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Electrochemistry of a Series of Hexakis(aryl isocyanide)chromium(0) Complexes

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Using cyclic voltammetry, $E_{1/2}$ values for the sequential one-electron oxidations

$$Cr(CNR)_6^- \xrightarrow{-e^-} Cr(CNR)_6 \xrightarrow{-e^-} Cr(CNR)_6^+ \xrightarrow{-e^-} Cr(CNR)_6^{2+}$$

have been measured for 11 complexes of substituted aryl isocyanides. These data are shown to give an unusually good correlation with the Hammett σ parameters assigned to substituent groups on the aryl ring. The implications of this correlation are discussed.

Introduction

Hexakis(aryl isocyanide)chromium(0) complexes have been known for over 20 years, their preparation and characterization first being described by Malatesta and co-workers.[1] These compounds are normally prepared from an alcoholic suspension of chromium(II) acetate together with the appropriate aryl isocyanide, disproportionation of the metal to the zero- and trivalent states occurring. No chromium(0) complexes of alkyl isocyanides have been prepared. The $Cr(CNR)_6$ complexes are now known to have a substantial redox chemistry. Oxidation to isolable chromium(I) and chromium(II) complexes $[Cr(CNR)_6]^{n+}$ ($n = 1, 2$) is accomplished using $AgPF_6$ as an oxidizing agent; air oxidation of solutions of the zerovalent complexes to $[Cr(CNR)_6]^+$ also occurs.[2] There is electrochemical evidence for a reversible one-electron reduction.[2]

Electrochemical studies have assumed an important role in the initial study of the redox behavior of these systems. Two preliminary reports on the cyclic voltammetry of $Cr(CNR)_6$ complexes preceded the synthetic studies cited above.[3,4] Both suggest that simple electron-transfer reactions should be easily accomplished with mild oxidizing agents, and both predict the stable existence of the resulting oxidized species.

One observation made in earlier work on the $Cr(CNR)_6$ complexes was that substituent groups on the aryl ring of the isocyanide have some influence on the $E_{1/2}$ value. The $E_{1/2}$ values (for the process $Cr(CNR)_6 \rightarrow [Cr(CNR)_6]^+ + e^-$), representative of the ease of one-electron oxidation of the complex, vary from 0.15 to 0.33 V vs. SCE; similar trends are observed for other oxidation–reduction processes in the $[Cr(CNR)_6]^{n+}$ systems. Data on the $[Mn(CNR)_6]^+ \rightarrow [Mn(CNR)_6]^{2+} + e^-$ oxidations show the same trends; here the existence of complexes of alkyl isocyanides allows their inclusion and comparison.[3,5] The ease of oxidation of both the chromium and manganese complexes is related to the donor ability of the ligand groups, their ability to cause a buildup of negative charge on the metal. Manganese complexes of alkyl isocyanides have lower $E_{1/2}$ values than comparable complexes of aryl isocyanides. This is in accord with the alkyl isocyanides being better donors, a fact determined in earlier infrared studies.[6] Differentiation in $E_{1/2}$ values among complexes of substituted aryl isocyanides follows the same trend, the ease of oxidation being related to aryl ring substituent group donor–acceptor parameters.

In previous work on $[Mn(CO)_{6-x}(CNCH_3)_x]^+$ complexes, this relationship between ligand donor–acceptor properties and ease of oxidation has been most clearly studied. Initially it was shown[3,5] that each substitution of CO, a better electron-withdrawing ligand, for $CNCH_3$ raises the value of $E_{1/2}$ in the complex by about 0.4 V. This result was rationalized by assuming that electron withdrawal to the carbonyl ligands stabilizes the metal 3d (primarily nonbonding) electrons, making their removal less energetically favorable. Subsequently a MO study on these complexes supported this idea; it was shown that $E_{1/2}$ was directly proportional to the HOMO energy in the complex.[7] More recently this correlation was extended to isomeric species, *mer*- and *fac*-$[Mn(CO)_3(CNCH_3)_3]^+$ and *cis*- and *trans*-$[Mn(CO)_2(CNCH_3)_4]^+$.[8]

It may be noted here that the measured $E_{1/2}$ values appear to be a remarkably sensitive probe to electronic properties of the ligands. At least for the $[M(CNR)_6]^{n+}$ species described above, other typical parameters such as the isocyanide stretching frequency, $\nu(CN)$, or the difference between stretching frequencies of the free and complexed ligand, $\Delta\nu(CN)$, are insensitive to ligand differences. This point will bear further comment later.

One general goal of our work has been the evaluation of ligand properties. Thus it seemed appropriate to extend the studies initiated earlier on substituted aryl isocyanides to include a larger number of examples and to seek particularly compounds with substituent groups which would extend the range of ligand donor–acceptor characteristics. This would presumably lead to complexes which undergo oxidations over a substantially larger range of $E_{1/2}$ values. The larger number of examples and the wider range of $E_{1/2}$ values would allow a determination of whether meaningful correlations of $E_{1/2}$ values with substituent parameters can be made. Additionally, the possibility existed for more quantitative correlations with theory, as had been seen in the $[Mn(CO)_{6-x}(CNCH_3)_x]^+$ series.[7,8]

The data in this study appear likely to be applicable in our further work. We are involved in a more general study of reaction chemistry of electron-rich metal compounds, compounds of good donor ligands, which seem to behave as if they have unusually high electron density at the metal.[9] The information derived from this study should be helpful in defining important ligand parameters for this work.

Thus we were led to synthesize and carry out electrochemical studies on an extended series of $Cr(CNR)_6$ compounds. Results of this study are reported here.

