18-electron species $[Mo(NO)(CNR)_5]I$ and $Mo(NO)(CNR)_4I$. This difference in synthetic strategy, namely, either the reaction of a nitrosyl precursor complex with excess RNC or the reaction of an isocyanide complex with nitric oxide, may be important in determining the reaction course. In view of the greater reducing propensity of the isocyanide ligands,[14] it is not surprising that the reaction of $[Cr(NO)(NCMe)_5](PF_6)_2$ with excess RNC gives 18-electron products.

We find that the use of the seven-coordinate homoleptic species $[Cr(CNR)_7](PF_6)_2$[6] in place of $[Cr(CNR)_6](PF_6)_2$ should be avoided, as the equilibrium $[Cr(CNR)_7]^{2+} \rightleftarrows [Cr(CNR)_6]^{2+} + CNR$ which exists in solution,[6] provides free isocyanide which we have found leads to its NO-induced polymerization, particularly in the case of the cyclohexyl isocyanide derivative.

Once isolated, the 17-electron Cr(I) complexes $[Cr(NO)(CNR)_5](PF_6)_2$ were found to undergo a facile one-electron reduction by Zn metal to form the violet, crystalline 18-electron Cr(0) compounds $[Cr(NO)(CNR)_5]PF_6$. This process is easily reversible by treatment of the Cr(0) compound (R = CMe_3) with $AgNO_3$ and KPF_6 in dichloromethane. An intriguing facet of this reduction is the apparent "catalytic" behavior of ethanol when the reaction is run in dichloromethane. Several drops of ethanol in the reaction mixture allow completion of a reaction within minutes which otherwise does not appear to proceed to completion at all.

Reduction of the 17-electron complexes is sufficiently facile ($E_{p,c} \sim +0.3$ V vs. SCE as measured by cyclic voltammetry) that it is observed to be a dominant process in certain substitution reactions. Thus reaction of yellow $[Cr(NO)(CNR)_5](PF_6)_2$ with amines in ethanol first leads to the rapid reduction (within a few minutes) of the starting material and formation of a dark purple solution. From this solution, the orange Cr(0) compounds $[Cr(NO)(CNR)_4(amine)]PF_6$ form over a period of days. For confirmation of this reduction–substitution reaction sequence, an authentic sample of 18-electron $[Cr(NO)(CNCMe_3)_5]PF_6$ was reacted with an ethanol solution of isopropylamine under identical reaction conditions as outlined for the dicationic species; by this means $[Cr(NO)(CNCMe_3)_4(NH_2CHMe_2)]PF_6$ was isolated in 22% yield.

Although reactions with other amines were attempted (e.g., cyclohexylamine and diethylamine) only with *tert*-butylamine, isopropylamine, and piperidine did substitution subsequently occur, even though dark purple solutions formed in all cases, indicating that reduction to $[Cr(NO)(CNR)_5]PF_6$ had occurred.

These amine-substituted compounds decompose in solution (acetone, chloroform, and dichloromethane) over periods ranging from a few minutes to several hours to yield the corresponding purple $[Cr(NO)(CNR)_5]PF_6$ complexes. This scavenging of an RNC ligand by the complex probably proceeds by initial dissociation of amine and the subsequent decomposition (with loss of RNC) by a small proportion of the molecules. For example, in the decomposition of $[Cr(NO)(CNCMe_3)_4(piperidine)]PF_6$, $[Cr(NO)(CNCMe_3)_5]PF_6$ is obtained in 67% yield, whereas the maximum possible yield (assuming quantitative release of RNC by a minimum number of molecules) is 80%. The ready loss of amine, which is necessary for the regeneration of the $[Cr(NO)(CNR)_5]^+$ species, is consistent with the long reaction times and high concentration of amine which are necessary to convert $[Cr(NO)(CNR)_5]PF_6$ to $[Cr(NO)(CNR)_4(amine)]PF_6$. The weakly bound nature of the amine ligands is observed in the gas phase as well, as noted from studies of the secondary ion mass spectra (SIMS) of these compounds, details of which will be reported elsewhere.[15]

It is important to note here the difference in reactivities between the chromium compounds and the analogous molybdenum species. McCleverty and Williams report[5] formation of carbene complexes $[Mo(NO)(CNR)_4\{C(NHR)(NHR')\}]^+$ from the action of primary amines ($R'NH_2$) on $[Mo(NO)(CNR)_5]^+$. This reaction proceeds at 0 °C and only upon refluxing the reagents do the substituted complexes $[Mo(NO)(CNR)_4(NH_2CMe_3)]^+$ form. The lower activity of the isocyanide carbon of the analogous chromium complexes to nucleophilic attack by amine should be commented upon, especially in light of the electrochemical properties of these two complexes.

