idine, the pyridine b_1 orbital is destabilized to the extent that it rather than the a_2 orbital is the highest occupied molecular orbital. On the other hand, only substitution of the strongest π electron donating group NH_2 leads to a significant destabilization of the pyridine n orbital.

6. The change in the dipole moment which occurs upon substitution in pyridine is determined by the polarity of the substituent and the orientation of the substituent dipole moment vector relative to that of pyridine, and by the electron redistribution in the molecule. Those substituents which enhance the dipole moment in the 2 isomer lower it in the 4, and vice versa. In 4-cyanopyridine, the dipole moment vector is reversed relative to pyridine.

Acknowledgments. The support of a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant (1974-1979) is gratefully acknowledged. Thanks are also due to the Youngstown State University Computer Center for continued support and assistance, and to Dr. Irwin Cohen for his comments and suggestions.

References and Notes

(1) R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Wiley, New York, 1975, pp 31-77.
(2) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976).
(3) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
(4) E. M. Arnett in ref 1, pp 79-101.
(5) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 318 (1976).
(6) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5729 (1977).
(7) I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1601 (1977).
(8) W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5821 (1977).
(9) J. E. Del Bene, *J. Am. Chem. Soc.*, **97**, 5330 (1975); *Chem. Phys.*, **15**, 463 (1976).
(10) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(12) L. E. Sutton, *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1965).
(13) The angle to the substituent (N_1-C_2-X) is also within ±1° of the N_1-C_2-H angle in pyridine except in 2-vinylpyridine, where it decreases by 3°.
(14) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).
(15) The N-H′ interaction should probably not be labeled an intramolecular hydrogen bond. The O-H′· · ·N arrangement is far from linear (73°) and the N_1-H overlap population is negative, whereas in an inter- or intramolecular A-H· · ·B hydrogen bond the B-H overlap population is always positive.
(16) The relative orientation of component dipole moments of the ring and of the substituent has been invoked as a factor influencing the relative stabilities of 2- and 3-monosubstituted furans. (See I. G. John and L. Radom, *J. Am. Chem. Soc.*, **100**, 3981 (1978). However, this factor does not stabilize the 2-substituted pyridine when the substituent is F or CN, in which cases the component dipole moments are unfavorably oriented.
(17) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
(18) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(19) These large errors arise primarily from an overestimation of the C_4-X distance by the standard model and from variations in angular coordinates within the substituent from standard model values, as evident from Table II.
(20) It should be noted that a nonplanar aniline structure with a pyramidal nitrogen was found to be 2.7 kcal/mol more stable than the planar standard-model structure (see ref 14). With the pyramidal structure as a reference, the computed ΔE_2 value would be reduced to 1.6 kcal/mol, but would still remain positive for 2-aminopyridine. A more detailed study of the effect of NH_2 substitution on the relative stabilities of aniline and the aminopyridines would require that similar pyramidal structures be investigated for the aminopyridines.
(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(22) R. Ditchfield, J. E. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 703 (1972).

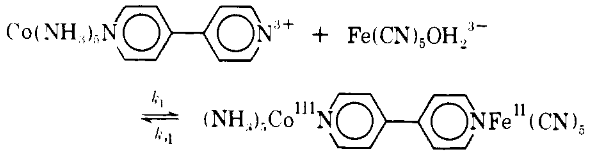
Intramolecular Electron Transfer from Pentacyanoferrate(II) to Pentaamminecobalt(III) Mediated by Various 4,4′-Bipyridines[1a]

Jing-Jer Jwo,[1b] P. L. Gaus, and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received March 19, 1979*

