Contribution from the Department of Chemistry, University of Missouri, Columbia, Missouri 65201,
and the Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, Brazil

Carbon-13 and Proton Nuclear Magnetic Resonance Spectra of Some Pentacyanoferrate(II) Complexes[1]

JOHN M. MALIN,*[2] CHARLES F. SCHMIDT, and HENRIQUE E. TOMA

Received May 7, 1975 AIC50303W

Carbon-13 and proton nuclear magnetic resonance spectra have been obtained for a number of iron(II) complexes $Fe(CN)_5L^{n-}$ in aqueous solution. For ligands L related to pyridine and pyrazine the effects of N-coordinated $Fe(CN)_5^{3-}$ on the proton and ^{13}C spectra are similar, showing downfield shifts for α carbons ($\sim$8 ppm) and hydrogens ($\sim$0.6 ppm) and smaller, upfield shifts for β and γ carbons and their substitutents. The cyano resonances in $Fe(CN)_5L^{n-}$(aq) are shifted upfield according to the sequence L = pyridine $\sim$ 4-methylpyridine < isonicotinamide $\sim$ cyanide $\sim$ pyrazine < *N*-methylpyrazinium $\sim$ dimethyl sulfoxide << NO^+. The results are discussed in terms of the character of the Fe^{II}–L bond and compared with the proton magnetic resonance spectra of several analogous Ru(II) complexes.

Introduction

Interest in the nature of metal-to-ligand π bonding has led us to the characterization of a number of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{n-}$.[3-5] Various lines of inquiry, utilizing visible–uv spectra and the relative susceptibilities of the complexes to oxidation and to ligand substitution, indicate an increase in $M \rightarrow L$ π back-donation from $Fe(CN)_5^{3-}$ to the ligand L in the order L = 4-methylpyridine < pyridine < isonicotinamide $\sim$ pyrazine < *N*-methylpyrazinium < S-bonded dimethyl sulfoxide.

We report here proton and carbon-13 chemical shifts for the above complex ions, as well as carbon-13 shifts for the ferrocyanide and nitroprusside ions. Variations in the shifts are systematic and can be compared with the complexes' other properties. The ordering of the cyano shifts is in some respects like trends that have been observed for $\delta(^{13}CO)$ in metal carbonyl complexes.

Experimental Section

Pentacyanoferrate(II) Complexes. The various organic ligands were purified and their pentacyanoferrate(II) complexes prepared as the sodium salts from $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ according to procedures described previously.[3,4] A new complex ion, the pyrazine-bridged binuclear species $[Fe(CN)_5pyrFe(CN)_5]^{6-}$ was prepared in solution from stoichiometric amounts of pyrazine and sodium pentacyanoammineferrate(II) hydrate. In all cases the starting material was synthesized from sodium nitroprusside[6] and recrystallized several times from saturated ammonia solution at 0°. Anal. Calcd for $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$: C, 18.4; N, 25.7; H, 2.7. Found: C, 18.3; N, 25.6; H, 2.6.[7]

Preparation of Pentaammine(*N*-methylpyrazinium)ruthenium(II) Tribromide. A 1.5-g amount of $Ru(NH_3)_5Cl_3$, prepared according to the method of Vogt et al.,[8] was dissolved in 1 l. of sodium acetate–acetic acid buffer solution (pH 4.5) and treated with zinc amalgam in argon atmosphere for 30 min. This solution was added to 100 ml of deaerated solution containing 5.5 g of *N*-methylpyrazinium iodide,[9] with continuous argon bubbling. A red-violet color developed slowly and after 5 hr the reaction was considered to be complete. The products were charged onto a column of cation-exchange resin (Bio-Rad AG 50W-X2, H^+ form) and were subsequently eluted with HCl solutions of increasing concentrations (0.5–5.0 *M*). At least two side products were obtained in small amounts in this preparation: a reddish fraction which was elutable with dilute acid solution and an intensely blue product which was released only on treatment with 5 *M* HCl. The major product, deep violet, was eluted with 3 *M* acid and concentrated by evaporation of the solution at room temperature and reduced pressure using a rotary evaporator. When the solution volume had been reduced to a few milliliters, 2 g of lithium bromide and 20 ml of ethanol were added and the solution was evaporated in vacuo to dryness. The residue was dissolved in the minimum quantity of water and 100 ml of methanol at 50°C was added. After maintaining the resulting solution at ice–salt bath temperature for 12 hr, small, hygroscopic violet–black crystals were collected by filtration and recrystallized several times from methanol–water solution. Anal. Calcd for $[Ru(NH_3)_5C_5H_2H_7]Br_3\cdot 2H_2O$: C, 10.7; N, 17.6; Br, 43.0. Found: C, 10.5; N, 17.9; Br, 42.8.[7]