Chatt and co-workers[16,17] have investigated nucleophilic attack on coordinated isocyanides and found that an increase in the oxidation state of the metal or of its positive charge should decrease the electron density at the isocyanide carbon and hence enhance the latter's reactivity toward nucleophiles. Our electrochemical investigations of $[Cr(NO)(CNCMe_3)_5]^+$ (vide infra) and the isoelectronic $[Mo(NO)(CNCMe_3)_5]^+$[18] indicate a greater positive charge at the molybdenum center. While both compounds are characterized by a reversible one-electron oxidation in the cyclic voltammograms of dichloromethane–0.2 M tetra-*n*-butylammonium hexafluorophosphate solutions, this occurs at $E_{1/2} = +0.62$ V vs. SCE for $[Mo(NO)(CNCMe_3)_5]^+$, whereas the related couple for the chromium complex is at $E_{1/2} = +0.35$ V. This difference demonstrates the relative ease of oxidizing the chromium complex, which may be a reflection of the smaller positive charge at the metal center. This perhaps goes some way in explaining why only amine-substituted compounds are isolated in the case of chromium, whereas for the molybdenum system, carbene complexes are known as well.

Formation of the halide derivatives $[Cr(NO)(CNR)_4X]PF_6$ is effected by direct reaction of halide ion with dichloromethane solutions of $[Cr(NO)(CNR)_5](PF_6)_2$. This simple ligand substitution process results in the formation of the orange, paramagnetic complexes $[Cr(NO)(CNR)_4X]PF_6$ for R = CMe_3, when X = Cl or Br, R = $CHMe_2$, when X = Cl, and R = C_6H_{11}, when X = Br. Only a small amount of purple complex (presumably $[Cr(NO)(CNR)_5]^+$) is obtained if a 1:1 stoichiometric ratio of reagents is used, and this may be easily separated from the orange complexes by chromatography on silica gel using dichloromethane as eluent. Yields are quite low for the chloride reactions (10–27%), and several bands, including considerable amounts of starting material, are observed on the column. If longer reaction times are used, more reduced (purple) product is formed and yields of the chloride-containing complexes suffer further.

Spectroscopic and Electrochemical Characterization. Infrared spectra of Nujol mulls and dichloromethane solutions of compounds prepared in this study are presented in Table I. The isocyanide $\nu(C{\equiv}N)$ and nitrosyl $\nu(NO)$ modes occur in the regions 2100–2250 cm^{-1} and

---

[14] Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* **1982**, *1*, 336.

[15] Pierce, J. L.; Wigley, D. E.; Walton, R. A., *Organometallics*, following paper in this issue.

[16] Chatt, J.; Richards, R. L.; Royston, G. H. D. *Inorg. Chim. Acta* **1972**, *6*, 669.

[17] Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1433.

[18] For this purpose a sample of $[Mo(NO)(CNCMe_3)_5]BF_4$ was prepared by the procedure published in ref 5. Cyclic voltammetric measurements were carried out as described in the Experimental Section.

Table I. Infrared Spectra and Voltammetric Half-Wave Potentials of Nitrosyl–Isocyanide Complexes of Cr(0) and Cr(I)