Experimental Section

All reactions were carried out under nitrogen. Melting points were determined on evacuated sealed samples of the compound using a Thomas-Hoover capillary melting point apparatus and are uncorrected. High-resolution infrared spectra (± 1 cm^{-1}) in the range of 2200–1850 cm^{-1} in dichloromethane solutions were recorded using a Digilab FTS-20 spectrometer; other infrared spectral measurements were made on a Perkin-Elmer Model 457 or Beckman IR-10 spectrometer, also employing dichloromethane solutions. ^1H NMR spectra were recorded on a Varian A-60A spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Electrochemical measurements were made using a three-electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counterelectrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research electrochemistry system, Model

Table I. Infrared and ^{1}H NMR Data for Hexakis(aryl isocyanide)chromium(0) Complexes

Compd	ν(CN),[a] cm^{-1}	τ (rel intens)[c]
$Cr(p\text{-}(CH_3)_2NC_6H_4NC)_6$	2030 m, 1935 s, br	2.73 m (4); 7.2 br, s (6)
$Cr(p\text{-}CH_3OC_6H_4NC)_6$[b]	1994 vs, br, 1927 s	*d*
$Cr(p\text{-}CH_3C_6H_4NC)_6$[b]	2049 w, 1970 vs, br	*d*
$Cr(m\text{-}CH_3C_6H_4NC)_6$	2050 sh, 1955 s, br	2.97 m (4); 7.78 s (3)
$Cr(C_6H_5NC)_6$[b]	2040 sh, 1975 vs, br	*d*
$Cr(p\text{-}FC_6H_4NC)_6$	2050 sh, 1975 vs, br	2.96 m
$Cr(m\text{-}CH_3OC_6H_4NC)_6$	2050 sh, 1965 vs, br	2.68 m (1); 3.48 m (3); 6.29 s (3)
$Cr(p\text{-}ClC_6H_4NC)_6$[b]	2020 m, 1970 vs, br, 1918 sh	*d*
$Cr(p\text{-}BrC_6H_4NC)_6)$	2010 m, 1970 vs, br, 1900 sh	2.78 m
$Cr(m\text{-}ClC_6H_4NC)_6$	2080 w, 1975 vs, br	2.56 m (1); 3.36 m (3)
$Cr(m\text{-}CF_3C_6H_4NC)_6$	2065 w, 1965 vs, br, 1935 sh	2.46 q, J = 8 Hz (1); 2.80 m (3)
$Cr(o\text{-}CH_3C_6H_4NC)_6$[b]	1993 vs, br, 1907 s, br	2.72 m (2); 3.32 m (2); 7.26 s (3)

[a] CH_2Cl_2 solutions. [b] High-resolution data. [c] $CDCl_3$; 1% TMS internal standard. [d] Reported earlier.[2]

170, incorporating compensation for internal resistive potential drop. Acetonitrile or dichloromethane was used as the solvent with the solution 5×10^{-3} M in substrate. Tetrabutylammonium perchlorate (0.1 M) was employed as the base electrolyte. Sweep rates were usually varied from 50 to 200 mV/s in order to achieve the optimum peak shapes. The ratios between the anodic and cathodic peak currents, $i_{p,a}/i_{p,c}$, in all cases were unity. However, since the peak separation $|E_{p,a} - E_{p,c}|$ generally exceeded 59 mV, the electrochemical nature of the complexes indicated a quasi-reversible system, i.e., moderately slow electron transfer compared to the rate potential change.[10] All measurements were made at 25 °C.

Benzene was dried by distillation from lithium aluminum hydride. Dichloromethane and acetonitrile used in the electrochemical measurements were dried by at least one distillation from phosphorus pentoxide.

Preparation of the Aryl Isocyanides. The *N*-aryl formamides, precursors in the isocyanide syntheses, were prepared in good yield (80–95%) according to the literature method[9] from the substituted aniline and formic acid.

The method of Appel and co-workers[12] was used to prepare a majority of the aryl isocyanides. Due to the offensive and very penetrating odors of these compounds, preparations were carried out in a good hood. Equimolar amounts of the appropriate *N*-arylformamide, carbon tetrachloride, and triethylamine, along with triphenylphosphine (20% excess), were dissolved in dichloromethane (0.1 mol of reactants in approximately 100 mL of solvent) and heated to 60 °C for at least 2.5 h. The solvent was distilled off at slightly reduced pressure and the residue was extracted 3–5 times with hot hexane. The extracts were combined and the solvent was removed on a rotary evaporator. The isocyanide was removed from this residue then by either fractional distillation at reduced pressure, vacuum sublimation, or crystallization.

The phosgene method of Ugi et al.[13,14] was employed for the preparation of $p\text{-}ClC_6H_4NC$ in 68% but in attempts to synthesize other isocyanides, this method was found to be generally less reliable. The modified Hoffmann carbylamine synthesis of Ugi and co-workers[15] employing the phase-transfer catalysis method of generating dihalocarbene was utilized for the preparation of $p\text{-}O_2NC_6H_4NC$.

Following the suggestion of Grundmann,[16] a trace of unreacted aniline was added to the isolated liquid isocyanides in order to retard their polymerization. All of the isocyanides were stored at −21 °C.

Detailed listings of the preparation and characterization of many isocyanides are available.[14,17]

Preparation of Known Compounds of Chromium. Chromium(II) acetate[16] was prepared by the published method. $Cr(CNR)_6$ complexes (R = phenyl, *p*-tolyl, *p*-anisyl, *p*-chlorophenyl, *m*-chlorophenyl, and *p*-bromophenyl) were prepared by the method of Malatesta and co-workers[1] from chromium(II) acetate and the corresponding aryl isocyanide. These compounds were recrystallized from a benzene–hexane mixture to give bright red crystalline compounds and their identity was confirmed by comparison of their infrared spectra, melting points, and cyclic voltammograms[3] to the literature values.

Preparation of New $Cr(CNR)_6$ Complexes. $Cr(o\text{-}CH_3C_6H_4NC)_6$. Utilizing a modification of the method of Malatesta and co-workers,[1] chromium(II) acetate (6 g, 0.16 mol) was suspended in 100 mL of deaerated methanol under nitrogen. A slight excess of the *o*-tolyl isocyanide (18 g, 0.154 mol) was added and the reaction was stirred for 1.5 h followed by heating the mixture to reflux for an additional 0.5 h. After cooling of the reaction mixture a bright red precipitate was removed via filtration. This product was recrystallized from a benzene–hexane mixture yielding bright red prisms with green reflectances (6.0 g, 75%). This product was washed with cold hexane and vacuum-dried; mp 148–149 °C.

Anal. Calcd for $C_{48}H_{42}N_6Cr$: C, 76.37; H, 5.61; N, 11.13. Found: C, 76.49; H, 5.60; N, 11.13.

Data on other compounds prepared by this route are given below.

Preparation of $Cr(p\text{-}(CH_3)_2NC_6H_4NC)_6$. This was obtained as a dusky reddish brown powdery precipitate from cold methanol in 48% yield after reaction for approximately 1.0 h at room temperature. The compound is apparently unstable over a period of weeks even stored under a nitrogen atmosphere. Upon heating the product melts at 173 °C accompanied by decomposition.