Proton Magnetic Resonance. Spectra were recorded using a Varian T-60 spectrometer at a probe temperature of 33°. Solutions of the sodium pentacyanoferrate(II) complexes (0.1–0.3 *M*) of pyridine, isonicotinamide, 4-methylpyridine, pyrazine, and *N*-methylpyrazinium and of the pentaammine(*N*-methylpyrazinium)ruthenium(II) bromide salt were prepared by dissolving each complex in deuterium oxide containing some free ligand (0.2–0.1 *M*). The chemical shifts of free and bound ligands were independent of concentration within the limited ranges employed and within experimental error (±0.05 Hz). Chemical shifts are given with respect to TMS. The methyl resonance of 10^{-2} *M tert*-butyl alcohol (δ_{TMS} 1.20 ppm) was used as the internal standard.

Carbon-13 Magnetic Resonance. Proton-decoupled carbon-13 Fourier transform spectra were taken at 31° with a Bruker HFX-90 spectrometer using methanol (δ_{TMS} 50.0 ppm) or dioxane (δ_{TMS} 67.4 ppm)[10] as internal standard. Aqueous solutions of the complexes (0.5–1 *M*, pH 7–8) were prepared with a small amount (ca. 10^{-2} *M*) of the unbound ligand present. Spectra of the aqueous, uncomplexed ligands at 1–2 *M* concentration were obtained separately. Small disagreements between our results for the free ligands and those already published are attributed to solvent effects.

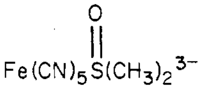
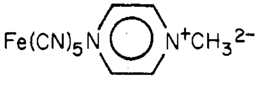
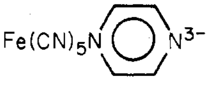
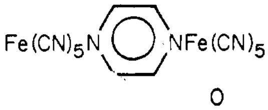
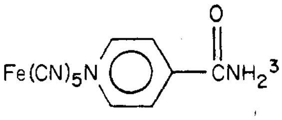
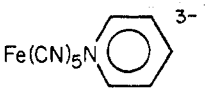
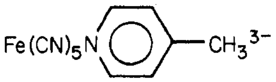
Results

^1H NMR Spectra of Pentacyanoferrate(II) Complexes. The δ values in this work were measured relative to internal *tert*-butyl alcohol and converted to the TMS scale by adding 1.2 ppm. Figure 1 shows the ^1H NMR spectra of aqueous pentacyano(pyridine)ferrate(II) and of free, aqueous pyridine. For the latter, the three multiplets with relative intensities 2:1:2 appearing at δ 8.45, 7.85, and 7.40 ppm have been assigned[11,12] to protons located at the α, γ, and β positions with respect to the pyridine nitrogen. In the spectrum of the complex the α-proton signal is centered at δ 8.78 ppm while those of the γ and β protons appear at 7.55 and 7.05 ppm, respectively.

These values are listed in Table I along with the results for complexes of 4-methylpyridine, isonicotinamide, pyrazine, *N*-methylpyrazinium, and dimethyl sulfoxide. Except for pyridine, free pyrazine, and the pyrazine-bridged binuclear complex, the aromatic ring protons showed A_2X_2 patterns with the multiplet due to the α protons in the complex always appearing downfield of the free ligand resonance. In the pentacyano(pyrazine)ferrate(II) complex, the single (free) pyrazine resonance at 8.55 ppm is split into two multiplets centered at 8.20 and 9.05 ppm. The downfield signal is assigned to the protons adjacent to $Fe(CN)_5^{3-}$.

In the spectrum of uncomplexed *N*-methylpyrazinium ion, the downfield multiplet is assigned to the proton α to the methylated nitrogen. However, based on the results described above, we expect that the Fe(II) substituent should exert a particularly strong influence on the proton shifts of methylated

Table I. Magnetic Resonance Spectra of Aqueous Pentacyanoferrate(II) Complexes[a]