	ν(NO),^{a} cm^{-1}		ν(C≡N),^{a} cm^{-1}		
complex	Nujol mull	CH_2Cl_2	Nujol mull	CH_2Cl_2	$E_{1/2}$,^{c} V
$[Cr(NO)(CNCMe_3)_5](PF_6)_2$	1805 br	1797 s	2229 s	2224 s	+0.35 (90), reduction
$[Cr(NO)(CNCHMe_2)_5](PF_6)_2$	1770 s	1790 s	2235 s	2233 s	+0.30 (100), reduction
$[Cr(NO)(CNC_6H_{11})_5](PF_6)_2$	1793 s	1791 s	2240 s	2233 s	+0.34 (130), reduction
$[Cr(NO)(CNCMe_3)_5]PF_6$	1680 s	1682 s	2210 m, 2135 s	2202 m, 2128 s	+0.35 (95), oxidation
$[Cr(NO)(CNCHMe_2)_5]PF_6$	1682 s	1680 s	2212 m, 2140 s	2209 m, 2138 s	+0.33 (105), oxidation
$[Cr(NO)(CNC_6H_{11})_5]PF_6$	*b*	1682 s	*b*	2208 m, 2133 s	+0.34 (140), oxidation
$[Cr(NO)(CNCMe_3)_4(NH_2CMe_3)]PF_6$	1646 s, 1630 s	1666 m	2128 s	2122 s	+0.24 (100), oxidation
$[Cr(NO)(CNCMe_3)_4$(piperidine)$]PF_6$	1640 s, 1623 s	1666 s	2130 s	2124 s	+0.23 (90), oxidation
$[Cr(NO)(CNCMe_3)_4(NH_2CHMe_2)]PF_6$	1647 s, 1632 s	1661 s	2128 s	2125 s	+0.21 (90), oxidation
$[Cr(NO)(CNCHMe_2)_4$(piperidine)$]PF_6$	1660 s, 1629 s	1665 m	2142 s	2136 s	+0.22 (90), oxidation
$[Cr(NO)(CNCMe_3)_4Cl]PF_6$	1742 s	1759 s	2224 s	2219 s	−0.46,^{d} reduction
$[Cr(NO)(CNCHMe_2)_4Cl]PF_6$	1746 s, 1737 sh	1757 s	2228 s	2225 s	−0.45,^{d} reduction
$[Cr(NO)(CNCMe_3)_4Br]PF_6$	1744 s	1760 s	2222 s	2217 s	−0.34 (90), reduction
$[Cr(NO)(CNC_6H_{11})_4Br]PF_6$	1734 s, br	1758 s	2224 s	2222 s	−0.34 (110), reduction

^{a} s, strong; m, medium; br, broad; sh, shoulder. ^{b} Not measured, see text. ^{c} In V vs. SCE with a Pt bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate(TBAH) as supporting electrolyte; values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. ^{d} $E_{p,c}$ reported.

1600–1850 cm^{-1}, respectively, and are of particular interest since they are seen to monitor changes in oxidation state of the metal as well as ligand substitution. An intense ν(NO) mode is observed at around 1800 cm^{-1} in the spectra of the formally Cr(I) complexes $[Cr(NO)(CNR)_5](PF_6)_2$. Although two ν(C≡N) bands might be predicted in the isocyanide stretching region, only one is seen in the spectra of the dications; this can be rationalized on the basis of the expected weakness of the A_1 mode (in C_{4v} symmetry) of the axial isocyanide stretch. Both the ν(C≡N) and ν(NO) peaks of $[Cr(NO)(CNR)_5]^{n+}$ sharpen in CH_2Cl_2 solution and are only very slightly solvent shifted (~5 cm^{-1}) to lower energies.

Reduction of the dicationic species to $[Cr(NO)(CNR)_5]PF_6$ results in a substantial decrease in the ν(C≡N) and ν(NO) energies (Table I), consistent with increased back-bonding to the π^* levels of the ligands. In each case the shift in nitrosyl energy is more pronounced than in the isocyanide ligand. In the reduced compounds, both IR-active ν(C≡N) modes are now discernible, both in the solid state and in solution, and are separated by about 75 cm^{-1}.

The amine-substituted series $[Cr(NO)(CNR)_4$(amine)$]PF_6$ exhibit values of ν(C≡N) and ν(NO) which are consistent with their formulation as unipositive, Cr(0) complex ions, and they may be considered as simple substitution products of the parent 18-electron compounds $[Cr(NO)(CNR)_5]PF_6$. A single, sharp isocyanide stretch is observed, both in Nujol mulls and dichloromethane solution, consistent with the assignment of these structures as *trans*-$[Cr(NO)(CNR)_4$(amine)$]PF_6$. Both ν(C≡N) and ν(NO) frequencies shift to lower energies compared to the parent $[Cr(NO)(CNR)_5]PF_6$ complexes, which is no doubt a reflection of the nonexistent π-accepting ability and greater σ-donating ability of the amine ligands as compared to the nitrosyl and isocyanide moieties.

