(18) P. Brand and J. Schmidt, *Z. Anorg. Allg. Chem.*, **348**, 257 (1966).
(19) E. G. M. Tornqvist, C. Cozewith, and W. F. Libby, to be submitted for publication.
(20) J. P. Dahl and H. Johansen, *Theor. Chim. Acta*, **11**, 26 (1968).

(21) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).
(22) C. A. L. Becker, C. J. Ballhausen, and I. Trabjerg, *Theor. Chim. Acta*, **13**, 355 (1969).
(23) C. A. L. Becker and J. P. Dahl, *Theor. Chim. Acta*, **14**, 26 (1969).

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Relative Bonding Characteristics of Cationic Isocyanide, Carbonyl, and Related Complexes of Iron as Determined by Mössbauer and Infrared Spectroscopy[1]

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Mössbauer-effect isomer shifts in cationic cyclopentadienyliron complexes identify ligand ($\sigma + \pi$) bonding capacities to increase in the order $PPh_3 < CNMe \simeq C(NHMe)_2 < CO$. An analysis of substitution effects on isomer shifts in varying ligand environments illustrates the compensating effect of both carbonyl and isocyanide groups on metal electron density. In contrast, infrared force constants for carbonyl stretching modes decrease uniformly for a given substitution in each metal environment. Consideration of both isomer shifts and stretching force constants for isocyanides and diaminocarbenes distinguishes enhanced σ-donor capacities for the carbene that are paralleled by increased π acceptance on the part of the isocyanide. Both σ and π bonding are reduced in indenyl analogues of the cyclopentadienyl complexes since isomer shifts increase despite negligible differences in carbonyl stretching frequencies.

Introduction

Although Mössbauer spectroscopy is frequently used to characterize iron carbonyl complexes, care must be exercised in interpreting isomer-shift variations, particularly when correlations with carbonyl stretching force constants are made. Complexes containing three or more carbonyls have been shown to exhibit minimal differences in δ due to the capacity of these ligands to absorb excess metal electron density via π back-bonding.[3-5] It is therefore not unusual for significant differences in $C{\equiv}O$ stretching frequencies to be accompanied by nearly identical Mössbauer δ values.[3,4] Further, a change in the overall charge of the iron complex complicates isomer-shift comparisons and often prohibits meaningful correlation with other spectroscopic data.[6] However, Mössbauer studies of several closely related series of neutral or cationic cyclopentadienyliron complexes have been reported[7-10] and have permitted comparisons of relative ($\sigma + \pi$) effects for a variety of ligands in specific carbonyl-containing metal environments.

Research in our laboratory has been concerned with isocyanide and diaminocarbene complexes of iron[11,12] for which no Mössbauer data have been reported. Recent photochemical investigations of cationic species have extended this system to include complexes in which all carbonyls have been replaced.[13] As a result, Mössbauer data for these complexes have the potential of not only characterizing ligand ($\sigma + \pi$) effects but also of comparing more subtle bonding differences in analogous isocyanide and carbonyl systems.

Infrared stretching frequencies are also sensitive to the σ-donating and π-accepting abilities of accompanying ligands, but, unlike the isomer shift, the two factors oppose each other in their effect on carbonyl stretching.[14] Thus, whereas each technique is incapable of an independent assessment of relative donor–acceptor effects, the two in concert offer the possibility of qualitatively separating these factors—particularly where overall differences in structure are minimized.

Experimental Section

The following compounds were synthesized by literature methods: $CpFe(CO)_3{}^+PF_6{}^-$,[15] $CpFe(CO)_2(CNMe)^+I^-$,[16] $CpFe(CO)(CNMe)(PPh_3)^+I^-$,[17] $CpFe(CO)(PPh_3)[C(NHMe)_2]^+I^-$,[17] $CpFe(CO)(CNMe)_2{}^+PF_6{}^-$,[18] $CpFe(CO)(CNMe)[C(NHMe)_2]^+PF_6{}^-$,[17] $CpFe(CNMe)_3{}^+I^-$,[16] $InFe(CO)(CNMe)_2{}^+I^-$.[11]

$CpFe(CO)_2(PPh_3)^+PF_6{}^-$ was conveniently prepared by combining $CpFe(CO)_3{}^+PF_6{}^-$ with an excess of triphenylphosphine in dry acetone