Complex	ΔE_{CT},[b] kK	$\Delta E(^1E(1) \leftarrow {}^1A_1)$,[c] kK	δ ($^{13}CN_{cis}$), ppm	δ ($^{13}CN_{trans}$), ppm	Position in L	δ(^{13}C),[d] ppm	δ(^{1}H),[d] ppm
$Fe(CN)_5NO^{2-}$		37.75[e]	135.1	133.2			
 $Fe(CN)_5\overset{\overset{O}{\parallel}}{S}(CH_3)_2^{3-}$		28.5	170.0	167.0	α	47.7 (39.7)	3.18 (2.65)
	15.1	26.3	172.3	166.2	α β γ-CH_3	159.8 (150.9) 133.2 (137.4) 49.0 (50.0)	9.70 (8.90) 8.20 (9.35) 4.15 (4.45)
	22.2		177.3	173.5	α β	153.2 (145.3) 143.0 (145.3)	9.05 (8.55) 8.20 (8.55)
	20.0		177.8	173	α	150.6 (145.3)	8.64 (8.55)
	23.0		180.0	175.8	α β γ γ-$CONH_2$	158.1 (150.0) 121.4 (122.8) 140.0 (142.1) 170.6 (171.2)	9.00 (8.60) 7.40 (7.65)
$Fe(CN)_6^{4-}$		37, 31[f]		177.0			
	27.6		180.2	177.1	α β γ	156.8 (149.3) 124.3 (125.2) 136.7 (138.3)	8.78 (8.45) 7.05 (7.40) 7.55 (7.85)
	28.1		179.3	176.7	α β γ γ-CH_3	156.3 (149.6) 125.1 (125.9) 148.2 (149.1) 20.9 (21.1)	8.60 (8.20) 6.95 (7.15) 2.30 (2.30)

[a] Chemical shifts measured relative to internal standards and computed relative to external TMS. [b] Energies of metal-to-ligand charge-transfer bands at λ_{max}.[2] [c] Reference 5b. [d] Chemical shifts in L, both complexed and free. Free values are in parentheses. [e] Reference 17. [f] Respectively $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^1T_{1g} \leftarrow {}^1A_{1g}$.[18]

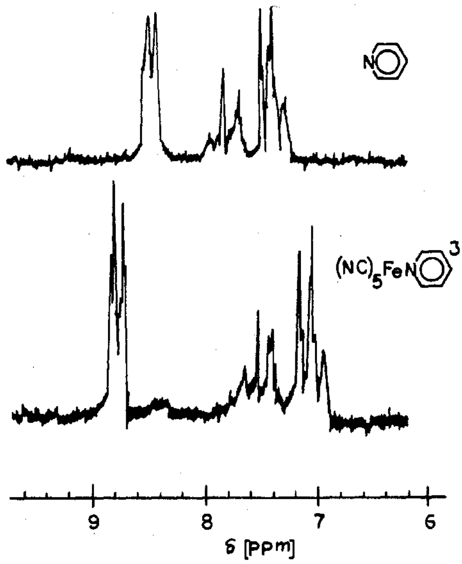


Figure 1. ^{1}H NMR spectra of pyridine and of pentacyano(pyridine)ferrate(II) in D_2O.

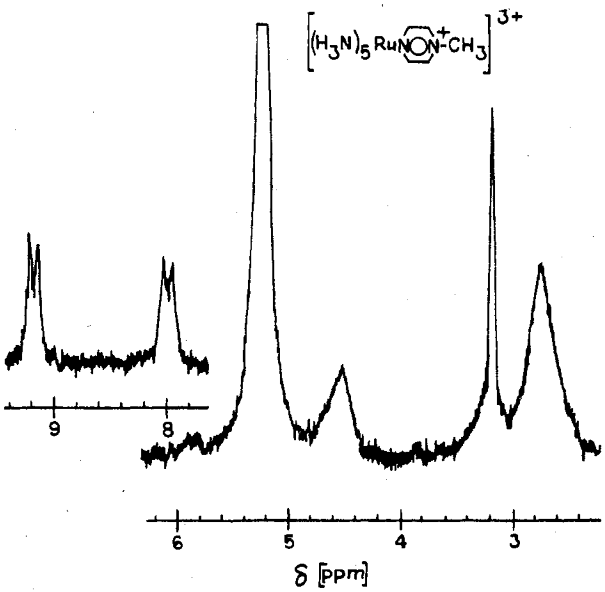
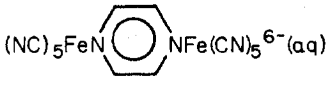


Figure 2. ^{1}H NMR spectrum of pentaammine(*N*-methylpyrazinium)ruthenium(II) in D_2O. Peaks are assigned as follows: ring protons ortho to Ru(II), 8.0 ppm; meta ring protons, 9.2 ppm; HDO, 5.2 ppm (shifted downfield by Co^{2+}); trans ammine, 4.5 ppm; *N*-methyl group, 3.2 ppm; and cis ammine, 2.7 ppm.

pyrazine. We therefore assign the downfield multiplet in the spectrum of the complex to the protons ortho to $Fe(CN)_5^{3-}$ and the upfield multiplet to the meta protons. In the binuclear species



only one proton resonance is seen, shifted 0.09 ppm downfield of the free pyrazine signal.