An apparent solid-state splitting is observed for ν(NO) in the Nujol mull spectra of the amine-substituted compounds, an effect that vanishes in dichloromethane solution. The comparable intensity of these twin peaks and the observation of this splitting in the case of a secondary amine, piperidine, precludes the assignment of one component of the doublets to a δ(HNH) bending mode. What is intriguing is the *increase* in the value of ν(NO) upon dissolution of these compounds. This would appear to reflect in one way or another a weakening of the amine–metal interaction in solution perhaps through the influence of hydrogen bonding effects involving the dichloromethane solvent.

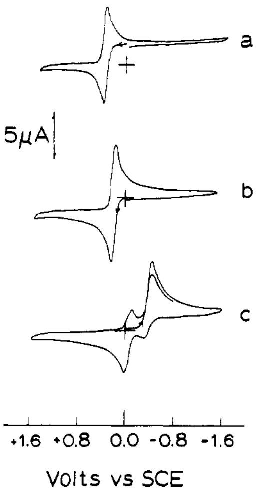

Figure 1. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of (a) $[Cr(NO)(CNCMe_3)_5](PF_6)_2$, (b) $[Cr(NO)(CNCMe_3)_4(NH_2CHMe_2)]PF_6$, and (c) $[Cr(NO)(CNCMe_3)_4Cl]PF_6$ recorded at 200 mV/s.

The IR spectral properties of the halide derivatives $[Cr(NO)(CNR)_4X]PF_6$ are seen (Table I) to reflect qualitatively the trends seen in the spectra of the related amine-containing salts. The trans-halide ligands induce a significant decrease in the value of ν(NO) compared to the analogous 17-electron cations $[Cr(NO)(CNR)_5]^{2+}$, reflecting the more potent σ-donor ability of X^- compared to RNC. A similar trend is observed in comparing the 18-electron species $[Cr(NO)(CNR)_4$(amine)$]^+$ with $[Cr(NO)(CNR)_5]^+$ (vide supra).[19]

Electrochemical properties of these complexes were investigated by using the cyclic voltammetry technique. Voltammetric half-wave potentials vs. SCE for dichloromethane–0.2 M tetra-*n*-butylammonium hexafluorophosphate solutions are presented in Table I. All complexes exhibit a single process, corresponding to a 17-electron/18-electron couple (Figure 1a). For the $[Cr(NO)(CNR)_5]^{n+}$ (n = 1 or 2) series, the $E_{1/2}$ values occur between +0.30 and +0.35 V vs. SCE and indicate the extreme ease of reducing $[Cr(NO)(CNR)_5]^{2+}$ to the corre-

---

[19] Many of the mixed nitrosyl–isocyanide complexes were also characterized on the basis of their ^1H NMR and electronic absorption spectra, details of which can be obtained from R.A.W. upon request. For example, $[Cr(NO)(CNCHMe_2)_5]PF_6$: ^1H NMR (acetone-d_6) δ 1.50 (d, CH_3, J_{CH_3CH} = 6 Hz); UV λ_{max} (CH_2Cl_2) 532 nm.

Table II. X-Band ESR Spectra and Magnetic Moments of Nitrosyl-Isocyanide Complexes of Chromium(I)

complex	g_{av}[a]	$A(^{53}Cr)$, G	$A(^{14}N)$, G	μ_{obsd}[b]
$[Cr(NO)(CNCMe_3)_5](PF_6)_2$	1.9936	18.0	4.5	1.51
$[Cr(NO)(CNCHMe_2)_5](PF_6)_2$	1.9931	18.1	4.7	1.53
$[Cr(NO)(CNC_6H_{11})_5](PF_6)_2$	1.9934	18.0	5.0	1.48
$[Cr(NO)(CNCMe_3)_4Cl]PF_6$	1.9927	18.8	4.8	1.51
$[Cr(NO)(CNCHMe_2)_4Cl]PF_6$	1.9925	18.7	5.2	1.66
$[Cr(NO)(CNCMe_3)_4Br]PF_6$	2.0146	~18	~4.5	1.22
$[Cr(NO)(CNC_6H_{11})_4Br]PF_6$	2.0144	~19	~4.5	1.45
$[Cr(NO)(CNCMe_3)_4(NH_2CMe_3)]^{2+}$[c]	1.9923	18.2	5.4[d]	