Table I. Mössbauer-Effect Parameters[a]

	L	L'	L''	δ, mm/s	ΔE_Q, mm/s
	CO	CO	CO	−0.006	1.85
	CO	CO	PPh₃	0.014	1.81
	CO	CO	CNMe	−0.004	1.84
	CO	PPh₃	PPh₃	0.146	1.85
	CO	PPh₃	CNMe	0.056	1.88
	CO	PPh₃	C(NHMe)₂	0.053	1.91
	CO	CNMe	CNMe	0.024	1.87
	CO	CNMe	C(NHMe)₂	0.018	1.93
	CNMe	PPh₃	PPh₃	0.204	1.90
	CNMe	CNMe	C(NHMe)₂	0.062	1.90
	CNMe	CNMe	PPh₃	0.100	1.93
	CNMe	CNMe	CNMe	0.059	1.92
	CO	CO	CO	0.029	1.85
	CO	CNMe	CNMe	0.045	1.96
	CNMe	CNMe	PPh₃	0.125	2.03

[a] Relative to natural α-iron foil.

for 15 min. Concentration of the solvent followed by addition of ethyl ether resulted in an 81% yield of the product. This method of synthesis offers a savings in time and an increased yield over that reported previously.[19]

$CpFe(CO)(PPh_3)_2{}^+PF_6{}^-$ was synthesized by irradiation of $CpFe(CO)_2(PPh_3)^+PF_6{}^-$ and excess triphenylphosphine in dichloromethane for 4 h. The reaction mixture was chromatographed on alumina, the product eluting with CH_2Cl_2 as a broad orange band. The nonoptimized yield was approximately 63%. The synthesis of this complex has been reported previously by Treichel,[19] with $CpFe(CO)(PPh_3)I$ and excess PPh_3 in the presence of $AlBr_3$. The photolysis reaction, however, requires considerably less time in addition to increased yield.

$CpFe(CNMe)_2[C(NHMe)_2]^+I^-$ was synthesized by the reaction of methylamine with $CpFe(CNMe)_3{}^+I^-$ as described for analogous compounds.[20]

$InFe(CO)_3{}^+PF_6{}^-$ was prepared in the same manner as $CpFe(CO)_3{}^+PF_6{}^-$ by using $[InFe(CO)_2]_2$.

$CpFe(CNMe)_2(PPh_3)^+PF_6{}^-$, $CpFe(CNMe)(PPh_3)_2{}^+PF_6{}^-$, and $InFe(CNMe)_2(PPh_3)^+PF_6{}^-$ were prepared by irradiation of the appropriate carbonyl complex in the presence of triphenylphosphine.[13]

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 II. Infrared Data[a]

compd	ν_{CO}, cm⁻¹	ν_{CNR}, cm⁻¹	k_{CO}, mdyn/Å	k_{CNR}, mdyn/Å	compd	ν_{CO}, cm⁻¹	ν_{CNR}, cm⁻¹	k_{CO}, mdyn/Å	k_{CNR}, mdyn/Å
CpFe(CO)₃⁺PF₆⁻ [b]	2125, 2079		17.71		CpFe(CNMe)(PPh₃)₂⁺PF₆⁻		2149		17.56
CpFe(CO)₂(PPh₃)⁺PF₆⁻ [b]	2055, 2010		16.68		CpFe(CNMe)₂[C(NHMe)₂]⁺I⁻		2167, 2130		17.55
CpFe(CO)₂(CNMe)⁺I⁻	2078, 2038	2242	17.10	19.11	CpFe(CNMe)₂(PPh₃)⁺PF₆⁻		2185, 2153		17.89
CpFe(CO)(PPh₃)₂⁺PF₆⁻ [b]	1970		15.67		CpFe(CNMe)₃⁺I⁻		2176, 2213		18.21
CpFe(CO)(PPh₃)(CNMe)⁺I⁻	1995	2208	16.07	18.54	InFe(CO)₃⁺PF₆⁻ [b]	2117, 2072		17.59	
CpFe(CO)(PPh₃)[C(NHMe)₂]⁺I⁻	1958		15.48						
CpFe(CO)(CNMe)₂⁺PF₆⁻	2024	2228, 2207	16.54	18.70	InFe(CO)(CNMe)₂⁺I⁻	2020	2224, 2202	16.47	18.62
CpFe(CO)(CNMe)[C(NHMe)₂]⁺I⁻	1978	2197	15.80	18.35	InFe(CNMe)₂(PPh₃)⁺PF₆⁻		2187, 2155		17.92

[a] Unless otherwise noted, all samples were run in chloroform. [b] Recorded in dichloromethane.