^{1}H NMR Spectrum of $Ru(NH_3)_5Mepyr^{3+}$(aq). The ^{1}H

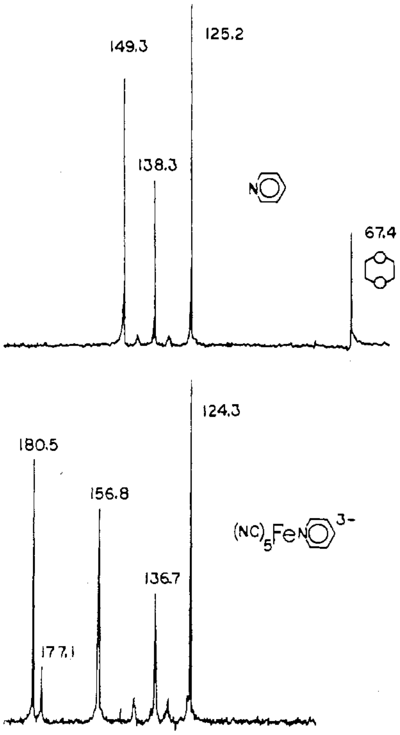


Figure 3. ^{13}C NMR spectra of aqueous pyridine (pH ~7.5) and the pentacyano(pyridine)ferrate(II) complex (1 *M*, pH ~7). The peaks at 180.5 and 177.1 ppm are assigned to the cis and trans cyano ligands, respectively.

NMR spectrum of the aqueous ion pentaammine(*N*-methylpyrazinium)ruthenium(II) is shown in Figure 2. At 9.2 and 8.0 ppm are seen peaks due to the ring protons of *N*-methylpyrazinium. The upfield signal is assigned to those ortho to Ru(II) by analogy with the results of Lavallee and Fleischer,[12] who found pronounced upfield shifts for aromatic ring protons at that location. The multiplet at 9.2 ppm is assigned to protons meta to Ru(II). The strong absorption at 5.2 ppm is due to HDO which, in this case, is shifted ca. 0.7 ppm downfield by addition of a small amount of cobalt(II) chloride.[13] Shifting of the solvent peak unmasks a new resonance at 4.5 ppm. This broad absorption and the similar, stronger signal at 2.7 ppm diminish with time ($t_{1/2} \approx 1$ week at pD 5–6). These two peaks are assigned respectively to the trans and cis ammines while the remaining, sharp resonance at 3.2 ppm is assigned to the *N*-methyl group.[14]

Carbon-13 Nuclear Magnetic Resonance Spectra of Pentacyanoferrate(II) Complexes. Proton-decoupled Fourier transform ^{13}C NMR spectra of aqueous pyridine (ca. 2 *M*) and the pentacyano(pyridine)ferrate(II) complex (1 *M*) are given in Figure 3. In the pyridine spectrum the peaks due to the α-, γ-, and β-carbon nuclei appear at 149.3, 138.3, and 125.2 ppm, respectively.[15] For the complex the corresponding signals appear at 156.8, 136.7, and 124.3 ppm. Separate resonances are observed for the cis and trans cyano groups. The latter, assigned because it is the smaller of the two, appears at 177.1 ppm while the former is seen at 180.5 ppm. Our results and assignments for nine iron(II) cyanide complexes are summarized in Table I.

A discrepancy exists between our value of the ^{13}C chemical shift of $Fe(CN)_6^{4-}$(aq) and the previously reported result, δ 71.3 ppm.[16] We suggest that the sign of the chemical shift relative to the external standard signal (C_6H_6) was listed incorrectly in the earlier work.

Discussion

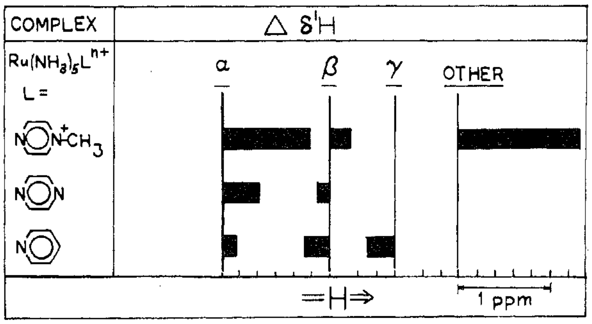
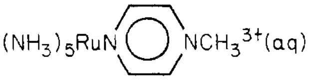


Figure 4. $\Delta\delta(^1H)$, the changes in proton chemical shifts at various positions in L for three $Ru^{II}(NH_3)_5L^{n+}$(aq) complexes, computed relative to the aqueous, free ligand resonances. Data for the pyridine and pyrazine complexes are from ref 12.