[a] At room temperature in CH_2Cl_2 solution. [b] Bohr magnetons; determined on dichloromethane solutions at room temperature by the Evans method. [c] Electrochemically generated dication (see text). [d] Coupling to ^{14}N of the nitrosyl ligand.

sponding monocations. For sweep rates (ν) between 50 and 400 mV/s, the ratio $i_p/\nu^{1/2}$ was constant and $i_{p,a}/i_{p,c} \simeq 1$ in accord with diffusion control. The potential separation between the anodic and cathodic peaks, ΔE_p, was in the range 90–140 mV for a sweep rate of 200 mV/s. With our cell configuration,[20] these properties are consistent with this being a reversible electron-transfer process.

Exhaustive electrolyses on dichloromethane solutions of both $[Cr(NO)(CNR)_5]^{n+}$ (n = 1 or 2 for R = $CHMe_2$ or CMe_3) afforded the corresponding oxidized or reduced species.[21] Both processes are accessible chemically, as we have already described.

In comparing the voltammetric half-wave potentials of $[Cr(NO)(CNR)_5]PF_6$ with those of their amine-substituted analogues (Table I and Figure 1),[22] we see that the $E_{1/2}$ values of the latter species are shifted to more negative potentials. This trend reflects the ability of NO and RNC ligands to better stabilize the lower oxidation state Cr(0), and amine ligands to better stabilize the Cr(I) oxidation state. This correlates with the coordinated amine being the better σ donor and poorer π acceptor.

The halide-substituted compounds are different in comparison to the previously discussed complexes (Table I and Figure 1c). The 17-electron chloride containing species exhibit an irreversible reduction at $E_{p,c} \simeq -0.45$ V. This is illustrated in Figure 1c for $[Cr(NO)(CNCMe_3)_4Cl]PF_6$. Following reduction at −0.46 V, the return sweep reveals the appropriate coupled oxidation wave at $E_{p,a} \simeq -0.32$ V ($i_{p,a}/i_{p,c} \ll 1$) and the appearance of a couple at $E_{1/2} = -0.06$ V ($E_{p,a} - E_{p,c}$ = 130 mV) associated with a new (and as yet unidentified) chemical species. Bulk electrolysis at a potential of −0.8 V produces a solution which is devoid of starting complex and now exhibits couples at $E_{1/2} = -0.06$ V (the major constituent) and $E_{1/2} \simeq +0.35$ V (presumably $[Cr(NO)(CNCMe_3)_5]^{n+}$), signifying the formation of chemical products. The electrochemical behavior of $[Cr(NO)(CNCHMe_2)_4Cl]PF_6$ and the bromide complexes $[Cr(NO)(CNR)_4Br]PF_6$ (R = CMe_3 or C_6H_{11}) are similar to this although the reduction of the bromides ($E_{1/2}$ = −0.34 V) more closely approaches reversibility. The chemical processes which follow these electrochemical reductions are the subject of a separate and more detailed study, the results of which we hope to make available in the near future.[23]