Abstract: The reactions of $Fe(CN)_5OH_2^{3-}$ with $Co(NH_3)_5L^{3+}$ (L = bis(4-pyridyl)methane, bis(4-pyridyl)ethane, bis(4-pyridyl)propane, bis(4-pyridyl)ethylene, and bis(4-pyridyl) ketone) produce binuclear complexes $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ that exhibit iron t_{2g} to ligand π^* charge transfer bands at (same order) 370, 365, 360, 500, and 555 nm. Comparison of these values with those for the corresponding $Fe^{II}(CN)_5L^{3-}$ complexes (370, 365, 360, 460, and 520 nm) suggests that the electron-withdrawing effect of the Co(III) moiety attached to the remote N is transmitted to the ring adjacent to the Fe(II) via π interactions, and that saturated hydrocarbon groups connecting the two pyridine rings insulate electronically the iron and cobalt centers. Rate constants for the formation and dissociation of the binuclear complexes have been measured and a dissociative mechanism is clearly indicated by the LFER of slope −1.0 between rate constants and equilibrium constants for the formation reactions. The rate constants for intramolecular electron transfer from Fe(II) to Co(III) in the binuclear complexes have been measured. At 25 °C, $\mu = 0.10$ M, the values are (same order of ligands) $<0.6 \times 10^{-3}$, 2.0×10^{-3}, 4.8×10^{-3}, 1.4×10^{-3}, and $<0.1 \times 10^{-3}\ s^{-1}$. It is suggested that conjugation between the two pyridine rings is essential for electron transfer mediated by the ligand. When the two rings are separated by insulating methylene groups, electron transfer through the ligand is precluded, but ligands that permit close approach of the metal centers lead to intramolecular, outer-sphere electron transfer.

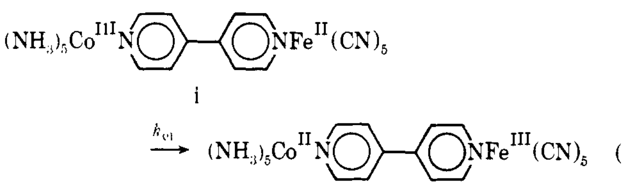
It was previously reported[2] that the redox reaction between 4,4′-bipyridinepentaamminecobalt(III) and aquopentacyanoferrate(II) proceeds via the *detectable* binuclear precursor complex i. The rate constants for the formation and dissociation of this intermediate (k_f and k_d in eq 1) and the rate constant for intramolecular electron transfer (k_{el} in eq 2) were measured.[2] In view of the importance of measuring intramo-



(1)

i

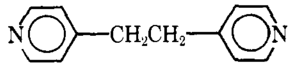
0002-7863/79/1501-6189$01.00/0 © 1979 American Chemical Societv

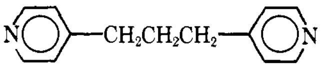


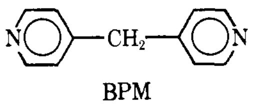
i

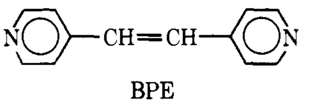
(2)

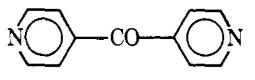
lecular electron transfer rates,[3-5] this work has been extended to include the bipyridines shown as bridging ligands. While the


BPA


BPP


BPM


BPE


BPK

present work was in progress, a study of the rates of intramolecular electron transfer from ruthenium(II) to cobalt(III) in $(NH_3)_4(H_2O)Ru^{II}LCo^{III}(NH_3)_5^{5+}$ where L = BPE, BPA, 4,4′-bipyridine (BP), 2,2′-dimethyl-4,4′-bipyridine (DMBP), and bis(4-pyridyl) sulfide (BPS) was published.[6]

Experimental Section

Materials. *trans*-1,2-Bis(4-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethane were recrystallized from hot water until white crystals were obtained (five and three times, respectively). 1,3-Bis(4-pyridyl)propane was recrystallized several times from hot ethanol. Distilled water was passed through a Barnstead ion-exchange demineralizer and then was distilled in a modified (all-glass) Corning Model AG-lb apparatus. Lithium perchlorate was prepared by the reaction of lithium carbonate with perchloric acid and purified by recrystallization. Bis(4-pyridyl)methane and bis(4-pyridyl) ketone were synthesized as described previously.[7] All other chemicals were reagent grade and used without further purification.

