been used to determine intranuclear distances and molecular conformations.[8]

We have previously assigned the resonances in the A_5CoImH^{3+} complex[3] based on the magnitude of the $\Delta\delta$ excursion on deprotonation of the coordinated imidazole. In comparison of the C-4 and C-5 H excursions, the site closest to the protonation (C-4 H) undergoes the largest excursion. The C-2 H is at lowest field by a considerable amount, and its assignment can be easily confirmed by deuterium exchange prior to complex synthesis.[3]

The T_1 values reported in Table I for compounds **1-6** confirm and extend our previous assignment. An isolated proton in the C-2 position (compounds **1**, **4**, and **5**) has a longer T_1 in the deuterium-exchanged complex by a factor of 3–4. With an adjacent methyl group (compound **2**) to provide a competitive relaxation source, the T_1 at C-2 H still lengthens by a factor of 2 in the deuterated ammine complex. The same trend follows for the T_1 values of protons at the C-5 position (compounds **1–4**, and **6**). When the adjacent ammine ligands are exchanged for deuterium, the T_1 values are much longer. A similar pattern is also reflected in the T_1 values of methyl (compound **3**, **5**, and **6**) adjacent to ammine ligands. In addition to the dipolar interaction with the ammine protons, other relaxation pathways are available to the protons of the methyl groups. Thus, the effect is not nearly as dramatic as in the more isolated aromatic protons.

The chemical shifts in compounds **4** and **5** have been assigned by Shepard et al.[4] based on an X-ray structure. Our assignments are of the same order, although the chemical shifts are slightly different due to pH and ionic strength effects.

The same pattern continues in the bis(ethylenediamine) complexes (compounds **7–9**), with imidazole protons adjacent to exchangeable ethylenediamine protons having much longer T_1's in the deuterium-exchanged complexes.

In the tridentate histidine complex (compound **10**) only the proton at C-2 and the proton at the α-carbon of the amino acid show a large T_1 change when the ethylenediamine and histidine amino protons are exchanged for solvent deuterium. This is consistent with the previously reported X-ray structure.[6]

Protons that are spatially close and interact by a dipolar relaxation mechanism show an enhancement of intensity in one peak when the other is saturated; the nuclear Overhauser effect.[8] The NOE's presented in Table III follow the T_1 trends in Table II. In each case where a T_1 lengthened on deuterium exchange of the ammine ligand protons, a NOE is observed on irradiation of the ammine ligand protons. A comparison of the tables shows that either method can be used to assign resonances or isomers.

The NOE results for the ethlenediamine complexes (compounds **7–9**) are surprisingly different. Although the NH resonances have quite similar chemical shifts, substantiating that these are all cis complexes, the NOE's to ligand imidazole protons are quite selective. One possible explanation is that the methyl imidazoles have different conformational rotamer populations than unsubstituted imidazole. The details of NOE's in these complexes will be the subject of a future study.

Conclusion

The T_1's and NOE's reported here result in unambiguous assignments of proton resonances and linkage isomers in Co(III) complexes. The methods should be general and apply to other ligands such as pyrazines, tetrazoles, and pyridines and other diamagnetic, exchange-inert metal centers such as Ru(II), Os(II), Pt(II), Pt(IV), Pd(II), and Pd(IV). Two-dimensional NMR techniques relying on the NOE (NOSEY)[10] can also be used to make the assignments. ^{13}C assignments can be made from the proton assignments by using single-frequency off-resonance decoupling or a two-dimensional heteroscalar-correlated $^{13}C\{^1H\}$ NMR spectra.[10] The method should also have potential for ligand assignment and NH resonance assignment in metalloproteins.

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Registry No. **1**, 38716-02-8; **2**, 91209-43-7; **3**, 89955-97-5; **4**, 89922-05-4; **5**, 89955-98-6; **6**, 91209-45-9; **7**, 60314-38-7; **8**, 60314-39-8; **9**, 95250-94-5; **10**, 88657-78-7; deuterium, 7782-39-0.