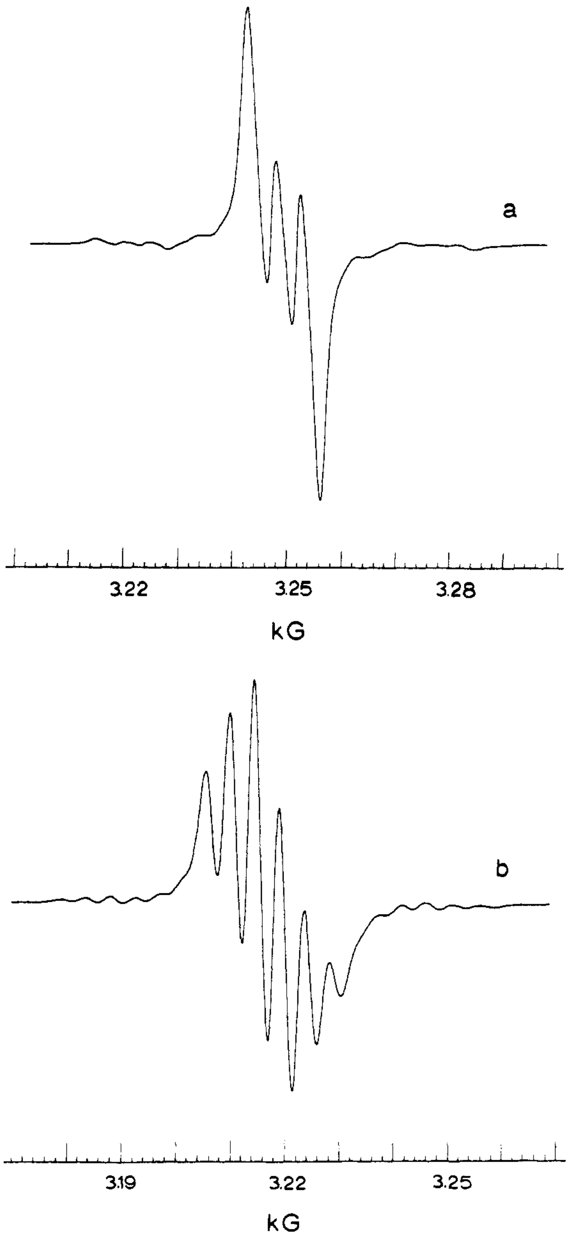

Figure 2. X-Band ESR spectra of dichloromethane solutions at room temperature containing (a) $[Cr(NO)(CNCMe_3)_4Cl]PF_6$ and (b) $[Cr(NO)(CNCMe_3)_4Br]PF_6$.

---

(20) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(21) Determination of n values for representative complexes (n is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials) confirmed that these are one-electron processes ($n = 1.0 \pm 0.1$). For example, n = 1.10 for the reduction at −0.2 V of $[Cr(NO)(CNC_6H_{11})_5](PF_6)_2$, while n = 1.05 for the corresponding reduction of $[Cr(NO)(CNCHMe_2)_5](PF_6)_2$.

(22) The $E_{1/2}$ value for the $[Cr(NO)(CNCMe_3)_5]^{1+,2+}$ couple (+0.35 V vs. SCE) agrees well with the value reported by Lloyd and McCleverty[4] in their earlier study of the monocationic salt $[Cr(NO)(CNCMe_3)_5]PF_6$ (+0.31 V vs. SCE in CH_2Cl_2–0.05 M Et_4NClO_4). However, these workers report a second couple (2+,3+) at +1.04 V which we do not observe. In a related electrochemical study of the methyl isocyanide derivative $[Cr(NO)(CNMe)_5]PF_6$ it was claimed[4] that the (1+,2+) and (2+,3+) couples were at +0.21 and +0.79 V vs. SCE. We prepared this complex by the method of Lloyd and McCleverty[4] and confirmed the couple at the lower potential (+0.27 V vs. SCE under our experimental conditions). Once again we did not find a second couple up to the potential limit of +1.6 V. Accordingly, we attribute the couples at the more positive potentials to contamination by impurities.

The decomposition of solutions containing the $[\mathrm{Cr(NO)(CNR)_4(amine)}]\mathrm{PF_6}$ complexes to $[\mathrm{Cr(NO)(CNR)_5}]^+$ (vide supra) can also be detected through cyclic voltammetric measurements. When a dilute solution of $[\mathrm{Cr(NO)(CNCMe_3)_4(NH_2CHMe_2)}]\mathrm{PF_6}$ was allowed to stand for several hours, the resulting cyclic voltammogram ($E_{1/2} = +0.21$ V) revealed a new couple due to $[\mathrm{Cr(NO)(CNCMe_3)_5}]\mathrm{PF_6}$ beginning to grow in at $E_{1/2} = +0.35$ V.