Chemical Shifts of L in $Ru^{II}(NH_3)_5L^{m-}$(aq). In the work of Lavallee and Fleischer[12] on the ^{1}H NMR spectra of pentaammineruthenium(II) complexes of pyridine and pyrazine, the signals of β and γ ring protons were observed downfield of the free ligand resonances. Since this result was important to our interpretations of the $Fe(CN)_5L^{N-}$(aq) spectra, we obtained for comparison the ^{1}H NMR spectrum of the pentaammine(*N*-methylpyrazinium)ruthenium(II) complex



In this species upfield shifts of the bound ligand signals were thought more likely than in the pyridine complex because *N*-methylpyrazinium is a stronger π acceptor and a weaker base than either pyridine or pyrazine. For the Ru(II) complex above, the β and *N*-methyl proton signals were observed to be shifted upfield of the free ligand resonances by 0.15 and 1.30 ppm, respectively. In Figure 4 the changes in chemical shift ($\Delta\delta(^1H)$) due to complex formation are compared for pyridine, pyrazine, and *N*-methylpyrazinium.

Two sets of authors[12,19] have discussed the electronic effects that are considered to be responsible for the chemical shifts of Ru(II)-coordinated aromatic N heterocycles. Both concluded that an increase in the shielding of γ and, possibly, β protons indicates increased electron density at the carbon atoms to which they are attached. Thus, in Figure 4 the trends at these positions, including the *N*-methyl group, are consistent with an increase in dπ–pπ back-donation which, in the case of the Mepyr$^+$ complex, overshadows the inductive effect of bipositive Ru(II). Observations that the complexes' metal-to-ligand electron-transfer band energies decrease and their Ru(II)–Ru(III) oxidation potentials become more negative in the order L = pyridine, pyrazine, N-methylpyrazinium support this conclusion.[20]

For the α protons of the pentaammineruthenium(II) complexes of pyridine and pyrazine, Lavallee and Fleischer observed marked upfield shifts, relative to the free ligand signals. These were ascribed to the "paramagnetic" anisotropy of Ru(II), arising because of temperature-independent paramagnetism expected of the metal center. We note in Figure 4 that the upfield α shifts of Ru(II)-coordinated ligands increase in the order pyridine < pyrazine < Mepyr$^+$. This result could perhaps be caused by variations in the "paramagnetic" anisotropy effect, but it suggests that the degree of dπ–pπ back-bonding also influences the chemical shifts of the α hydrogens.

Chemical Shifts of L in $Fe^{II}(CN)_5L^{m-}$(aq). The effects of N-coordinated $Fe(CN)_5^{3-}$ on the proton and carbon nuclear magnetic resonance spectra of several aromatic N heterocycles are represented in Figure 5. As with the Ru(II) complexes, measurements of relative oxidation potentials, complexation constants, and the energies of the metal-to-heterocycle electron-transfer transitions (ΔE_{CT} in Table I) have been

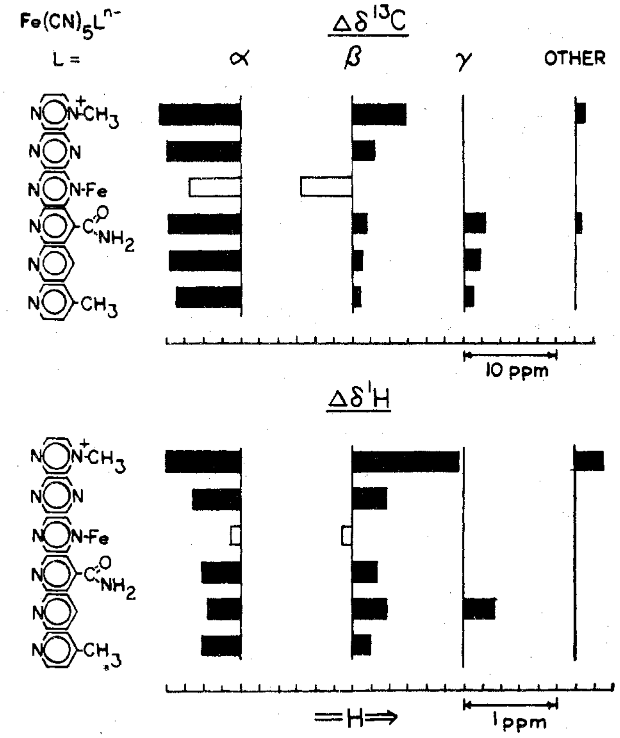


Figure 5. Effects of the $Fe(CN)_5{}^{n-}$ substitutent on the carbon and proton chemical shifts of five aqueous aromatic N heterocycles.