Table III. Effects of Carbonyl Substitution

complex	L = CO → PPh₃			L = CO → CNMe		
	$\Delta\delta$, mm/s	Δk_{CO}, mdyn/Å	Δk_{CNR}, mdyn/Å	$\Delta\delta$, mm/s	Δk_{CO}, mdyn/Å	Δk_{CNR}, mdyn/Å
CpFe(CO)₂L⁺	0.020	−1.03		0.002	−0.61	
CpFe(CO)(CNMe)L⁺	0.060	−1.03		0.028	−0.56	
CpFe(CO)(PPh₃)L⁺	0.132	−1.01		0.042	−0.61	
CpFe(CNMe)₂L⁺	0.076		−0.82	0.035		−0.50
CpFe(CNMe)(PPh₃)L⁺	0.148		−0.99	0.044		−0.66

Results

Room-temperature Mössbauer-effect parameters of 15 cationic complexes are given in Table I. In general complexes exhibited well-resolved quadrupole doublet spectra with full widths at half-height between 0.26 and 0.31 mm/s. Values of the isomer shift are estimated to be accurate to ±0.005 mm/s.

Mössbauer spectra of two of the complexes in Table I, CpFe(CO)₃⁺PF₆⁻ and CpFe(CO)₂(PPh₃)⁺PF₆⁻, have been reported previously but for comparative purposes were re-measured under the experimental and calibration conditions of this study. Results for the two complexes are nonetheless in good agreement with those previously reported.[7-9] Cationic complexes were prepared as either I⁻ or PF₆⁻ salts. Differences in the identity of the anion did not affect Mössbauer parameters significantly, as verified by analysis of several of the complexes as both PF₆⁻ and I⁻ salts.

Infrared spectra 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.[21]

Discussion

Mössbauer isomer shifts of transition-metal complexes are useful in providing a sensitive indication of metal s electron density. A decrease in the value of δ reflects an increase in s density which can be prompted by enhanced ligand σ donation (to metal s orbitals) or by greater retrodative π bonding from filled metal d orbitals to empty ligand orbitals. A comparison of shift values before and after a given substitution thus distinguishes the (σ + π) character of the substituted ligand. Examination of the series of complexes CpFe(CO)₂L⁺ (Table I) reveals an increase in (σ + π) bonding in the order L = PPh₃ < CNMe ≃ C(NHMe)₂ < CO. Variation of the cationic metal environment does not alter the relative effect of these ligands on metal s density; the same order is evident in the series of compounds CpFe(CNMe)₂L⁺, CpFe(CO)- (CNMe)L⁺, CpFe(CO)(PPh₃)L⁺, and CpFe(CNMe)- (PPh₃)L⁺. The isocyanide and diaminocarbene (σ + π) properties can therefore be directly compared to the ligands

examined by Bancroft et al.[8] in the CpFe(CO)₂L⁺ series, where it was found that MeCN < C₂H₄ < C₅H₅N < PPh₃ < CO < CS. The description of isocyanides as better (σ + π) ligands than phosphines in cyclopentadienyliron compounds agrees with earlier data by Bancroft[22] and also by Mosbaek[23] for other iron systems.

The most striking aspect in comparing the values of Table I is the extent to which isomer shifts change as a function of metal environment upon carbonyl substitution. The changes in δ for replacement of carbonyl by triphenylphosphine and methyl isocyanide are summarized in Table III. The first three series show that as the carbonyl content of the metal environment decreases, ligand substitution exerts a greater effect. This type of compensating ability has been observed previously to be characteristic of carbonyl groups.[7,9] (It is not surprising that δ values of tricarbonyl Fe(CO)₃L₂ and tetracarbonyl Fe(CO)₄L complexes are essentially independent of the identity of L.[4,23]) The increase in electron density at iron from isocyanide substitution is less than that from phosphine substitution because of the closer correlation of (σ + π) effects of the former with carbonyls, as noted above.