Magnetic moments were determined on dichloromethane solutions of the complexes by the Evans method (Table II).[10,11] The 18-electron $[\mathrm{Cr(NO)(CNR)_5}]\mathrm{PF_6}$ and $[\mathrm{Cr(NO)(CNR)_4(amine)}]\mathrm{PF_6}$ series were, as expected, diamagnetic, while $[\mathrm{Cr(NO)(CNR)_5}](\mathrm{PF_6})_2$ and chloride-substituted $[\mathrm{Cr(NO)(CNR)_4X}]\mathrm{PF_6}$ complexes exhibited magnetic moments of 1.5–1.7 μ_B.

The X-band ESR spectra of the paramagnetic complexes were also recorded and are presented in Table II. The ligand hyperfine interaction with the nitrosyl nitrogen ($I(^{14}\mathrm{N}) = 1$) is the salient feature of the spectra, as each signal is split into a triplet with $A(^{14}\mathrm{N}) \simeq 5$ G. This is illustrated in Figure 2a in the case of a dichloromethane solution of $[\mathrm{Cr(NO)(CNCMe_3)_4Cl}]\mathrm{PF_6}$. Hyperfine interaction with the active chromium nuclei ($I(^{53}\mathrm{Cr}) = {}^3/_2$; 9.54% abundance) is in accord with the spin Hamiltonian $H = -g\beta HS + AIS$. Four signals of equal intensity are predicted from this interaction, but the center two peaks are obscured by the much more intense signal associated with the nonactive nuclei. Each signal of this quartet, for which $A(^{53}\mathrm{Cr}) \simeq 18$ G, is further split by ligand hyperfine interaction with the nitrosyl nitrogen and finally presents itself as a weak quartet of triplets overlayed by the much more intense triplet signal associated with the nonactive chromium nuclei (Figure 2a).

For further examination of this ligand hyperfine splitting, a solution of $[\mathrm{Cr(NO)(CNCMe_3)_4(NH_2CMe_3)}]\mathrm{PF_6}$ was oxidized electrochemically to the 17-electron $[\mathrm{Cr(NO)(CNCMe_3)_4(NH_2CMe_3)}]^{2+}$ species. Once again, the characteristic ligand hyperfine splitting by only one nitrogen ($A(^{14}\mathrm{N}) = 5.4$ G) was seen at the expected g value of 1.99. Additional ligand hyperfine interaction due to the amine nitrogen was not detected.

In the case of $[\mathrm{Cr(NO)(CNCMe_3)_4Br}]\mathrm{PF_6}$ and its cyclohexyl isocyanide analogue, a six-line ESR spectrum is observed (Figure 2b) in addition to the weak side bands resulting from hyperfine interaction with the spin-active nuclei of chromium. The increase in complexity of these spectra relative to the chloride-containing derivatives almost certainly results from additional ligand hyperfine interaction with the bromine nuclei ($I(^{79}\mathrm{Br}) = I(^{81}\mathrm{Br}) = {}^3/_2$). That this additional splitting is due to the increased sensitivity of bromine relative to chlorine in detecting spin density and not to changes in the distribution of unpaired spin is suggested for several reasons. First, the inherently greater sensitivity of bromine is seen in the predicted hyperfine coupling constants. For an unpaired valence s electron on bromine the isotropic coupling is 7800 G (^{79}Br) or 8400 G (^{81}Br) while for chlorine the value is only 1680 G (^{35}Cl) or 1395 G (^{37}Cl).[25] In addition, the consistency in $\mathrm{A}(^{14}\mathrm{N})$ between the chloride and bromide complexes, as well as the pentakis(isocyanide) compounds, suggests that the distribution of spin density is relatively constant throughout this series. Further evidence for this is seen in the IR spectra of the chloride and bromide complexes which are quite similar (see ν(NO) and ν(C≡N) values in Table I), implying a similar effect of chloride and bromide upon the Cr–NO bonding. A signal split into six components (as in the bromide complexes) could result if $A(^{14}\mathrm{N}) \simeq A(^{79}\mathrm{Br}), A(^{81}\mathrm{Br}) \simeq 5$ G. In such an event, the triplet of quartets which is expected if $\mathrm{A}(^{14}\mathrm{N}) > \mathrm{A}(^{79}\mathrm{Br}), \mathrm{A}(^{81}\mathrm{Br})$ would coalesce to a signal comprising six lines with approximate relative intensities 1:2:3:3:2:1 (Figure 2b).[26]

Acknowledgment. We thank the National Science Foundation (Grant CHE79-09233) for support of this research.