Anal. Calcd for $C_{54}H_{60}N_{12}Cr$: C, 69.80; H, 6.51; N, 18.09. Found: C, 68.85; H, 6.33; N, 17.47.

Preparation of $Cr(m\text{-}CH_3C_6H_4NC)_6$. This compound was obtained as a red-orange needlelike precipitate having green reflectances. The reaction was allowed to proceed for 3 h at room temperature and the product was recovered in a 30% yield after recrystallization from a benzene–hexane mixture; mp 127–128.5 °C.

Anal. Calcd for $C_{48}H_{42}N_6Cr$: C, 76.37; H, 5.61; N, 11.13. Found: C, 76.21; H, 5.58; N, 10.67.

Preparation of $Cr(p\text{-}FC_6H_4NC)_6$. This was obtained as orange crystals with green reflectances in 35% yield after reaction for 1.5 h at room temperature. The product was recrystallized from a benzene–hexane mixture; mp 180 °C dec.

Anal. Calcd for $C_{42}H_{24}N_6F_6Cr$: C, 64.78; H, 3.11, N, 10.79. Found: C, 65.33; H, 3.28; N, 10.50.

Preparation of $Cr(m\text{-}CH_3OC_6H_4NC)_6$. This compound was obtained as a red fluffy precipitate after reaction for 1.5 h at room temperature followed by recrystallization from a benzene–hexane mixture; mp 58-59 °C.

Anal. Calcd for $C_{48}H_{42}O_6N_6Cr$: C, 67.75; H, 4.98; N, 9.88. Found: C, 68.01; H, 4.85; N, 9.24.

Preparation of $Cr(m\text{-}CF_3C_6H_4NC)_6$. This was obtained as a bright orange fluffy precipitate from a reaction for 1.5 h at room temperature in which there was an excess of the isocyanide present. The yield was 78% and the product was recrystallized from a benzene–hexane mixture; mp 113-113.5 °C.

Anal. Calcd for $C_{48}H_{24}N_6F_{18}Cr$: C, 53.44; H, 2.24; N, 7.79. Found: C, 53.59; H, 1.93; N, 7.83.

Attempts to prepare $Cr(CNR)_6$ complexes by this route from $p\text{-}O_2NC_6H_4NC$, $p\text{-}NCC_6H_4NC$, and $p\text{-}C_6H_5C_6H_4NC$ were unsuccessful. Several other methods were tried but were also unsuccessful.

Infrared and ^{1}H NMR data for these compounds are presented in Table I. Cyclic voltammetry data are found in Tables II (CH_3CN) and III (CH_2Cl_2). A previous study on the effect of scan rate on potential separation for the compound $Cr(o\text{-}CH_3C_6H_4NC)_6$ is noted.[2]

Discussion

Synthesis of the various $Cr(CNR)_6$ compounds used in this study was accomplished by the method of Malatesta et al.,[1] viz.

$$3Cr_2(OAc)_4(H_2O)_2 + 12CNR \rightarrow 2Cr(CNR)_6 + 4Cr^{3+} + 12OAc^- + 6H_2O$$

Yields of the red, crystalline chromium(0) complexes were generally good. Except for the complex derived from $p\text{-}(CH_3)_2NC_6H_4NC$ the metal complexes were thermally stable

Table II. Cyclic Voltammetric Data[a] (CH_3CN) for Hexakis(aryl isocyanide)chromium(0) Complexes

Compd	$\frac{1}{2}[E_{p,c} + E_{p,a}]$	$E_{p,a}$	$E_{p,c}$	$E_{p,c} - E_{p,a}$	Process
$Cr(p\text{-}(CH_3)_2NC_6H_4NC)_6$	−0.178	−0.125	−0.230	0.105	0 → 1+
	+0.700	+0.765	+0.635	0.130	1+ → 2+
$Cr(p\text{-}CH_3OC_6H_4NC)_6$	−0.385[b]	−0.355	−0.415	0.060	1− → 0
	+0.038[b]	+0.070	+0.005	0.065	0 → 1+
	+0.820	+0.865	+0.775	0.090	1+ → 2+
$Cr(p\text{-}CH_3C_6H_4NC)_6$	−0.392[b]	−0.360	−0.425	0.065	1− → 0
	+0.070[b]	+0.100	+0.040	0.060	0 → 1+
	+0.790[c]	+0.825	+0.755	0.070	1+ → 2+
$Cr(m\text{-}CH_3C_6H_4NC)_6$	−0.323	−0.285	−0.360	0.075	1− → 0
	+0.120	+0.155	+0.070	0.085	0 → 1+
	+0.840	+0.890	+0.790	0.100	1+ → 2+
$Cr(C_6H_5NC)_6$	−0.320[b]	−0.275	−0.365	0.090	1− → 0
	+0.150[b]	+0.190	+0.110	0.080	0 → 1+
	+0.902	+0.945	+0.850	0.095	1+ → 2+
$Cr(p\text{-}FC_6H_4NC)_6$	−0.315	−0.248	−0.315	0.067	1− → 0
	+0.151	+0.183	+0.118	0.065	0 → 1+
	+0.891	+0.938	+0.843	0.095	1+ → 2+
$Cr(m\text{-}CH_3OC_6H_4NC)_6$	−0.240	−0.150	−0.240	0.090	1− → 0
	+0.230	+0.268	+0.192	0.076	0 → 1+
	+0.945	+0.990	+0.900	0.090	1+ → 2+
$Cr(p\text{-}ClC_6H_4NC)_6$	−0.212[b]	−0.165	−0.260	0.095	1− → 0
	+0.270[b]	+0.310	+0.230	0.080	0 → 1+
	+1.015	+1.110	+0.920	0.190	1+ → 2+
$Cr(p\text{-}BrC_6H_4NC)_6$	−0.204	−0.157	−0.250	0.093	1− → 0
	+0.238	+0.282	+0.195	0.087	0 → 1+
	+1.092	+1.130	+1.055	0.075	1+ → 2+
$Cr(m\text{-}ClC_6H_4NC)_6$	−0.105	−0.080	−0.130	0.050	1− → 0
	+0.347	+0.377	+0.317	0.060	0 → 1+
	+1.007	+1.040	+0.975	0.065	1+ → 2+
$Cr(m\text{-}CF_3C_6H_4NC)_6$	−0.055	+0.020	−0.130	0.150	1− → 0
	+0.365	+0.410	+0.320	0.090	0 → 1+
	+1.142	+1.265	+1.020	0.245	1+ → 2+
$Cr(o\text{-}CH_3C_6H_4NC)_6$	−0.292	−0.255	−0.330	0.075	1− → 0
	+0.227	+0.267	+0.187	0.080	0 → 1+
	+1.042	+1.085	+1.000	0.085	1+ → 2+