The ability of isocyanide ligands to exert compensatory effects similar to carbonyls is also evident from Table III. A comparison of CpFe(CNMe)₂L⁺ and CpFe(CNMe)(PPh₃)L⁺ complexes shows that substitution effects on δ increase as isocyanide content decreases, particularly in the case of phosphine substitution. Similarly, the differences between the monocarbonyl complexes CpFe(CO)(CNMe)L⁺ and CpFe- (CO)(PPh₃)L⁺ must be attributed to the ability of the isocyanide ligand, relative to the phosphine, to partially offset the loss of one carbonyl in relieving metal d electron density. These observations parallel previous evidence from Mössbauer data for the participation of isocyanides as significant π receptors.[24] A leveling of the π-acceptor capacities of CNR and CO groups appears in CpFe(CO)(PPh₃)L⁺ and CpFe- (CNR)(PPh₃)L⁺ complexes. The effect of CO → PPh₃ or CO → CNMe substitution in L produces similar changes in δ in the two series of compounds, indicating that a majority of the charge increase remains on the metal.

Quadrupole splittings (ΔE_Q) of the complexes reported in Table I were essentially unaffected by changes in ligand

identity. The same observation has been made for other cyclopentadienyliron complexes.[7-9] Bancroft et al.[8] describe this invariance as a consequence of the cyclopentadienyl and carbonyl ligands' ability to substantially change their bonding properties so as to neutralize the changes in electron asymmetry. Clearly, in view of the consistency of ΔE_Q values in Table I, isocyanide and indenyl groups must adapt similarly. The failure to observe significant trends precludes further analysis of quadrupole splitting data.

The influence of π-acceptor ligands on Mössbauer isomer shifts can be corroborated by infrared spectra, since the occupation of ligand antibonding orbitals in groups such as CO and CNR decreases the bond order of the coordinated molecule. As a result, stretching force constants decrease markedly. Substitution of a carbonyl by triphenylphosphine results in an increase in metal electron density, presumably due to increased σ donation by the phosphine and failure of the same to act as a significant π acceptor. As a result, the excess electron density is conducted to the remaining carbonyl(s) and k_{CO} decreases. A similar though smaller decrease is anticipated for CO → CNMe substitution.[25] As seen in Table III, decreases in k_{CO} for isocyanide vs. phosphine substitution differ as expected. However, for a given carbonyl substitution k_{CO} of the remaining carbonyl(s) decreases uniformly despite considerable differences in metal environment. The Mössbauer isomer shift in these compounds then reflects the extent to which back-bonding has offset increased metal d electron density. In the case of the monocarbonyl complexes $CpFe(CO)(CNMe)(PPh_3)^+$ and $CpFe(CO)$-$(PPh_3)_2^+$ considerable density remains on the metal, but due to the π-acceptor ability of the isocyanide, as noted above, the increase in δ is only half as much in the former as in the latter compound. These observations explain why attempts to derive linear plots of k_{CO} vs. δ are frequently unsuccessful. Obviously differences in compensatory effects of compounds having unequal numbers of carbonyls would prohibit their quantitative comparison. Further, where carbonyl content is consistent, the presence of any other π-acceptor ligands would yield lower isomer shifts than anticipated, resulting in large deviations from linearity. Such deviations have been reported for neutral iron complexes containing the π-acceptor CN ligand.[7]

Isocyanide stretching frequencies also decrease notably upon CO → CNMe or CO → PPh$_3$ substitution, particularly in $CpFe(CNMe)_2L^+$ and $CpFe(CNMe)(PPh_3)L^+$ where carbonyls are absent and relative δ increases suggest partial compensatory π acceptance by isocyanide. It should be pointed out that coordinated isocyanides, unlike carbonyls, often exhibit stretching frequencies higher than the free ligand, a result attributed to the dominance of the σ-donor component of the metal–isocyanide bond.[26] Within the present series of complexes, the values of k_{CNR} for coordinated methyl isocyanide are also generally higher than the free ligand, which is not surprising in view of the overall positive charge on the complex. However, in $CpFe(CNMe)_2(PPh_3)^+$ the values of k_{CNR} for free and coordinated isocyanide are comparable, and in $CpFe(CNMe)(PPh_3)_2^+$ the value of the force constant has dropped below that of free methyl isocyanide, despite the positive charge of the complex.