interpreted to mean that back-bonding to L increases in the order 4-methylpyridine ~ pyridine < isonicotinamide ~ pyrazine < Mepyr+. Moving up this series of pentacyanoferrate(II) complexes one sees in Figure 5 that the upfield shifts observed at the β, γ, and "other" positions tend to increase. This trend is offered as evidence for an increasing importance of shielding due to dπ–pπ back-bonding, relative to deshielding caused by the inductive effect of iron(II). The close resemblence in the carbon and hydrogen chemical shift patterns is consistent with a common chemical shift mechanism, based on charge density at the β- and γ-carbon atoms. In the pentacyano(*N*-methylpyrazinium)ferrate(II) ion, the upfield shift of the *N*-methyl protons (0.3 ppm) is smaller than that observed for the pentaammine(*N*-methylpyrazinium)-ruthenium(II) complex (1.3 ppm). This supports an earlier conclusion[5a] that back-bonding from $Fe(CN)_5{}^{3-}$ is less extensive than in the pentaammineruthenium(II) complexes.

In considering a solvent effect on the chemical shifts of β and γ carbons we find that for pyridine in deuteriochloroform solution these signals appear at 124.2 and 136.2 ppm, respectively, slightly upfield of the corresponding resonances in the aqueous $Fe(CN)_5{}^{3-}$ complex. However, in the pyrazine case[21] an analogous comparison yields an upfield shift on complex formation that is slightly larger than that shown in Figure 5. Thus, when the shifts of pyridine and pyrazine in an aprotic solvent are compared with those in the aqueous pentacyanoferrate(II) complexes, the observation remains that complexation of the more strongly π-accepting ligand produces a larger upfield shift.

Figure 5 shows that the resonances of the α carbons and hydrogens in the pentacyanoferrate(II) complexes lie downfield of those of the free, aqueous ligands. A factor that could be partly responsible is the magnetic anisotropy of the neighboring cyanide ligands. This field-induced effect, which is observed in alkynes and nitriles, may be considered to arise from the movement of π electrons in a loop perpendicular to the triple-bond axis.[22,23] The circulating electrons generate a magnetic field that opposes the applied field experienced by nuclei located on the CN bond axis, producing a shielding effect. For nuclei localized at some distance perpendicular to the triple bond the induced field reinforces the applied field and the effect is a deshielding one. By construction of molecular models, one can show that the α hydrogens of aromatic heterocycles bound to $Fe(CN)_5{}^{3-}$ lie in the deshielded region. Similarly, the methyl protons of S-bonded dimethyl sulfoxide should be deshielded. We note in Table I that this is observed.

A downfield shift also would be predicted for the α-carbon atoms in the complexes. However, these are located at a greater distance from the cyano ligands than are the α protons. The predicted anisotropic effect would therefore be smaller for carbon than that observed for hydrogen (ca. 0.6 ppm). In fact, it is much larger (ca. 8 ppm).

The α-carbon and -hydrogen shifts cannot be understood as a simple inductive effect. Although the metal center in the complexes probably carries a fractional positive charge,[24] protonation of aromatic heterocycles at nitrogen normally produces a downfield α-proton shift and an upfield shift of the α carbons.[25] We suggest that the α shifts may be caused by the "paramagentic" anisotropy of Fe(II). In addition, they may be influenced by electric field effects arising from the dipole moments of the cyano ligands or of the iron(II)–cyanide bonds. Further experiments are planned to determine the relative importance of these and other possible influences in mixed metal–cyano complexes.

Cyano ^{13}C Resonances in $Fe^{II}(CN)_5L^{n-}(aq)$. Positions of the cis and trans cyano resonances for eight aqueous pentacyanoferrate(II) complexes and for ferrocyanide ion are given in Table I. The $^{13}CN^-$ chemical shifts range from δ 180.5 ppm (L = pyridine) to δ 133.2 ppm (in $Fe(CN)_5NO^{2-}(aq)$). In every case the cis cyano signal appears downfield of the smaller trans resonance.

Inspection of Table I reveals that as the ligands L become better π acceptors and poorer bases, the cyanide signals move upfield. The large shift for the nitroprusside ion is particularly interesting because NO^+ can be considered, on the basis of molecular orbital calculations[17,26] and from photoelectron spectroscopic measurements,[27] to be a powerful π acceptor in $Fe(CN)_5NO^{2-}$. Because the cyanide resonances are shifted to higher field for complexes in which the charge carried by the metal ion should be comparatively positive, a normal inductive effect cannot be invoked.