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Gas-Phase Structure of Pentacarbonyl(trifluoromethyl isocyanide)chromium, $(CF_3NC)Cr(CO)_5$

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Although alkyl and aryl isocyanides and their transition-metal complexes have been known for a long time and have been studied extensively,[2] very little is known about isocyanides bearing strong electron-withdrawing groups, especially perfluoroalkyl or -aryl groups. The availability of an efficient method for preparing trifluoromethyl isocyanide[3] has led to studies of this molecule,[4] including its ligand behavior. The IR spectra of the complexes $(CF_3NC)M(CO)_5$ (M = Cr, W)[5] indicate that CF_3NC is a strong π acceptor ligand. The PE spectra[6] and XPS spectra[7] of $(CF_3NC)Cr(CO)_5$ confirm this result. Since the structure of the CF_3NC ligand provides direct information on the π acceptor properties of this ligand,[8] we have studied the gas-phase structure of the chromium complex by electron diffraction. Our prime interest in this study is the geometry of the CF_3NC group.

The scattering intensities have been recorded with the Balzers gas diffractograph KD-G2[9] at two camera distances (25 and 50 cm) and an accelerating voltage of about 60 kV. The sample was kept at 35 °C during the experiment (mp 26 °C), and the inlet system and nozzle were kept at 40 °C. The pressure in the diffraction camera was about 10^{-6} torr. Two plates for each camera distance were evaluated by the usual procedures,[10] and the averaged molecular intensities are presented in Figure 1.

A preliminary structural model was derived from the analysis of the radial distribution function (Figure 2). For a linear $CNCF_3$ ligand a strong peak around 5.1 Å, corresponding to the three Cr...F distances, is expected. Such a strong peak, however, is not observed in this distance range, indicating a bent $CNCF_3$ structure.

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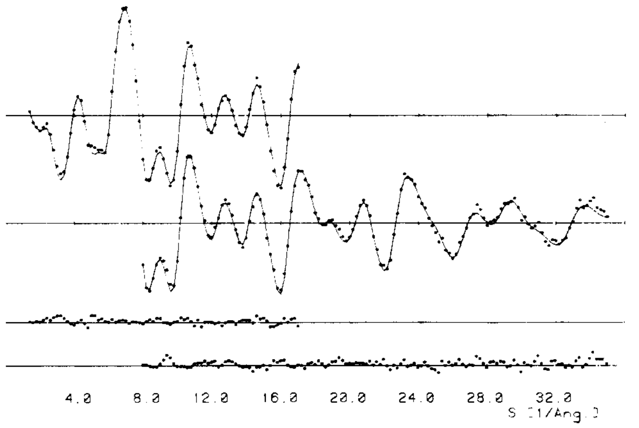


Figure 1. Experimental (...) and calculated (—) molecular intensities and differences.

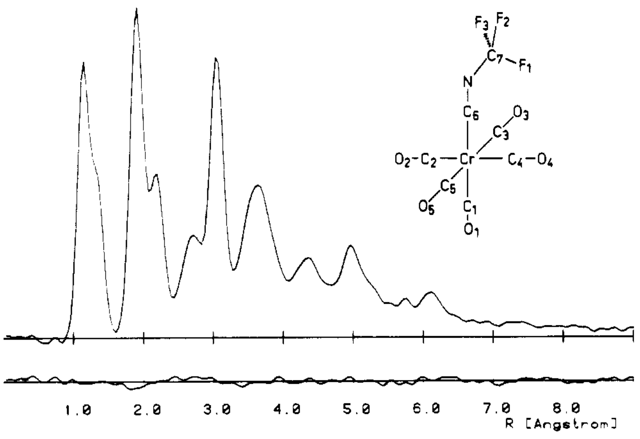


Figure 2. Experimental radial distribution function and difference curve.

