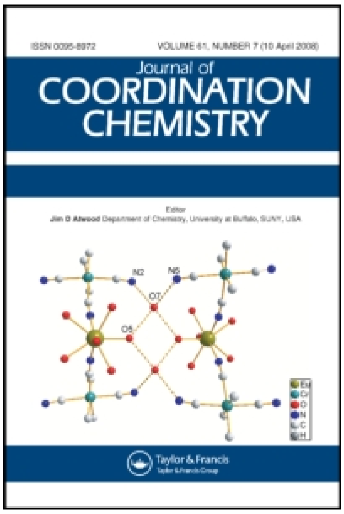

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ANALYSIS OF BONDING IN CATIONIC CYCLOPENTADIENYLIRON COMPLEXES BY MÖSSBAUER AND INFRARED SPECTROSCOPY

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ANALYSIS OF BONDING IN CATIONIC CYCLOPENTADIENYLIRON COMPLEXES BY MÖSSBAUER AND INFRARED SPECTROSCOPY

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The σ and π bonding characteristics of acetonitrile, pyridine, ethylene and triphenylphosphine have been studied in several metal environments by combined use of Mössbauer and infrared spectroscopy. Comparisons with earlier studies identify ligand $(\sigma + \pi)$ capacities that increase in the order $CH_3CN < C_5H_5N \simeq C_2H_4 < PPh_3 < CNMe \simeq C(NHMe)_2 < CO$. Pyridine is found to be a stronger σ donor than either acetonitrile or ethylene but weaker than triphenylphosphine. Significant π acceptor capacity is evident in both ethylene and triphenylphosphine. Spectroscopic analyses of relative ligand bond strengths are corroborated by the differing tendencies of the complexes in the study to undergo dissociation and disproportionation.

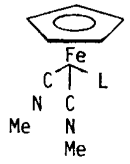
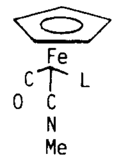
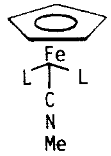
INTRODUCTION

Mössbauer isomer shift data has been found to be useful in comparing relative $(\sigma + \pi)$ effects of specific ligands in compounds where the remaining metal environment is fixed and where changes in metal electron density are not masked by the presence of too many strong π acceptor ligands.[1-4] Under these conditions infrared stretching frequencies of carbonyls and isocyanides are also sensitive to metal electron density and will reflect differences in the donor/acceptor capacities $(\sigma - \pi)$ of adjacent ligands. In closely related complexes the two methods may be combined to qualitatively separate donor/acceptor effects, as we have done for isocyanide, carbonyl, phosphine and diaminocarbene ligands in a series of cationic cyclopentadienyliron compounds.[5] Photochemical substitutions in this system have produced new complexes combining carbonyls and/or isocyanides with acetonitrile, pyridine, and ethylene ligands which, unlike earlier members of the series, display considerable differences in their tendency to dissociate the weaker ligand and disproportionate.[6] The relative σ donor and π acceptor bonding effects of these ligands can now be compared to those studied previously and can be related to the observed differences in complex stabilities.

EXPERIMENTAL

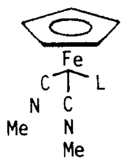
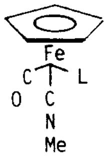
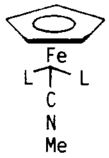
Our preparation of all of the compounds in Tables I and II has been described elsewhere in the literature.[6] A Mössbauer drive in the constant-acceleration mode was used for the experiments; the system was calibrated by using natural α-iron foil. All spectra were recorded at room temperature. Isomer shifts and quadrupole splittings were obtained by a least-squares fit to the Lorentzian. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer calibrated in the CO region with gaseous DCl.

TABLE I
Mössbauer — effect parameters[a] for the complexes.

Metal Environment	L	δ, mm/s	ΔE_Q, mm/s
	CH_3CN	0.224	2.08
	C_2H_4	0.181	1.79
	C_5H_5N	0.178	2.00
	PPh_3[b]	0.100	1.93
	CH_3CN	0.166	1.99
	C_5H_5N	0.157	1.98
	C_2H_4	0.149	1.75
	PPh_3[b]	0.056	1.88
	CH_3CN	0.371	2.26
	C_5H_5N	0.339	2.15
	PPh_3[b]	0.204	1.90

[a] Relative to natural α-iron foil. [b] Reference 5.

TABLE II
Infrared data[a] for the complexes.

Metal Environment	L	νCO cm^{-1}	νCNR cm^{-1}	k_{CO} mdyn/A	k_{CNR} mdyn/A
	CH_3CN		2202 2173		18.22
	C_2H_4		2214 2186		18.43
	C_5H_5N		2187 2154		17.94
	PPh_3[b]		2185 2153		17.89
	CH_3CN	2028	2222	16.45	18.76
	C_5H_5N	1999	2214	16.14	18.62
	C_2H_4	2029	2246	16.62	19.17
	PPh_3[b]	1995	2208	16.07	18.54
	CH_3CN		2208 2180		18.06
	C_5H_5N		2146		17.50
	PPh_3[b]		2149		17.56

[a] Recorded in chloroform. [b] Reference 5.