[a] Solutions in CH_3CN; concentration of compound approximately 5×10^{-3} M; $[Bu_4N][ClO_4]$ (0.1 M) used as supporting electrolyte. Cathodic and anodic peak potentials are in volts vs. saturated calomel electrode (aqueous KCl). [b] Value reported previously but without internal *IR* compensation.[3] [c] Value reported previously.[4]

Table III. Cyclic Voltammetric Data[a] (CH_2Cl_2) for Hexakis(aryl isocyanide)chromium(0) Complexes

Compd	$\frac{1}{2}[E_{p,c} + E_{p,a}]$	$E_{p,a}$	$E_{p,c}$	$\lvert E_{p,a} - E_{p,c}\rvert$	Process
$Cr(p\text{-}CH_3OC_6H_4NC)_6$	−0.447[b]	−0.320	−0.575	0.255	1− → 0
	+0.110[b]	+0.220	+0.000	0.220	0 → 1+
	+0.842	+0.945	+0.740	0.205	1+ → 2+
$Cr(p\text{-}CH_3C_6H_4NC)_6$	−0.376[b]	−0.275	−0.478	0.203	1− → 0
	+0.224[b]	+0.318	+0.130	0.188	0 → 1+
	+1.001[c]	+1.085	+0.918	0.167	1+ → 2+
$Cr(m\text{-}CH_3C_6H_4NC)_6$	−0.350	−0.250	−0.461	0.211	1− → 0
	+0.242	+0.368	+0.115	0.153	0 → 1+
	+1.042	+1.118	+0.965	0.153	1+ → 2+
$Cr(C_6H_5NC)_6$	−0.315[b]	−0.273	−0.357	0.084	1− → 0
	+0.266[b]	+0.305	+0.227	0.078	0 → 1+
	+0.982	+1.020	+0.945	0.075	1+ → 2+
$Cr(p\text{-}FC_6H_4NC)_6$	−0.263	−0.190	−0.337	0.147	1− → 0
	+0.294	+0.370	+0.218	0.152	0 → 1+
	+1.004	+1.078	+0.930	0.148	1+ → 2+
$Cr(p\text{-}ClC_6H_4NC)_6$	−0.200[b]	−0.135	−0.265	0.130	1− → 0
	+0.308[b]	+0.375	+0.240	0.135	0 → 1+
	+0.986	+1.052	+0.920	0.132	1+ → 2+
$Cr(m\text{-}ClC_6H_4NC)_6$	−0.218	−0.077	−0.360	0.283	1− → 0
	+0.432	+0.580	+0.285	0.295	0 → 1+
	+1.120	+1.300	+0.941	0.395	1+ → 2+
$Cr(o\text{-}CH_3C_6H_4NC)_6$	−0.356	−0.258	−0.455	0.197	1− → 0
	+0.336	+0.420	+0.253	0.167	0 → 1+
	+1.121	+1.180	+1.062	0.118	1+ → 2+

[a] Solutions in CH_2Cl_2; concentration of compound approximately 5×10^{-3} M; $[Bu_4N][ClO_4]$ (0.1 M) used as supporting electrolyte. Cathodic and anodic peak potentials are in volts vs. saturated calomel electrode (aqueous KCl). [b] Value reported previously but without internal *IR* compensation.[3] [c] Value reported previously.[4]

and easily characterized by analytical and spectroscopic techniques. The compound $Cr(p\text{-}(CH_3)_2NC_6H_4NC)_6$ was less stable, decomposing over several weeks. It proved not to be possible to prepare complexes by this route from aryl isocyanides such as $p\text{-}NCC_6H_4NC$ and $p\text{-}O_2NC_6H_4NC$ which have strongly electron-withdrawing groups. Several other attempted preparations of the chromium(0) complexes of these ligands were also unsuccessful. There is no obvious reason for this lack of success. We would have liked to include these compounds in this study since they would substantially extend the range of ligand parameters, but eventually synthetic attempts were abandoned when results seemed not to be forthcoming. Fortunately synthesis of the $[Mn(CNR)_6]^+$ complexes of these ligands was accomplished, allowing their inclusion in another study.[19]

A study of the electrochemistry of these complexes by cyclic voltammetry was the primary intent of this work. All of the complexes studied exhibit three peaks on the current–potential scans; a figure illustrating such a trace is given in a previous paper.[2] The three oxidation and reduction processes have been assigned to the simple one-electron-transfer processes[2]

$$[Cr(CNR)_6]^- \rightleftharpoons Cr(CNR)_6 + e^-$$

$$Cr(CNR)_6 \rightleftharpoons [Cr(CNR)_6]^+ + e^-$$

$$[Cr(CNR)_6]^+ \rightleftharpoons [Cr(CNR)_6]^{2+} + e^-$$

[The measured peak potentials for these processes will be designated as $E_{(n)}(1- \rightarrow 0)$, $E_{(n)}(0 \rightarrow 1+)$, and $E_{(n)}(1+ \rightarrow 2+)$, respectively, where $E_{(n)}$ refers to the particular measured value, i.e., $E_{1/2}$, $E_{p,c}$, or $E_{p,a}$.] In each process cathodic and anodic currents are equal. The peak separations $|E_{p,a} - E_{p,c}|$ generally exceed 59 mV but are otherwise well defined. The processes are thus defined as nearly reversible or quasi-reversible, in which there is moderately slow electron transfer relative to the rate of potential change.[10] A study on peak separation as a function of scan rate which tends to confirm this was reported earlier.[2]