A series of models with various C_6NC_7 bond angles and positions of the CF_3 group were considered. Good agreement between model and experiment was obtained for C_6NC_7 at ~140°, the CF_3 group eclipsing the $C_6{=}N$ bond and the N—C_7 bond eclipsing one of the equatorial Cr—C bonds. The calculated radial distribution function, however, is not very sensitive toward slight torsion of the CF_3 group around the N–C_7 bond or torsion of the NCF_3 group around the Cr–C_6 bond. The preliminary structural model was then refined in a least-squares analysis of the molecular intensities. A diagonal-weight matrix[10] was applied to the intensities, and scattering amplitudes and phases of J. Haase[11] were used. All Cr–C bond lengths were assumed to be equal. Attempts to refine the Cr–C_6 bond length seperately resulted in large correlations and standard deviations larger than the difference between Cr–C_6 and the other Cr–C bond lengths. C_{3v} symmetry was assumed for the CF_3 group and C_{4v} symmetry for the $Cr(CO)_5$ rest. Constraints for the vibrational amplitudes are evident from Table I. In the final least-squares analysis eight geometric parameters were refined simultaneously together with the vibrational amplitudes. The results are summarized in Table I. Some bond lengths (C=N/C=O and C—F/N—C) are not resolved in the radial distribution function. Since the number of "characteristic features" (peaks or shoulders) is larger than the number of geometric parameters, these bond lengths are determined indirectly through nonbonded distances. Nevertheless, error limits (3σ values) for some of the relevant bond lengths in the isocyano group are large due to high correlations between parameters (Table II). The value for the CNC angle is, of course, an "effective" value due to vibrational effects. Such shrinkage effects may be large for quasilinear molecules but are by experience small for bent molecules or groups. In the microwave spectrum no symmetric top μ_a transitions were observed, thus excluding the possibility of a quasilinear CNC group.

Table I. Results of Least-Squares Analysis (Atom Numbering in Figure 2; Error Limits in Last Digit, 3σ Values)

(a) Geometric Parameters (r_a Values): Distances (Å) and Angles (deg)

C=O (p_1)	1.140 (3)	$(Cr{-}C)_{av}$ (p_5)	1.918 (3)
C=N (p_2)	1.220 (16)	FCF (p_6)	108.2 (1.1)
C–F (p_3)	1.338 (11)	C_6NC_7 (p_7)	142 (4)
N–C (p_4)	1.40 (3)	C_1CrC_2 (p_8)	87.2 (1.4)

(b) Vibrational Amplitudes (Å)

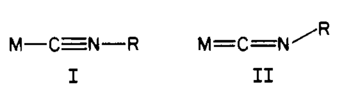
atom pr	dist		amp	atom pr	dist		amp
C=O	1.14	u_1	0.038 (4)	$C_2\cdots C_4$	3.82		0.070^a
C=N	1.22			$C_1\cdots C_6$	3.83		
C–F	1.34	u_2	0.051 (9)	$O_1\cdots O_2$	4.21	u_8	0.223 (44)
N–C	1.40			$O_2\cdots O_3$	4.31		
Cr–C	1.92	u_3	0.058 (3)	$O_2\cdots N$	4.48		
F···F	2.16	u_4	0.058 (17)	$Cr\cdots C_7$	4.33	u_9	0.206 (68)
N···F	2.25			$Cr\cdots F_1$	4.40		
$C_6\cdots C_7$	2.48			$C_2\cdots O_4$	4.96	u_{10}	0.085 (21)
$C_1\cdots C_2$	2.64	u_5	0.141 (17)	$C_6\cdots O_1$	4.96		
$C_2\cdots C_5$	2.70			$C_1\cdots N$	5.04		
$C_2\cdots C_6$	2.77			$Cr\cdots F_2$	5.15	u_{11}	0.237 (76)
$C_6\cdots F_1$	2.88		0.075^a	$O_2\cdots O_4$	6.09		0.100^a
Cr···O	3.05	u_6	0.060 (4)	$O_1\cdots N$	6.18		
Cr···N	3.13			$X\cdots Y^b$	3.95–4.90		0.250^a
$C_6\cdots F_2$	3.33		0.150^a	X···Y	5.14–5.94		0.280^a
$C_1\cdots O_2$	3.52	u_7	0.169 (22)	X···Y	6.15–8.14		0.400^a
$C_2\cdots O_3$	3.60						
$C_6\cdots O_2$	3.68						
$C_2\cdots N$	3.75						

[a] Not refined. [b] X, Y = C, O, F.