Registry No. $[\mathrm{Cr(NO)(CNCMe_3)_5}](\mathrm{PF_6})_2$, 76482-54-7; $[\mathrm{Cr(NO)(CNCHMe_2)_5}](\mathrm{PF_6})_2$, 82583-25-3; $[\mathrm{Cr(NO)(CNC_6H_{11})_5}](\mathrm{PF_6})_2$, 82583-27-5; $[\mathrm{Cr(NO)(CNCMe_3)_5}]\mathrm{PF_6}$, 51406-87-2; $[\mathrm{Cr(NO)(CNCHMe_2)_5}]\mathrm{PF_6}$, 82583-29-7; $[\mathrm{Cr(NO)(CNC_6H_{11})_5}]\mathrm{PF_6}$, 82583-31-1; $[\mathrm{Cr(NO)(CNCMe_3)_4(NH_2CMe_3)}]\mathrm{PF_6}$, 82583-33-3; $[\mathrm{Cr(NO)(CNCMe_3)_4(piperidine)}]\mathrm{PF_6}$, 82583-35-5; $[\mathrm{Cr(NO)(CNCMe_3)_4(NH_2CHMe_2)}]\mathrm{PF_6}$, 82583-37-7; $[\mathrm{Cr(NO)(CNCHMe_2)_4(piperidine)}]\mathrm{PF_6}$, 82583-39-9; $[\mathrm{Cr(NO)(CNCMe_3)_4Cl}]\mathrm{PF_6}$, 82089-40-5; $[\mathrm{Cr(NO)(CNCHMe_2)_4Cl}]\mathrm{PF_6}$, 82583-41-3; $[\mathrm{Cr(NO)(CNCMe_3)_4Br}]\mathrm{PF_6}$, 82583-43-5; $[\mathrm{Cr(NO)(CNC_6H_{11})_4Br}]\mathrm{PF_6}$, 82583-45-7; $[\mathrm{Cr(CNCMe_3)_6}](\mathrm{PF_6})_2$, 75215-52-0; $[\mathrm{Cr(CNCHMe_2)_6}](\mathrm{PF_6})_2$, 82583-47-9; $[\mathrm{Cr(CNC_6H_{11})_6}](\mathrm{PF_6})_2$, 80083-26-7.

---

(23) Room-temperature conductivity measurements were carried out on $\sim 10^{-3}$ M acetonitrile solutions of representative complexes. Molar conductivity values (in Ω^{-1} cm^2 mol^{-1}) are as follows: $[\mathrm{Cr(NO)(CNCMe_3)_5}](\mathrm{PF_6})_2$, $\Lambda_M = 263$; $[\mathrm{Cr(NO)(CNCMe_3)_5}]\mathrm{PF_6}$, $\Lambda_M = 128$; $[\mathrm{Cr(NO)(CNCMe_3)_4Cl}]\mathrm{PF_6}$, $\Lambda_M = 126$; $[\mathrm{Cr(NO)(CNCMe_3)_4Br}]\mathrm{PF_6}$, $\Lambda_M = 195$. The first three values characterize these complexes as 2:1 or 1:1 electrolytes[24] and demonstrate the covalently bound nature of the chloride. The somewhat larger value for the bromide complex most likely reflects its partial decomposition in this solvent, a conclusion that is supported by cyclic voltammetry measurements on acetonitrile solutions of this complex (containing 0.1 M TBAH as supporting electrolyte).

(24) Geary, W. J. *Coord. Chem. Rev.* 1971, *7*, 81.

(25) Atkins, P. N.; Symons, M. C. R. "The Structure of Inorganic Radicals"; Elsevier: Amsterdam, 1967; p 21.

(26) **Note added in proof**: Since this paper was submitted, a study of nitrosylchromium complexes has been reported (Herberhold, M.; Haumaier, L. *Chem. Ber.* 1982, *115*, 1399) in which the Cr(I) species $[\mathrm{Cr(NO)(CNCMe_3)_5}](\mathrm{PF_6})_2$ and $[\mathrm{Cr(NO)(CNCMe_3)_4Cl}]\mathrm{PF_6}$ were synthesized by a procedure different from ours.