An analysis of Mössbauer and infrared data is especially useful in comparing isocyanide and diaminocarbene ligands. Replacing an isocyanide with a diaminocarbene results in only slight changes in isomer shift (e.g., $CpFe(CNMe)_3^+$ → $CpFe(CNMe)_2[C(NHMe)_2]^+$; $\Delta\delta = +0.003$ mm/s), leading to the previous observation that total $(\sigma + \pi)$-bonding characteristics are very similar. However, stretching force constants for the remaining carbonyl and/or isocyanide ligands decrease drastically ($\Delta k_{CO} > 0.58$ mdyn/Å; $\Delta k_{CNR} > 0.34$ mdyn/Å) when CNMe → C(NHMe)$_2$ substitution occurs,

indicating that $(\sigma - \pi)$ effects are considerably different. Table II shows that decreases in k_{CO} and k_{CNR} for diaminocarbene substitution exceed even those resulting from replacement of isocyanide by triphenylphosphine. The only interpretation of these changes that is compatible with the Mössbauer data is that σ-donor ability of the carbene is much stronger than that of the isocyanide, but enhanced π acceptance by the isocyanide equalizes the effect of the two ligands on overall metal s electron density. This conclusion is in excellent agreement with Mössbauer studies of $[Fe(CNMe)_5(carbene)](PF_6)_2$ and $[Fe(CNMe)_4(carbene)_2](PF_6)_2$ complexes where partial center shifts and partial quadrupole splittings were used to compare relative donor and acceptor properties of carbene and isocyanide ligands.[27] Comparisons of k_{CO} and k_{CNR} for the complexes in Table II further imply considerably greater σ-donating ability for diaminocarbene ligands relative to triphenylphosphine and suggest that π bonding to vacant ligand orbitals in both is negligible relative to carbonyl and isocyanide coordination.

A reversal of the comparative Mössbauer and infrared effects occurs when one considers indenyl and cyclopentadienyl ligands. Complexes differing only in ring identity have virtually identical carbonyl and isocyanide force constants ($\Delta k_{max} = 0.11$ mdyn/Å), but isomer shifts increase by 0.20–0.35 mm/s upon indenyl substitution. The similarity of force constants in light of increased δ values implies nearly equal decreases in σ and π factors so that the difference (affecting ν_{CO} and ν_{CNR}) remains constant but the overall sum $(\sigma + \pi)$ is reduced. The result is the prediction of a weaker metal–indenyl vs. metal–cyclopentadienyl bond. Noting a similar invariance of ν_{CO} in cyclopentadienyl-, indenyl-, and fluoroenylmanganese tricarbonyl complexes, despite decreased stability in the latter cases, King and Efraty[28] have already suggested that both donor and acceptor characteristics of the cyclopentadienyl ligand decrease upon successive fusing of benzene rings. The increased Mössbauer isomer shifts confirm this to be the case in iron complexes, where similar decreases in indenyl complex stabilities are common.

The use of Mössbauer spectroscopy to assess the factors contributing to metal–ligand coordination is thus considerably aided by infrared force constant data. Analyzing differences in the variation of k and δ can often be more useful in delineating specific bonding properties than attempting their linear correlation.

Registry No. $CpFe(CO)_3^+PF_6^-$, 38834-26-3; $CpFe(CO)_2$-$(PPh_3)^+PF_6^-$, 12100-39-9; $CpFe(CO)_2(CNMe)^+I^-$, 53419-34-4; $CpFe(CO)(PPh_3)_2^+PF_6^-$, 12104-28-8; $CpFe(CO)(PPh_3)(CNMe)^+I^-$, 70130-43-7; $CpFe(CO)(PPh_3)[C(NHMe)_2]^+I^-$, 70130-44-8; $CpFe(CO)(CNMe)_2^+PF_6^-$, 70130-45-9; $CpFe(CO)(CNMe)[C(NHMe)_2]^+I^-$, 70130-46-0; $CpFe(CNMe)(PPh_3)_2^+PF_6^-$, 70130-48-2; $CpFe(CNMe)_2[C(NHMe)_2]^+I^-$, 70130-49-3; $CpFe(CNMe)_2$-$(PPh_3)^+PF_6^-$, 70130-51-7; $CpFe(CNMe)_3^+I^-$, 53419-37-7; InFe-$(CO)_3^+PF_6^-$, 70130-53-9; $InFe(CO)(CNMe)_2^+I^-$, 70130-54-0; $InFe(CNMe)_2(PPh_3)^+PF_6^-$, 70130-56-2.