Table II. Correlation Coefficients with Values Larger Than 0.6

p_3/p_4	−0.83	p_3/u_2	0.81
p_3/p_6	0.66	p_4/u_2	−0.79
p_4/p_6	−0.74	p_6/u_2	0.78
p_7/p_8	−0.76	p_7/u_7	0.68
p_2/u_1	−0.65	p_8/u_7	−0.86

The structure of the $Cr(CO)_5$ group compares well with the parameters for $Cr(CO)_6$ obtained in an early electron diffraction study:[12] Cr—C = 1.918 (3) vs. 1.92 (4) Å and C=O = 1.140 (3) vs. 1.16 (5) Å. The slight distortion of the $Cr(CO)_5$ group from the octahedral configuration (C_1CrC_2 = 87.2 (1.4)°) is possibly an effect of large amplitude bending vibrations. The prime interest in this study is the structure of the trifluoromethyl isocyanide ligand. The bonding in metal isocyanide complexes can be discussed on the basis of two resonance forms:[2,8]



Increasing contribution of II decreases the CNR angle, and according to ab initio calculations,[8] this angle decrease is directly related to the amount of π back-donation from the metal to the ligand. Thus, the strong bending of the $CNCF_3$ group in the chromium complex (CNC = 142 (4)°) indicates strong π back-donation from chromium to the C=N bond. Parallel with the bending of the trifluoromethyl isocyanide we observe lengthening of the C=N bond (1.220 (16) vs. 1.171 (3) Å for the free molecule[4a]). Similar CN bond lengths (1.22 (1) and 1.24 (1) Å) have been determined in a crystal structure analysis of $Fe_3(\mu\text{-}CNCF_3)(CO)_{11}$,[13] which contains the isocyanide ligand in a bridging position. The weakening of this bond is also demonstrated by the vibrational frequency, which decreases from 2133 cm^{-1} in the free molecule[3] to 1950 cm^{-1} in the complex.[5] Entirely different ligand properties of CF_3NC and CH_3NC are demonstrated by the shift of the vibrational C=N stretching frequencies, which

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in the later case *increase* from 2158 cm^{-1} in the free molecule to 2195 cm^{-1} in the complex.[14]

To our knowledge the structure of $(CO)_5Cr(CNCH_3)$ has not been determined. The CNC angle in pentacarbonyl(isocyanide)chromium complexes with known structure is between 168.5 (4)° in $(CO)_5CrCNCN$[15] and 176.0 (3)° in $(CO)_5CrCNCCo(CO)_3$,[16] and the C═N bonds (1.160 (5) and 1.167 (5) Å) are not lengthened. Small CNC angles down to 133.1 (8)° have been observed in $Fe(CN\text{-}t\text{-}Bu)_5$,[17] but there are no competing strong π acceptors present in this complex.

The strong difference between CH_3NC and CF_3NC in ligand behavior can be rationalized by the difference in the energies of the π^* LUMO. The energy of the π^* orbital is considerably lower in CF_3NC (0.125 au[18]) than in CH_3NC (0.215 au[8]), and lowering of this orbital increases the π acceptor ability of the ligand.

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Registry No. $(CF_3NC)Cr(CO)_5$, 88902-50-5.

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Effect of Nitrogenous Bases on the Electrochemical Oxidation of a Bis(phosphine)-Bridged Tetrakis(isocyanide)rhodium(I) Dimer

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In recent years there have been several reports of studies involving bis(phosphine)-bridged tetrakis(isocyanide)rhodium(I) dimers.[1-4] We have previously reported that the electrochemical behavior of binuclear Rh(I) complexes of the type $[Rh_2(dpm)_2(RNC)_4][PF_6]_2$ (dpm = $Ph_2PCH_2PPh_2$) is strongly solvent dependent.[1] In the noncoordinating solvent CH_2Cl_2, a quasi-reversible one-electron transfer is observed at +0.60 V (vs. SCE). An irreversible electron transfer corresponding to the removal of a second electron is observed near the solvent limit. In CH_3CN, the second one-electron oxidation occurs at less positive potentials and is more readily observed. It was concluded that the removal of a second electron from the $[Rh_2(dpm)_2(RNC)_4][PF_6]_2$ complexes in the coordinating solvent CH_3CN leads to a binuclear Rh(II) species that is stabilized by the coordination of solvent molecules. The dimeric cation was formulated as $[Rh_2(dpm)_2(RNC)_4(CH_3CN)_2]^{4+}$.