From the electrochemical values recorded in Tables II and III, it can be seen that a substituent on the phenyl ring can substantially modify the $E_{1/2}$ value of a given process. This result is not unexpected; however, the range of the electrochemical values for a particular process is indeed surprising. For example, for the $E_{1/2}(0 \rightarrow 1+)$ process, a range of 0.543 V is noted. The range might be larger but for the unavailability of complexes with strongly electron-withdrawing substituents; indeed a wider range of $E_{1/2}$ values is noted for the manganese(I) complexes.[19] Qualitatively, the variation of $E_{1/2}$ values occurs in a manner predicted with a knowledge of substituent group effects. Substituent groups which are electron donating cause $E_{1/2}$ to decrease, the complex thus being easier to oxidize; electron-withdrawing substituents increase $E_{1/2}$ values, oxidation becoming more difficult. The same observation had been made in this laboratory on a limited series of $[Mn(CNR)_6]^+$ and $Cr(CNR)_6$ compounds[3,4] and elsewhere in another electrochemical study on $Cr(CO)_{6-x}(CNR)_x$ compounds.[20]

It had been our hope when this work was initiated that a meaningful relationship could be developed between $E_{1/2}$ data and parameters related to substituent groups on the aryl isocyanide ligand. Indeed it would have been surprising not to find such a result. Although not extensively studied, correlations of electrochemical data with substituent group parameters are known in several organic systems.[21] In the organometallic area, the same sort of correlation is reported for oxidations of substituted ferrocenes.[22-24] Similar correlations of substituent group parameters with other physical properties are known. For example, a recent paper noted the relationship between $\nu(CO)$ (or force constant data) and the substituent group R in a series $Cr(C_6H_5R)(CO)_3$.[25]

Table IV. Linear Regression Analysis for $E_{(n)}$(process)-σ Correlations[a]

$E_{(n)}$[b]	σ	N	a	b	s	r
A. Process: $Cr(RNC)_6^- \rightarrow Cr(RNC)_6^0 + e^-$ (CH_3CN)						
$E_{1/2}$	σ_I	10	−0.340	0.312	0.129	0.628
$E_{p,a}$		10	−0.298	0.338	0.138	0.634
$E_{1/2}$	σ_p or σ_m	10	−0.300	0.482	0.041	0.969
$E_{p,a}$		10	−0.253	0.516	0.046	0.965
$E_{1/2}$	σ_R	10	−0.220	0.155	0.182	0.273
$E_{p,a}$		10	−0.171	0.151	0.200	0.247
$E_{1/2}$	σ_p° or σ_m°	10	−0.328	0.513	0.072	0.922
$E_{p,a}$		10	−0.284	0.550	0.077	0.921
$E_{1/2}$	σ_R°	10	−0.216	0.208	0.233	0.285
$E_{p,a}$		10	−0.171	0.184	0.254	0.235
B. Process: $Cr(RNC)_6^0 \rightarrow Cr(RNC)_6^+ + e^-$ (CH_3CN or CH_2Cl_2[c])						
$E_{1/2}$	σ_I	11	0.055	0.429	0.168	0.628
$E_{p,a}$		11	0.094	0.427	0.165	0.633
$E_{1/2}$	σ_p or σ_m	11	0.148	0.511	0.019	0.993
$E_{p,a}$		11	0.187	0.506	0.017	0.994
$E_{1/2}$	σ_R	11	0.264	0.377	0.178	0.556
$E_{p,a}$		11	0.301	0.374	0.176	0.558
$E_{1/2}$	σ_p° or σ_m°	11	0.116	0.555	0.047	0.966
$E_{p,a}$		11	0.155	0.549	0.047	0.966
$E_{1/2}$	σ_R°	11	0.271	0.489	0.228	0.562
$E_{p,a}$		11	0.308	0.484	0.225	0.562
$E_{1/2}$[c]	σ_p or σ_m	7	0.259	0.416	0.055	0.951
$E_{p,a}$[c]		7	0.353	0.436	0.097	0.879
C. Process: $Cr(RNC)_6^+ \rightarrow Cr(RNC)_6^{2+} + e^-$ (CH_3CN)						
$E_{1/2}$	σ_I	11	0.817	0.416	0.133	0.704
$E_{p,a}$		11	0.848	0.491	0.155	0.711
$E_{1/2}$	σ_p or σ_m	11	0.910	0.417	0.049	0.937
$E_{p,a}$		11	0.958	0.460	0.077	0.883
$E_{1/2}$	σ_R	11	1.000	0.292	0.161	0.498
$E_{p,a}$		11	1.066	0.327	0.177	0.504
$E_{1/2}$	σ_p° or σ_m°	11	0.883	0.463	0.057	0.932
$E_{p,a}$		11	0.936	0.493	0.077	0.897
$E_{1/2}$	σ_R°	11	0.007	0.386	0.204	0.512
$E_{p,a}$		11	1.059	0.396	0.249	0.450

[a] For the regression line $E_{(n)}$(process) = $a + b\sigma$; N = number of data sets, a = y intercept, b = slope, s = standard deviation of estimate, r = correlation coefficient. [b] Reported in volts vs. SCE. [c] $E_{(n)}$ values recorded in CH_2Cl_2. [d] Including Shorter's value[27] for ortho CH_3 as $\sigma_o = -0.17$.

There is a predictive advantage gained with the ability to correlate $E_{1/2}$ with substituent group parameters. Apart from this, the degree of correlation with various σ or modified σ parameters is of interest. A high degree of correlation with a given series of parameters could define whether there is dominance of inductive or resonance factors in the transmission of a substituent group effect. Thus we elected to look at possible correlations of $E_{1/2}$ values with three sets of parameters.[26] The Hammett σ_p and σ_m parameters were the first values chosen, representing the total inductive and mesomeric effect of the substituent group. Also chosen were the insulated parameters σ_p° and σ_m°, which reflect only direct or nonconjugative interactions, σ_I, the Taft purely inductive parameter, and σ_R, the pure resonance parameter calculated from Hammett σ and σ_I parameters;[27] σ_R°, which is the insulated resonance constant, involves the conjugative effect but is operative in the restricted domain of the substituent and the benzene ring.[25] The values of these parameters were obtained from standard sources.[28]

The relationship between $E_{1/2}$(process) and $E_{p,a}$(process) (Tables II and III) and the specific substituent constants was investigated via a linear regression analysis. The $E_{p,a}$ values were included since the accepted prerequisite for reversibility, i.e., $|E_{p,c} - E_{p,a}|$ = 59 mV, had not been met for most systems. For each process $E_{(n)}$ was expressed in terms of the equation $E_{(n)}$(process) = $a + b\sigma$. The results, presented in Table IV, summarize the statistical information derived from the correlations of $E_{1/2}$ or $E_{p,a}$ for each of the processes with each substituent parameter. The data were obtained by least-squares fitting and are listed as the number of pairs of data points (N), the intercept and slope labeled a and b, respectively, the estimate of standard deviation s, and the correlation coefficient r. The convention of Jaffe[24] which assesses the reliability of the relationship between the two variables in terms of the correlation coefficient will be employed. For information on the computations used, see ref 27.