The results can be related to recent work on the carbon-13 magnetic resonance spectra of metal carbonyl complexes.[28–32] Several workers have attributed upfield shifts of bound ^{13}CO to a decrease in dπ–pπ back-donation from the metal center to CO. In this regard the results reported here are consistent with the calculations of Gray and coworkers[17,24] who found that back-bonding to the cyano ligands is greater in $Fe(CN)_6{}^{4-}$ than in $Fe(CN)_5NO^{2-}$.

However, the utility of the back-bonding argument in rationalizing ^{13}CO chemical shifts has been questioned.[33] Also, it is instructive to compare the δ values of some simpler cyanides. For $CN^-(aq)$ and neat CH_3CN and HCN these are 168.6,[34] 117.2,[35] and 110.9[36] ppm, respectively. Although various solvents and temperatures were employed in making these measurements, the perturbations from those sources are expected to be small within the wide range of chemical shifts that is covered. The comparison shows that the resonance of cyanide can be shifted to high field when an electron-withdrawing substituent is attached at carbon *even though π-bonding with that group is impossible.* The origin of the upfield shifts in $\delta(^{13}CN^-)$ may be an increase in the anisotropic shielding at carbon caused by polarization of cyano π electrons toward the carbon atom. Although this does not rule out the back-bonding chemical shift mechanism for metal complexes, it suggests that the degree of σ donation from the cyano carbon to the metal center is important in determining $\delta(^{13}\mathrm{CN})$. This concept seems to be useful in understanding not only our results but also the substantial trans effects observed in substituted cyanocobalamines.[37] Its significance for metal carbonyl complexes has been considered.[28-32] However, we note that a sophisticated analysis of $^{13}\mathrm{CN}^-$ and $^{13}\mathrm{CO}$ chemical shifts, such as one given recently for hydrocarbons by Ellis, Maciel, and McIver,[38] is needed.

In Table I, systematic variations can be seen in the splitting between cis and trans cyanide signals. Among the complexes of aromatic N heterocycles (C_{2v} symmetry) this splitting increases as the back-bonding ability of L increases. The effect diminishes abruptly as the series of ligands reaches dimethyl sulfoxide and NO$^+$. It is evidently related to the fact that the π-acceptor orbitals of the latter two ligands are not prevented by symmetry from interacting simultaneously with all four cis cyano groups.

The known values of ΔE_{CT}, the energy of the metal-to-heterocycle electron-transfer band, and of $\Delta E(^1\mathrm{E}(1) \leftarrow {}^1\mathrm{A}_1)$, corresponding to the lowest observable d–d transition in each of the complexes, are given in Table I. We find no comprehensive relationship between the energies of either of these electronic transitions and the measured values of $\delta(^{13}\mathrm{CN}^-)$ in the complexes. The result can be contrasted with the outcome of a Mössbauer study of several of the complexes[5b] in which a linear relationship was found between the d–d excitation energies and measured isomer shifts. In that instance, the correspondence was expected because, for the set of Fe(CN)$_5$L^{n-} complexes, d–d transition energies normally increase and isomer shifts decrease according to the ability of the ligand L to augment the ligand field of Fe(II). On the other hand, the factor controlling the measured values of $\delta(^{13}\mathrm{CN})$ in the complexes appears to be the inductive influence of L, transmitted via the iron center. In this case the net effect of σ donation plus π back-donation in the Fe(II)–L bond need not correlate with the position of L in the spectrochemical series.

Acknowledgment. The authors gratefully acknowledge the assistance of Professor R. N. Loeppky in obtaining some of the carbon-13 spectra.

Registry No. Fe(CN)$_5$NO^{2-}, 15078-28-1; Fe(CN)$_5$S=O(CH$_3$)$_2$$^{3-}$, 56533-28-9; Fe(CN)$_5$(NC$_4H_4NCH_3$)$^{2-}$, 40299-79-4; Fe(CN)$_5$(NC$_4H_4$N)$^{3-}$, 40299-78-3; Fe(CN)$_5$(NC$_4H_4$N)Fe(CN)$_5$$^{6-}$, 56533-29-0; Fe(CN)$_5$(NC$_4H_4$C(C=O)NH$_2$)$^{3-}$, 40299-77-2; Fe(CN)$_6$$^{4-}$, 13408-63-4; Fe(CN)$_5$(NC$_5H_5$)$^{3-}$, 37475-75-5; Fe(CN)$_5$(NC$_5H_4$-4-CH$_3$)$^{3-}$, 37475-65-3; (H$_3$N)$_5$Ru(NC$_4H_4NCH_3$)Br$_3$, 48135-76-8; Ru(NH$_3$)$_5Cl_3$, 18532-87-1; ^{13}C, 14762-74-4.