The ability of CH_3CN to facilitate the removal of a second electron from the binuclear Rh(I) complex suggested that there might be a correlation between the peak potential for the removal of the second electron and the basicity of the ligands coordinating in the transannular positions of the dimeric cation shown in Figure 1. To test this hypothesis we have investigated the electrochemical behavior, via cyclic voltammetry, of $[Rh_2(dpm)_2(n\text{-}C_4H_9NC)_4][PF_6]_2$ in the presence of pyridine and several substituted pyridines with different σ donor abilities. During our investigation of the tetrakis(isocyanide)rhodium(I) dimers a report of a similar study involving tetrakis(carboxylato)rhodium(II) dimers appeared.[5]

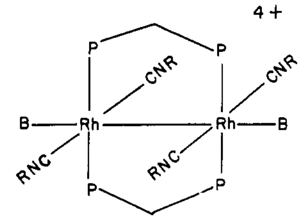

Figure 1. Proposed structure of the rhodium(II) diadduct $[Rh_2(RNC)_4(dpm)_2(B)_2][PF_6]_4$. The phenyl groups have been omitted from the bis(phosphine) ligands.

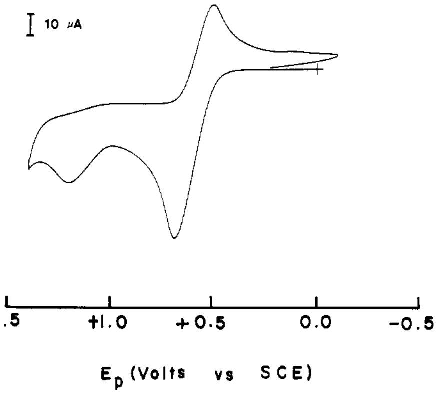

Figure 2. Cyclic voltammogram of $[Rh_2(n\text{-}C_4H_9NC)_4(dpm)_2][PF_6]_2$ in CH_2Cl_2 and 0.1 M TBAH (sweep rate 100 mV s^{-1}).

Experimental Section

Materials. The $[Rh_2(dpm)_2(n\text{-}C_4H_9NC)_4][PF_6]_2$ was prepared according to literature procedures.[2,3] Pyridine was stored over KOH and distilled from BaO immediately before use. All substituted pyridines (Aldrich) were reagent grade and were used as received. The dichloromethane (Fisher) was the spectroanalyzed grade and was used without further purification. The tetrabutylammonium hexafluorophosphate (TBAH) was prepared from $(n\text{-}C_4H_9)_4NI$ and KPF_6 in water and was recrystallized five times from acetone–water and dried under vacuum.

Instrumentation. All cyclic voltammetric experiments were performed at 25 °C with a function generator of the design of Woodward and co-workers[6] and a Princeton Applied Research Model 364 polarographic analyzer. The experiments were conducted with a Pt-inlay (Beckman) working electrode, a Pt-grid counter electrode, and a saturated calomel reference electrode (SCE). All voltammograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder.

Results and Discussion

The cyclic voltammogram of a 1.0 mM solution of $[Rh_2(n\text{-}C_4H_9NC)_4(dpm)_2][PF_6]_2$ in CH_2Cl_2 and 0.1 M TBAH is shown in Figure 2. The quasi-reversible couple at +0.60 V has been previously shown[1] to result from a one-electron transfer. The oxidation process occurring at +1.3 V is the irreversible transfer of a second electron. In the presence of a coordinating species, the second oxidation peak moves to less positive potentials, indicating that the oxidation process occurs more readily in the presence of a Lewis base. This shift in oxidation potential is indicative of stabilization of the Rh(II) dimer through coordination of the Lewis base. The Lewis bases used in this study are substituted pyridines.

Figure 3 shows the oxidation peaks for $[Rh_2(n\text{-}C_4H_9NC)_4(dpm)_2][PF_6]_2$ in the presence of the weak base 3-cyanopyridine and the stronger base 3,4-dimethylpyridine. There are two general trends evident from the voltammograms, with each trend being a function of the basicity of the substituted pyridine. The first is the decrease in the cathodic peak current for the quasi-reversible couple as the base strength increases. This behavior is consistent

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