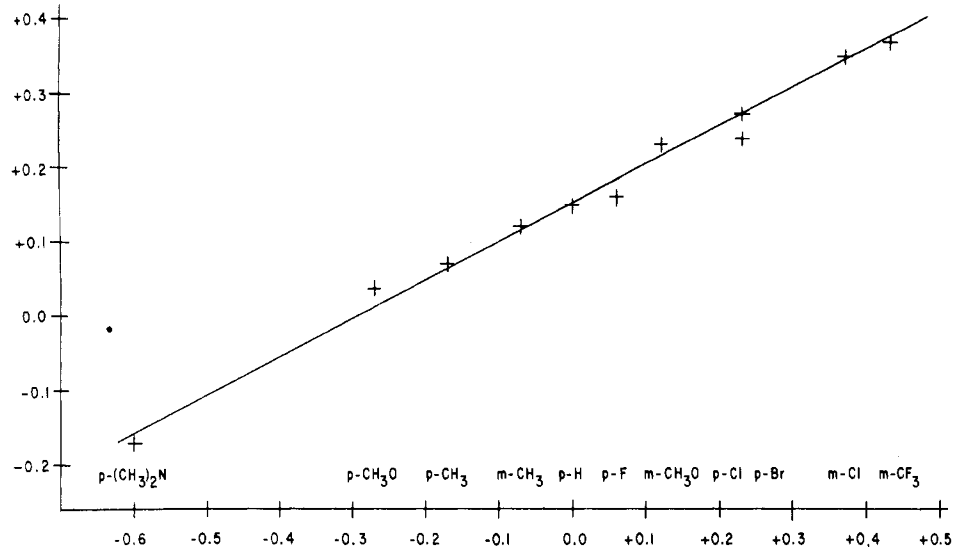

Figure 1. $E_{1/2}(0 \rightarrow 1+)$ data in acetonitrile vs. Hammett σ_p or σ_m parameters for the hexakis(aryl isocyanide)chromium(0) series.

Several observations can be made concerning these results.

(1) The poorest correlation seems to exist between $E_{(n)}$ and σ_R or $\sigma_R°$, the purely polar resonance constant or the insulated polar resonance constant (r = 0.273–0.562, s = 0.182–0.228 V). The lack of any significant correlation indicates that a substituent interaction that invokes electron delocalization or polarization transmitted *entirely* through a conjugative mechanism is not very meaningful.

(2) A slightly better correlation is exhibited in the relationship between $E_{(n)}$ and Taft's inductive parameter, σ_I (r = 0.628–0.704, s = 0.168–0.133 V). Even though the statistical analysis implies a poor relationship, there exists a better correlation between $E_{(n)}$ and σ_I than between $E_{(n)}$ and σ_R or $\sigma_R°$. This suggests that the substituent effect involves more of a direct or through-bond polarization than a resonance effect.

(3) An excellent correlation is observed between $E_{(n)}$ and σ_p or σ_m (r = 0.993–0.937, s = 0.019–0.049 V), especially in the case of $E_{1/2}(0 \rightarrow 1+)$ vs. σ_p or σ_m. This correlation is illustrated further in Figure 1. Clearly the substituent effect affects the electrochemical process through a combined inductive and resonance interaction. Furthermore, since there exists a better correlation between $E_{(n)}$ and σ_p or σ_m than between $E_{(n)}$ and $\sigma_p°$ or $\sigma_m°$ (e.g., for $E_{1/2}(0 \rightarrow 1+)$: σ_p or σ_m, r = 0.993, s = 0.019 V; $\sigma_p°$ or $\sigma_m°$, r = 0.966, s = 0.047 V), the mechanism by which the transmission of substituent effects is relayed must be considered to be a combination of both direct and conjugative effects between the detection center and the aromatic ring.

That there is a good correlation of $E_{1/2}$ values with Hammett σ constants is probably not surprising; earlier it was noted that such relationships have been defined in other systems.[21-24] Nonetheless, it is desirable to probe the meaning of this result in more detail. To do this it is necessary to consider simple bonding models for metal isocyanide complexes.

Molecular orbital calculations on the members of the series $[Mn(CO)_{6-x}(CNCH_3)_x]^+$ show that a good correlation can be made between $E_{1/2}$ and the energies of the highest occupied molecular orbital (HOMO) in the complex.[7] In these complexes the HOMO's are primarily the metal d_{xy}, d_{xz}, and d_{yz} orbitals. They are more or less nonbonding but are stabilized to some extent by π interaction with the carbonyl ligands and to a lesser extent with the isocyanides. It may be presumed that a similar model of bonding pertains to $Cr(CNR)_6$ complexes. It is easy to visualize how the energies of these metal orbitals can be influenced by changes on the aryl ring. Through an inductive mechanism charge transfer from substituent group on the ligand will cause buildup of negative charge on the metal, and as a consequence the metal orbitals should be destabilized. At the same time the extent of π delocalization from the metal orbitals to the antibonding ligand orbitals will also vary. Substituent groups on the aryl ring will split the degeneracy of the π symmetry orbitals of the ring-NC group and alter their energies. As a consequence of the change in energy of π^*, the extent of electron transfer from the metal to these orbitals will also be altered. Delocalization from the metal to π^* ligand orbitals will decrease the HOMO (d_{xz}, d_{yz}, d_{xy}) orbital energies and cause the complex to be less easily oxidized. [In alkyl isocyanides the π^*(CN) orbitals are degenerate. However, in aryl isocyanides one π^*(CN) orbital will mix with a ring π^* orbital to generate lower energy and higher energy π^* orbitals.[29,30] The former interacts with the metal orbitals to allow π donation to the ligand from the metal.]