References and Notes

(1) Presented in part at the 30th Southeastern Regional Meeting of the American Chemical Society, Savannah, GA, Nov 1978; see Abstracts No. 180.
(2) To whom correspondence should be addressed.
(3) H. L. Clarke and N. J. Fitzpatrick, *J. Organomet. Chem.* **66**, 119 (1974).
(4) L. Korecz, K. Burger, *Acta Chim. Acad. Sci. Hung.*, **58**, 253 (1968).
(5) D. H. Gibson, R. L. Vonnahme, P. J. Ouseph, and B. C. Parakkat, *J. Inorg. Nucl. Chem.*, **37**, 2340 (1975).
(6) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).

(7) G. L. Long, D. G. Alway, and K. W. Barnett, *Inorg. Chem.*, **17**, 486 (1978).
(8) G. M. Bancroft, K. D. Butler, L. E. Manzer, A. Shaver, and J. E. H. Ward, *Can. J. Chem.*, **52**, 782 (1974).
(9) K. Burger, L. Korecz, P. Mag, U. Belluco, and L. Busetto, *Inorg. Chim. Acta*, **5**, 362 (1971).
(10) M. J. Mays and P. L. Sears, *J. Chem. Soc., Dalton Trans.*, 1973 (1973).
(11) B. V. Johnson, D. P. Sturtzel, and J. E. Shade, *J. Organomet. Chem.*, **154**, 89 (1978).
(12) B. V. Johnson, J. E. Shade, and D. P. Sturtzel, *Inorg. Chim. Acta*, **32**, 243 (1979).
(13) B. V. Johnson and A. L. Steinmetz, to be submitted for publication.
(14) M. Bigorgne, *J. Organomet. Chem.*, **94**, 161 (1975).
(15) L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 39 (1968).
(16) J. A. Dineen and P. L. Pauson, *J. Organomet. Chem.*, **71**, 77 (1974).
(17) R. J. Angelici, P. A. Christian, B. D. Dombek, and G. A. Pfeffer, *J. Organomet. Chem.*, **67**, 287 (1974).
(18) C. E. Coffey, *J. Inorg. Nucl. Chem.*, **25**, 179 (1963).
(19) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).
(20) R. J. Angelici and L. M. Charley, *J. Organomet. Chem.*, **24**, 205 (1970).
(21) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); *Inorg. Chem.*, **2**, 533 (1963); F. A. Cotton, *ibid*, **3**, 702 (1964).
(22) G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, *J. Chem. Soc., A*, 3165 (1971).
(23) H. Mosbaek, *Acta Chem. Scand., Ser. A*, **29**, 957 (1975).
(24) G. M. Bancroft and E. T. Libbey, *J. Chem. Soc., Dalton Trans*, 2110 (1973).
(25) Quantitative comparisons of k_{CO} and k_{CNR} calculated from the Cotton–Kraihanzel approximation in mixed CO,CNR complexes are complicated by interaction between the ν_{CO} and ν_{CNR} frequencies: R. B. King and M. S. Saran, *Inorg. Chem.*, **13**, 74 (1974), and references therein. The values listed in Table II ignore these interactions for the same reasons cited by King. This approach is further justified by the lack of significant deviation in k_{CO} and k_{CNR} changes when substitutions in mixed CO,CNR complexes are compared with those of analogous CO or CNR complexes (e.g., Table III; effect of CO → PPh$_3$ on $\Delta k(CO)$).
(26) P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973).
(27) G. M. Bancroft and P. L. Sears, *Inorg. Chem.*, **14**, 2716 (1975).
(28) R. B. King and A. Efraty, *J. Organomet. Chem.*, **23**, 527 (1970).

