_6]\text{PF}_6$ recorded in 0.1 M TBAH/ CH_3CN at 50 mV s^{-1} (electrode area 1.74 cm^2). Peaks labeled a are assigned to $\text{Cr}(\text{CNR})_{6-n}(\text{CH}_3\text{CN})_n^{m+}$ complexes. The peaks labeled with asterisks are assigned to uncoordinated CNR by comparison to the voltammetry of authentic CNR.

suggesting that solvent molecules and/or supporting anions have entered the Cr(III) coordination sphere.

Consistent with these arguments, we attribute the new waves observed in CH_3CN or ClO_4^- -containing media to substitutional processes yielding species such as $[\text{Cr}(\text{CNR})_{6-n}(\text{ClO}_4)_n]^{(m-n)+}$ and $[\text{Cr}(\text{CNR})_{6-n}(\text{CH}_3\text{CN})_n]^{m+}$. This interpretation is further supported by the observation of waves due to the reduction of the electrochemical oxidation products of free CNR after the Cr(III) complex is produced. (In Figures 5–8, these peaks due to free ligand are marked with an asterisk). Comparisons of the cyclic voltammetric behavior in CH_3CN solutions with ClO_4^- present (Figure 8) with the behavior observed in media where either CH_3CN (Figure 7) or ClO_4^- (Figure 6) is present show that both acetonitrile and ClO_4^- compete favorably with one another as the entering ligand while PF_6^- and methylene chloride do not.

The relative extent of substitution in the series 2-methylphenyl, 2,6-dimethylphenyl, and 2,6-diisopropylphenyl can be roughly estimated by comparison of the ratios of the anodic to cathodic peak currents of the (2+ ↔ 3+) couple. These ratios are 2.0, 1.3, and 7.7, respectively ($\text{CH}_2\text{Cl}_2/\text{TBAP}$), showing that the 2,6-diisopropylphenyl complex is most easily substituted while the 2,6-dimethylphenyl complex is the least easily substituted. We cannot confidently explain this unexpected inversion of the 2-methylphenyl and 2,6-dimethylphenyl compounds at this time.

Conclusions

We have confirmed that a linear correlation exists between the Hammett σ_p parameter and E° values for a series of substituted aryl isocyanide complexes of chromium(0), -(I), -(II), and -(III). Shifts in the observed E° values due to changes in the donor properties of the solvent were found to be relatively small. Ion-pairing differences between the oxidized and reduced forms of a given couple were found to be significant, especially in methylene chloride solutions. An interaction significantly stronger than that described by the ion-pairing formalism was observed between the Cr(III) complexes and perchlorate ion.

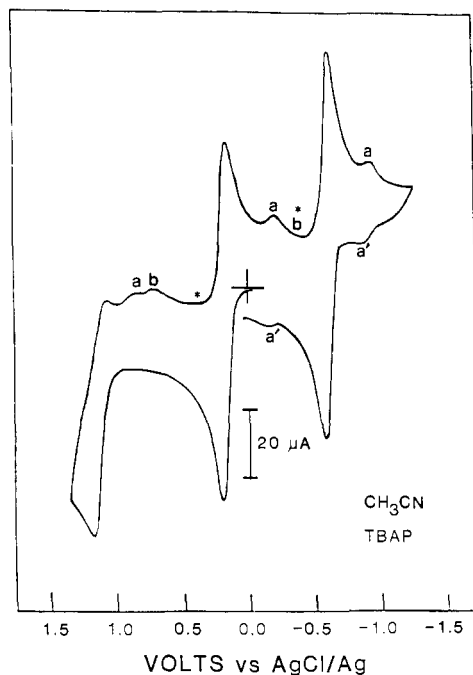


Figure 8. Cyclic voltammogram of 0.82 mM $[\text{Cr}(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{NC})_6]\text{PF}_6$ recorded in 0.1 M TBAP/ CH_3CN at 50 mV s^{-1} (electrode area 0.26 cm^2). Peaks labeled a are assigned to $\text{Cr}(\text{CNR})_{6-n}(\text{CH}_3\text{CN})_n^{m+}$ complexes. Peaks labeled b are assigned to $\text{Cr}(\text{CNR})_{6-n}(\text{ClO}_4)_n^{(m-n)+}$ complexes. The peaks labeled with asterisks are assigned to uncoordinated CNR by comparison to the voltammetry of authentic CNR.