Table V. Reaction Constants, ρ, for the Electrochemical Processes of Hexakis(aryl isocyanide)chromium(0) Complexes

Process[a]	ρ[b]
$E_{1/2}(1- \rightarrow 0)$ in CH_3CN	+0.0803
$E_{p,a}(1- \rightarrow 0)$ in CH_3CN	+0.0803
$E_{1/2}(0 \rightarrow 1+)$ in CH_3CN	+0.0851
$E_{p,a}(0 \rightarrow 1+)$ in CH_3CN	+0.0843
$E_{1/2}(0 \rightarrow 1+)$ in CH_2Cl_2	+0.0693
$E_{p,a}(0 \rightarrow 1+)$ in CH_2Cl_2	+0.0727
$E_{1/2}(1+ \rightarrow 2+)$ in CH_3CN	+0.0695
$E_{p,a}(1+ \rightarrow 2+)$ in CH_3CN	+0.0767

[a] From data in Table IV. [b] Calculated from $\Delta E_{1/2} = 6\sigma\rho$.

It is obvious that σ and π (inductive and resonance) effects work in tandem, varying in such a way as to minimize the overall variation of charge at the metal. The $E_{1/2}$ measurement must be particularly sensitive to this small effect to give the pronounced variation observed here.

The value of $E_{1/2}$ is determined by a free energy difference between reactants and products, the reduced and oxidized species in the electrochemical reaction. The fact that correlations can be made with bonding parameters associated with one of these species implies that the significant orbitals are not grossly distorted or perturbed in going from one species to the other. Were this otherwise, a predictable variation in $E_{1/2}$ value would probably not emerge.

The reaction constants ρ for each electrochemical process can be calculated for the slopes of the least-squares plots of $E_{1/2}$ vs. σ. In this calculation it is necessary to take into

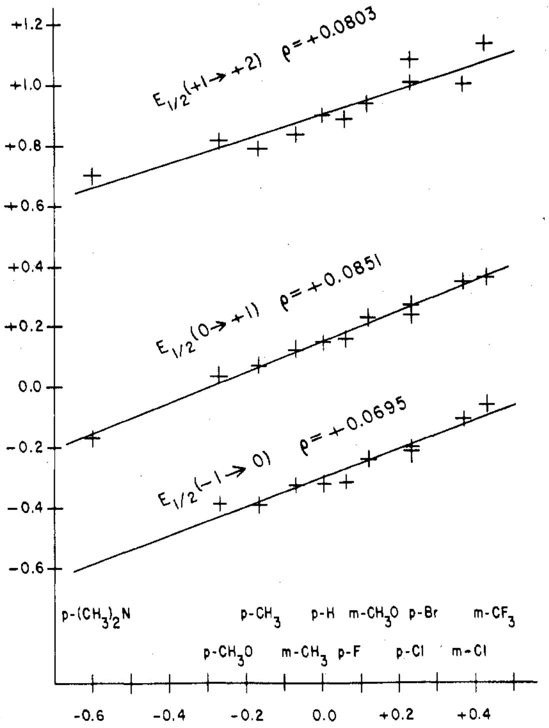

Figure 2. $E_{1/2}$(process) data in acetonitrile vs. Hammett σ_p or σ_m parameters for the hexakis(aryl isocyanide)chromium(0) series.

account the cumulative effect of the six ligands.[31] Values of ρ for the various electrochemical processes are given in Table V. The positive sign of the reaction constant which is found concurs with the vast majority of electrochemical correlations investigated. This is indicative of a reaction facilitated by a high electron density.[31] The relative magnitude of the reaction constant, relating the effectiveness of the transmission of the substituent effect, is associated with the proximity of the substituent to the reaction center. This can be clearly seen from the values of the reaction constants obtained from the correlations found between the $E_{1/2}$ values and the substituent constants for the three substituted series X–Ar–OH,[32] X–ferrocene,[33] and X–Ar–ferrocene.[33] The series have been arranged in order with respect to the distance between the substituent and the reaction center and, as expected, the calculated reaction constants decrease as the distance between the substituent and detection center increases: +0.52, +0.26, and +0.13, respectively. Compared to these data, the calculated value of +0.0851 from the $E_{1/2}(0 \rightarrow 1+)$ vs. σ_p or σ_m regression analysis for the hexakis(aryl isocyanide)chromium(0) series seems to be a very consistent value considering the number of bonds actually separating the substituents from the metal center.

From a comparison of the calculated ρ values for the processes $E_{1/2}(1- \rightarrow 0)$, $E_{1/2}(0 \rightarrow 1+)$, and $E_{1/2}(1+ \rightarrow 2+)$ it can be determined that the formal oxidation state of the complex does not exert a significant influence on the effectiveness of the transmission of the substituent effect. This can be seen by comparing the slopes of the regression lines for the respective processes in acetonitrile as shown in Figure 2. The fact that ρ for the process $E_{1/2}(1+ \rightarrow 2+)$ is slightly smaller than those for the other two processes, indicating diminished conjugate interaction of the substituent, may be due to the decrease in π interaction through successive oxidations. The fact that the electrode reaction $E_{1/2}(1- \rightarrow 0)$ is not as susceptible to the substituent effect as the electrode process $E_{1/2}(0 \rightarrow 1+)$ even though theoretically there should be more metal electron density available to enter into extended conjugation through back-donating is surprising, but the difference in ρ values is small and perhaps not significant. It is noted that attempts to reduce the hexakis(*p*-tolyl isocyanide)chromium(0) complex were unsuccessful.

The choice of solvents, acetonitrile or dichloromethane, seems to have an important influence. The $E_{1/2}$ values in dichloromethane are higher than the corresponding $E_{1/2}$ measured employing acetonitrile as the solvent. Also the peak separations, $|E_{p,c} - E_{p,a}|$, the measure of reversibility, are less in acetonitrile than those in dichloromethane. A better correlation seems to exist when relating the $E_{(n)}$ values to the total polar substituent constant for those values taken in acetonitrile than for the data reported in dichloromethane. Finally, the reaction constants calculated for the reaction series in acetonitrile are larger than those obtained for the series in dichloromethane. These results may be explained in an interrelated manner. Different solvent interactions, besides altering the *IR* drop through the cell and the liquid junction potential between the reference electrode and the solution, are known to affect the processes involved in the electrochemical couple to varying degrees depending upon the charges of the oxidized and reduced forms and the dielectric constant of the medium.[34] This could account for the contrast in the $E_{(n)}$ values as well as the deviation in the peak separations for the different solvent processes. The fact that the reaction constant for the series in acetonitrile is larger than the value for the series in dichloromethane (0.085 vs. 0.0693 for $E_{1/2}(0 \rightarrow 1+)$ in acetonitrile and dichloromethane, respectively), implies that the transmission of the substituent effect is facilitated to a larger degree in a more polar environment. This is also substantiated by noting that a better correlation exists between the $E_{(n)}$ values and the substituent constants, as measured by the relative magnitudes of the correlation coefficient. The more significant the transmission of the substituent is, the greater any correlations involving a series of compounds should be. Since the conveyance of the substituent effect has been described in terms of interactions associated with the aromatic ring π orbitals, it is interesting to observe an enhancement of this effect in a more polar medium.