Thermal Intramolecular Cobalt(III)–Iron(II) and Cobalt(III)–Titanium(III) Electron-Transfer Reactions Involving Outer-Sphere and Inner-Sphere Precursor Complexes
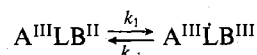
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Two binuclear cobalt(III) complexes containing a μ-[pyridine-4-carboxylato(O,O')-2,6-dicarboxylate] bridge (**1, 2**) react rapidly with [Fe(OH$_2$)$_6$]$^{2+}$ and [Ti(OH$_2$)$_6$]$^{3+}$, respectively, to form 1:1 complexes ([Co^{III}$_2$-L-M(OH$_2$)$_3$], L = bridging ligand, M = Fe(II) and Ti(III)) at pH 2–3 and 2:1 complexes ([Co^{III}$_2$-L-M-L-Co^{III}$_2$], M = Fe(II) and Ti(III)) at pH >4. Intramolecular rate constants for the one-electron transfer (ET) within the inner-sphere precursor complexes containing a Ti(III) center have been measured. No influence of the differing oxidizing abilities of the Co(III) centers (the nonbridging NH$_3$ ligands of **1** are substituted by 1,4,7-triazacyclononane in **2**) on the intramolecular reaction rate has been observed; alteration of the reducing power of Ti(III) in going from 1:1 to 2:1 complexes **6, 7** and **8, 9** exhibits a marked effect. This behavior is interpreted in terms of a "chemical" (two-step) mechanism: formation of a radical intermediate (i.e., the reduced bridging ligand) is considered to be the rate-determining step. In contrast, the transient 2:1 precursor complex **4** (Fe(II) being the weaker reductant) appears to react via resonance transfer. Outer-sphere reductions of some binuclear μ-carboxylato-cobalt(III) complexes by [Fe(dipic)$_2$]$^{2-}$ or [Ti(dipic)$_2$]$^-$ (dipic = pyridine-2,6-dicarboxylate) have also been studied. An outer-sphere association constant, K_o, and an intramolecular ET rate constant, k_{et}, have been determined for the reduction of the μ-(pyridine-4-carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)] cation by [Fe(dipic)$_2$]$^{2-}$ (74 M^{-1}, 3.7 × 10^{-3} s^{-1} at 25 °C; μ = 0.1 M). No difference in the reactivity of the outer-sphere (ion-pair) precursor complex and the structurally very similar inner-sphere precursor complex **4** is observed. This is taken as evidence that the uninterrupted bond system from Fe(II) to Co(III) in **4** does not provide a favorable electron pathway. A resonance transfer exhibiting the characteristics of an outer-sphere process is proposed for the intramolecular ET within **4**. In contrast, outer-sphere reductions of binuclear Co(III) complexes by [Ti(dipic)$_2$]$^-$ via ion-pair precursor complexes are shown to be less favorable than the corresponding intramolecular ET within the inner-sphere complexes **8** and **9**.

Introduction

The mechanism of thermal intramolecular electron transport between two metal ions which are connected by chemical bonds via an organic bridging ligand within a binuclear complex (inner-sphere precursor complex) has been conceptualized in terms of a "two-step" or "chemical" mechanism or, alternatively, a resonance transfer.[1,2] The former mechanism implies the transient reduction of the organic bridging ligand and formation of an intermediate radical species, whereas in the latter case no intermediates are thought to be generated.[3] The "radical-ion" mechanism may be formulated as

$$A^{III}LB^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^{III}LB^{III}$$

$$A^{III}LB^{III} \xrightarrow{k_2} A^{II}LB^{III} \xrightarrow{\text{rapid}} \text{products}$$

A, B = transition metals; L = organic bridging ligand

Radical intermediates of the proposed type have been directly observed in only very few instances with strong reductants such as [Cr(OH$_2$)$_6$]$^{2+}$[4] or the hydrated electron.[5] The observed first-order rate constant for the intramolecular ET can represent two limiting situations according to the above scheme by assuming the steady-state approximation to be valid for the concentration of the radical intermediate. If $k_{-1} \gg k_2$, then $k_{obsd} = (k_1/k_{-1})k_2$, but if $k_2 \gg k_{-1}$, then $k_{obsd} = k_1$; i.e., the formation of the radical intermediate is rate determining. The first limiting case should lead to a marked dependence of the rate on both the oxidizing power of the oxidant and the reducing ability of the reductant, whereas in the latter case only a marginal influence of the oxidizing transition-metal ion is expected—provided the oxidant does not change the reducibility of the bridging ligand greatly. It is noted that for a resonance-transfer mechanism a dependence of the intramolecular ET rate on the nature of the oxidant *and* the reductant is predicted. This mechanistic possibility is kinetically not distinguishable from the first limiting case of the chemical mechanism.