RESULTS AND DISCUSSION

The Mössbauer-effect parameters of the cationic complexes are listed in Table I. In general, the complexes exhibited well-resolved symmetric quadrupole doublet spectra; both lines in each pair have equal area. The full width at half maximum showed no systematic variations, lying between 0.26 and 0.31 mm/s with a possible error of ±0.005 mm/s. A typical spectrum, that of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)(PPh_3)]I$, is reproduced in Figure 1. Infrared spectral data in the carbonyl and isocyanide stretching region are reported in Table II. Solution spectra exhibited sharp intense CO and CNR bands from which stretching force constants were calculated according to the Cotton-Kraihanzel method.[7]

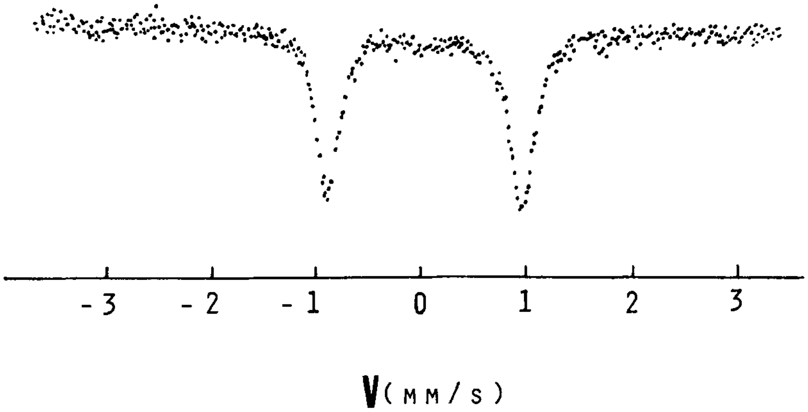


FIGURE 1 Mössbauer Spectrum of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)(PPh_3)]I$.

The relationship between Mössbauer isomer shifts and metal s electron density permits comparison of the total donor/acceptor capacity of two ligands when they are measured in otherwise identical environments. Lower values of δ reflect enhanced σ donation to metal d orbitals or greater retrodative π bonding from filled metal orbitals to empty ligand orbitals. A comparison of the δ values for acetonitrile, pyridine, ethylene, and triphenylphosphine in Table I with those of our previous work (identical experimental conditions) yields a series of $(\sigma + \pi)$ strengths where $CH_3CN < C_5H_5N \simeq C_2H_4 < PPh_3 < CNMe \simeq C(NHMe)_2 < CO$. The ordering is consistent in three separate metal environments and is similar to that reported for $[\eta^5\text{-}C_5H_5Fe(CO)_2L]^+$ complexes.[2] However, differences in isomer shifts are somewhat greater in the metal environments in Table I because π acceptance of excess metal electron density characteristic of the dicarbonyl complexes is reduced by isocyanide substitution.[5]

Quadrupole splittings of cyclopentadienyliron carbonyl or isocyanide complexes have generally varied little from a range of 1.9 ± 0.1 mm s^{-1} and have not been useful in analyzing bonding effects.[5] Adjustments in the bonding characteristics of these ligands, which can mask large increases in metal s electron density, are also believed to be effective in neutralizing changes in electron asymmetry about the metal.[2] While most of the complexes in Table I do show splittings in the expected range, values for the two disubstituted pyridine and acetonitrile complexes are considerably higher, as are their isomer shifts. Both parameters thus show the reduced compensating effect of the remaining isocyanide on the metal electron density.

The decreased value in isomer shift of pyridine complexes relative to those containing acetonitrile is due to the stronger σ-donating ability of pyridine since the π capacity of both ligands is considered to be negligible.[8,9] As a result isocyanide and carbonyl ligands in the pyridine complexes accept more electron density into antibonding orbitals and their ν_{CNR} and ν_{CO} values are also lower (Table II). The difference in donating strengths of the two ligands is reflected in the relative stabilities of their complexes, particularly in the $[\eta^5\text{-}C_5H_5Fe(CNMe)(L)_2]^+$ environment where dissociation of L and disproportionation to $[\eta^5\text{-}C_5H_5Fe(CNMe)_2L]^+$ occurred so much more rapidly for L = CH_3CN that ^{13}C characterization at 213 K was possible only for the pyridine complex.[6]

Combined Mössbauer and infrared data provide insight into the relative bonding properties of pyridine and ethylene since their $(\sigma + \pi)$ characteristics judged by isomer shifts are nearly identical but $(\sigma - \pi)$ differences cause ethylene complexes to have higher ν_{CN} and ν_{CO} values. Pyridine is therefore a stronger σ donor but π bonding to ethylene π^* orbitals equalizes the net effect of the two ligands on metal s density. However, differences in the nature of the bonding components resulted in the ethylene-metal bond being the weakest of those studied. Ethylene complexes disproportionated faster than those of either pyridine or acetonitrile and the *bis*ethylene complex was too unstable to be detected. Whereas the relative σ strengths of pyridine and ethylene are evident from the data in Tables I and II, a comparison of the ethylene and acetonitrile data shows only that $\pi C_2H_4 > \pi CH_3CN$. The increased stability of the acetonitrile complexes is therefore most likely due to a stronger σ bond.

Pyridine and triphenylphosphine complexes in all three metal environments have virtually the same carbonyl and isocyanide stretching frequencies but Mössbauer isomer shifts show PPh_3 to have much stronger $(\sigma + \pi)$ characteristics. Since the infrared data suggests that $\sigma_{PPh_3} - \pi_{PPh_3} = \sigma_{Pyr}(\pi_{Pyr}$ assumed to be O), isomer shifts are logical only if triphenylphosphine is a better σ donor than pyridine. Thus both σ and π components of the iron-phosphine bond should be stronger than those of iron-pyridine, a fact supported by the complete resistance of the phoshine complexes to dissociation.

A summary of the individual comparisons made possible by the combined Mössbauer and infrared data shows that the ligand $(\sigma + \pi)$ bonding characteristics in these cyclopentadienyl-iron complexes appear to stem from σ donation that increases in the series $C_2H_4 < CH_3CN < C_5H_5 < PPh_3$ combined with significant π acceptor capacity on the part of triphenylphosphine and ethylene.

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