Interestingly, there is no correlation between $E_{1/2}$ values and infrared data. Neither the value for ν(CN) in these complexes nor the change, $\Delta\nu$(CN), upon coordination to the metal varies in a predictable manner. Whether there should be some correlation of these data is not clear. Carbonyl stretching frequencies invariably change in a predictable manner with ability of the ligands to donate or accept electron density. Isocyanide stretching frequencies should also correlate, and since $E_{1/2}$ values are known to be determined by ligand donor–acceptor ability, a regular relationship between the two would not have been surprising. Probably the lack of a correlation is a consequence of the minimal variation of ν(CN) and the difficulty of identifying the center of the ν(CN) broad absorptions. The possible occurrence of vibrational coupling between CN and ring C═C vibrations of similar energy and appropriate symmetry would also interfere with such a correlation. It is not unreasonable to suggest that vibrational coupling is probably the reason, for the broadness and multiplicity of ν(CN) absorptions would not be expected to reflect C≡N force constants accurately and thus detract from any correlation of $E_{1/2}$ with ν(CN).

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Registry No. Cr(p-(CH$_3$)$_2$NC$_6$H$_4$NC)$_6$, 61506-02-3; Cr(p-(CH$_3$)$_2$NC$_6$H$_4$NC)$_6^{1+}$, 61505-75-7; Cr(p-(CH$_3$)$_2$NC$_6$H$_4$NC)$_6^{2+}$, 61505-76-8; Cr(p-CH$_3$OC$_6$H$_4$NC)$_6^{1-}$, 61528-34-5; Cr(p-CH$_3$OC$_6$H$_4$NC)$_6$, 18115-32-7; Cr(p-CH$_3$OC$_6$H$_4$NC)$_6^{1+}$, 57016-46-3; Cr(p-CH$_3$OC$_6$H$_4$NC)$_6^{2+}$, 57016-48-5; Cr(p-CH$_3$C$_6$H$_4$NC)$_6^{1-}$, 61506-03-4; Cr(p-CH$_3$C$_6$H$_4$NC)$_6$, 15531-15-4; Cr(p-CH$_3$C$_6$H$_4$NC)$_6^{1+}$, 57016-42-9; Cr(p-CH$_3$C$_6$H$_4$NC)$_6^{2+}$, 57016-44-1; Cr(m-CH$_3$C$_6$H$_4$NC)$_6^{1-}$, 61528-33-4; Cr(m-CH$_3$C$_6$H$_4$NC)$_6$, 61528-36-7;

Cr(*m*-CH$_3$C$_6$H$_4$NC)$_6{}^{1+}$, 61506-04-5; Cr(*m*-CH$_3$C$_6$H$_4$NC)$_6{}^{2+}$, 61506-05-6; Cr(C$_6$H$_5$NC)$_6{}^{1-}$, 61506-06-7; Cr(C$_6$H$_5$NC)$_6$, 17375-15-4; Cr(C$_6$H$_5$NC)$_6{}^{1+}$, 57016-32-7; Cr(C$_6$H$_5$NC)$_6{}^{2+}$, 57016-35-0; Cr(*p*-FC$_6$H$_4$NC)$^{1-}$, 61506-07-8; Cr(*p*-FC$_6$H$_4$NC), 61528-35-6; Cr(*p*-FC$_6$H$_4$NC)$_6{}^{1+}$, 61506-08-9; Cr(*p*-FC$_6$H$_4$NC)$_6{}^{2+}$, 61506-09-0; Cr(*m*-CH$_3$OC$_6$H$_4$NC)$_6{}^{1-}$, 61506-10-3; Cr(*m*-CH$_3$OC$_6$H$_4$NC)$_6$, 61528-37-8; Cr(*m*-CH$_3$OC$_6$H$_4$NC)$_6{}^{1+}$, 61506-11-4; Cr(*m*-CH$_3$OC$_6$H$_4$NC)$_6{}^{2+}$, 61506-12-5; Cr(*p*-ClC$_6$H$_4$NC)$_6{}^{1-}$, 61506-13-6; Cr(*p*-ClC$_6$H$_4$NC)$_6$, 36732-52-2; Cr(*p*-ClC$_6$H$_4$NC)$_6{}^{1+}$, 57016-50-9; Cr(*p*-ClC$_6$H$_4$NC)$_6{}^{2+}$, 57016-52-1; Cr(*p*-BrC$_6$H$_4$NC)$_6{}^{1-}$, 61506-14-7; Cr(*p*-BrC$_6$H$_4$NC)$_6$, 61506-01-2; Cr(*p*-BrC$_6$H$_4$NC)$_6{}^{1+}$, 61506-15-8; Cr(*p*-BrC$_6$H$_4$NC)$_6{}^{2+}$, 61506-16-9; Cr(*m*-ClC$_6$H$_4$NC)$_6{}^{1-}$, 61506-17-0; Cr(*m*-ClC$_6$H$_4$NC)$_6$, 15531-14-3; Cr(*m*-ClC$_6$H$_4$NC)$_6{}^{1+}$, 61506-18-1; Cr(*m*-ClC$_6$H$_4$NC)$_6{}^{2+}$, 61506-19-2; Cr(*m*-CF$_3$C$_6$H$_4$NC)$_6{}^{1-}$, 61506-20-5; Cr(*m*-CF$_3$C$_6$H$_4$NC)$_6$, 61505-66-6; Cr(*m*-CF$_3$C$_6$H$_4$NC)$_6{}^{1+}$, 61506-21-6; Cr(*m*-CF$_3$C$_6$H$_4$NC)$_6{}^{2+}$, 61505-66-6; Cr(*o*-CH$_3$C$_6$H$_4$NC)$_6{}^{1-}$, 61506-22-7; Cr(*o*-CH$_3$C$_6$H$_4$NC)$_6$, 57016-37-2; Cr(*o*-CH$_3$C$_6$H$_4$NC)$_6{}^{1+}$, 57016-38-3; Cr(*o*-CH$_3$C$_6$H$_4$NC)$_6{}^{2+}$, 57016-40-7.

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