Complexes that have ortho substituents were found to have $E^\circ_{2+/1+}$ and $E^\circ_{3+/2+}$ values that did not correlate well with the Hammett σ_o parameter. The deviations observed for these $E^\circ_{2+/1+}$ and $E^\circ_{3+/2+}$ values are consistent with significant destabilization of the higher oxidation state species of the couple. This destabilization of the higher oxidation state species is thought to arise from unfavorable steric interactions among the ortho-substituted ligands. This destabilization also causes a dramatic increase in the ligand substitution rate in the sterically hindered Cr(III) complexes.

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Registry No. $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-NMe}_2)_6]^0$, 61506-02-3; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-NMe}_2)_6]^+$, 61505-75-7; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-NMe}_2)_6]^{2+}$, 61505-76-8; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-NMe}_2)_6]^{3+}$, 82456-63-1; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-OMe})_6]^0$, 18115-32-7; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-OMe})_6]^+$, 57016-46-3; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-OMe})_6]^{2+}$, 57016-48-5; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-OMe})_6]^{3+}$, 82456-64-2; $[\text{Cr}(\text{CN-2,6-diMeC}_6\text{H}_3)_6]^0$, 82456-65-3; $[\text{Cr}(\text{CN-2,6-diMeC}_6\text{H}_3)_6]^+$, 82456-66-4; $[\text{Cr}(\text{CN-2,6-diMeC}_6\text{H}_3)_6]^{2+}$, 82456-67-5; $[\text{Cr}(\text{CN-2,6-diMeC}_6\text{H}_3)_6]^{3+}$, 82456-68-6; $[\text{Cr}(\text{CN-2,6-di}(\text{Pr-}i)\text{C}_6\text{H}_3)_6]^0$, 61770-86-3; $[\text{Cr}(\text{CN-2,6-di}(\text{Pr-}i)\text{C}_6\text{H}_3)_6]^+$, 82456-69-7; $[\text{Cr}(\text{CN-2,6-di}(\text{Pr-}i)\text{C}_6\text{H}_3)_6]^{2+}$, 82456-70-0; $[\text{Cr}(\text{CN-2,6-di}(\text{Pr-}i)\text{C}_6\text{H}_3)_6]^{3+}$, 82456-71-1; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^0$, 15531-15-4; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^+$, 57016-42-9; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^{2+}$, 57016-44-1; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^{3+}$, 82456-72-2; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^0$, 57016-37-2; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^+$, 57016-38-3; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^{2+}$, 57016-40-7; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}o\text{-Me})_6]^{3+}$, 82469-01-0; $[\text{Cr}(\text{CNC}_6\text{H}_3)_6]^0$, 17375-15-4; $[\text{Cr}(\text{CNC}_6\text{H}_3)_6]^+$, 57016-32-7; $[\text{Cr}(\text{CNC}_6\text{H}_3)_6]^{2+}$, 57016-35-0; $[\text{Cr}(\text{CNC}_6\text{H}_3)_6]^{3+}$, 70801-01-3; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-Cl})_6]^0$, 36732-52-2; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-Cl})_6]^+$, 57016-50-9; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-Cl})_6]^{2+}$, 57016-52-1; $[\text{Cr}(\text{CNC}_6\text{H}_4\text{-}p\text{-Cl})_6]^{3+}$, 82456-73-3; methylene chloride, 75-09-2; acetonitrile, 75-05-8; propylene carbonate, 108-32-7; tetrabutylammonium perchlorate, 1923-70-2; tetrabutylammonium hexafluorophosphate, 3109-63-5.