References and Notes

(1) Presented at the 1974 Midwest Regional Meeting of the American Chemical Society, Iowa City, Iowa, Nov 6–8, 1974.

(2) To whom correspondence should be addressed at the University of Missouri.

(3) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039, 2080 (1973); **13**, 1772 (1974).

(4) H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, **12**, 2084 (1973).

(5) (a) H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, **97**, 288 (1975); (b) H. E. Toma, E. Giesbrecht, J. Malin, and E. Fluck, *Inorg. Chim. Acta.*, **14**, 11 (1975).

(6) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, 2nd ed., Academic Press, New York, N.Y., 1965, p 1511.

(7) Micoanalysis performed by Stanford Microanalytical Laboratory, Stanford University.

(8) L. H. Vogt, J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1167 (1965).

(9) C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, **72**, 2881 (1950).

(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 49.

(11) H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 1487 (1957).

(12) D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, **94**, 2583 (1972).

(13) J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 553 (1960); F. W. Breivogel, *Inorg. Chem.*, **9**, 983 (1970).

(14) A virtually identical spectrum has been obtained by R. Magnuson, Ph.D. Dissertation, Stanford University, 1973.

(15) R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc.*, **90**, 697 (1968).

(16) M. Schporer, G. Ron, A. Loenstein, and G. Navon, *Inorg. Chem.*, **4**, 358 (1965). Quoted in ref 10, p 216.

(17) P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).

(18) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

(19) R. D. Foust and P. C. Ford, *J. Am. Chem. Soc.*, **94**, 5686 (1972).

(20) (a) R. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970); (b) R. E. Shepherd and H. Taube, *ibid.*, **12**, 1392 (1973); (c) R. E. Shepherd, Ph.D. Dissertation, Stanford University, 1972; (d) C. Creutz and H.. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).

(21) Reference 10, p 240.

(22) L. M. Jackmann and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, U.K., 1969, p 93.

(23) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 441 (1971).

(24) A positive charge has been calculated for iron in Fe(CN)$_6$$^{4-}$ and in Fe(CN)$_5$NO^{2-}: J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 4260 (1968), and ref 17.

(25) References 10 (p 247) and 15.

(26) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **11**, 437 (1972).

(27) A. Calabrese and R. G. Hayes, *J. Am. Chem. Soc.*, **96**, 5054 (1974).

(28) O. A. Gansow, D. Schexnayder, and B. Y. Kunvia, *J. Am. Chem. Soc.*, **94**, 3406 (1972).

(29) B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 2012 (1973).

(30) P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1027 (1973).

(31) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973); G. M. Bodner and L. J. Todd, *ibid.*, **13**, 1335 (1974); G. M. Bodner, *ibid.*, **13**, 2563 (1974).

(32) H. Mahnke, R. K. Sheline, and H. W. Spiess, *J. Chem. Phys.*, **61**, 55 (1974).

(33) J. Evans and J. Norton, *Inorg. Chem.*, **13**, 3042 (1974).

(34) G. E. Maciel and D. A. Beatty, *J. Phys. Chem.*, **69**, 3920 (1965).

(35) G. A. Gray, G. E. Maciel, and P. D. Ellis, *J. Magn. Reson.*, **1**, 407 (1969).

(36) G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **90**, 4666 (1968).

(37) T. E. Needham, N. A. Matwiyoff, T. E. Walker, and H. P. C. Hogenkamp, *J. Am. Chem. Soc.*, **95**, 5019 (1973).

(38) P. D. Ellis, G. E. Maciel, and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **94**, 4069 (1972).

Contribution from the Departments of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5,
and the State University of New York at Binghamton, Binghamton, New York 13901

Ortho Metalation and Donor Ligand Complexation Reactions of *O*-Alkyl Thioesters with Diiron Enneacarbonyl

HOWARD ALPER*[1] and CHEN KAO FOO

Received April 17, 1975 AIC50270K

Reaction of various *O*-methyl aryl thioesters with diiron enneacarbonyl in benzene at room temperature afforded a sulfur-donor ligand ortho-metalated complex as the minor product, the major component being an isomeric oxygen, sulfur-donor diiron hexacarbonyl complex. For different *O*-alkyl thiobenzoates, increasing the effective bulk of the alkoxy group afforded more of the ortho-metalated complex. The effect of ring strain on the course of these reactions is noted.

The intramolecular ortho metalation of nitrogen, phosphorus, sulfur, and oxygen ligands is a subject of considerable current interest.[2] For example, treatment of thiobenzophenones with diiron enneacarbonyl [Fe$_2$(CO)$_9$] affords