Preparation of Complexes. The BPE and BPA complexes of $Co(NH_3)_5^{3+}$ were prepared by a slight modification of the literature procedure. Following the formation of the desired complex in solution by reaction of $[Co(NH_3)_5OH_2](ClO_4)_3$[9] with the appropriate ligand in dimethylformamide, the dark orange-red solution was allowed to cool to room temperature and then extracted with several 50-mL portions of ether. The remaining viscous oil was mixed with 15 mL of methanol and filtered. In the case of the BPA complex, the filtrate was used directly. In the case of the BPE complex, the filtrate was discarded and the residue was treated with several 5-mL portions of methanol and filtered. The combined filtrate was 30 mL. In both cases the methanolic filtrate was treated with a saturated solution of NaI in methanol.[8] The resulting yellow precipitate was dissolved in the minimum amount of water and filtered if necessary, and then the perchlorate salt was precipitated by addition of concentrated perchloric acid and cooling in an ice-water bath. The resulting crystals were recrystallized three times from aqueous perchloric acid. Anal. Calcd for $[Co(NH_3)_5NC_5H_4CHCHC_5H_4NH](ClO_4)_4$: Co, 8.13; ClO_4, 54.86. Found: Co, 7.89, 8.11; ClO_4, 54.33. Calcd for $[Co(NH_3)_5NC_5H_4CH_2CH_2C_5H_4NH](ClO_4)_4 \cdot H_2O$: Co, 7.91; ClO_4, 53.39. Found: Co, 7.78, 7.92; ClO_4, 53.52.

The BPK and BPP complexes were prepared in the following manner. $[Co(NH_3)_5Me_2SO](ClO_4)_3 \cdot 2H_2O$[10] (0.5 g) in 1.0 mL of dimethyl sulfoxide was heated to ca. 90 °C under nitrogen; 1.0 g of the desired ligand was added and, after 10-15 min, the resulting clear orange solution was cooled to 0 °C and treated with 30 mL of dilute hydrochloric acid in the case of BPP or 30 mL of water in the case of BPK. The resulting mixture was filtered if necessary and the solution was loaded on a column of Dowex 50-X2, 200-400 mesh, H^+ form. The resin was rinsed with water and with 2 M HCl, and then the desired product was eluted with 4 M HCl. The resulting orange solution was evaporated to near dryness in a rotary evaporator at ca. 45 °C. The resulting orange paste was dissolved in the minimum amount of water, and the desired product was precipitated by addition of perchloric acid and cooling to 0 °C, yield 50-60%. The product was recrystallized three to four times from aqueous perchloric acid. Anal. Calcd for $[Co(NH_3)_5NC_5H_4COC_5H_4NH](ClO_4)_4 \cdot H_2O$: C, 17.78; H, 3.53; N, 13.19; Co, 7.93. Found: C, 17.73; H, 3.28; N, 12.84; Co, 7.90. Calcd for $[Co(NH_3)_5NC_5H_4CH_2CH_2CH_2C_5H_4NH](ClO_4)_4$: C, 21.07; H, 4.08; N, 13.23; Co, 7.95. Found: C, 21.70; H, 3.92; N, 13.16; Co, 7.83.

The BPM complex was prepared by a somewhat different procedure since the reaction of $Co(NH_3)_5Me_2SO^{3+}$ in Me_2SO with BPM at 90 °C resulted in a rapid decomposition of the cobalt complex with copious evolution of ammonia. The following procedure was found to produce less decomposition, but still ammonia was detected at the end of the reaction. An anhydrous solution of $[Co(NH_3)_5Me_2SO](ClO_4)_3$ in Me_2SO was prepared by dissolving 0.50 g of $[Co(NH_3)_5Me_2SO](ClO_4)_3 \cdot 2H_2O$[10] in 2.0 mL of Me_2SO and storing (48 h) under N_2 over molecular sieves. Using a glovebag (N_2 gas and P_2O_5 as desiccant), 1.0 g of bis(4-pyridyl)methane was sealed in a round-bottom flask fitted with a serum cap. The anhydrous solution of $[Co(NH_3)_5Me_2SO](ClO_4)_3$ was transferred to the flask containing the ligand, and the reaction was allowed to proceed at room temperature, in the dark, for 72 h. A gradual color change took place, from purple to orange. The product solution was added rapidly to 200 mL of 0.06 M HCl and the resulting orange solution was added to a column of Dowex 50-X2, 200-400 mesh ion exchange resin in the H^+ form. The resin was rinsed with 200 mL of water and 250 mL of 2 M HCl. An orange component was eluted from the column with 4 M HCl. The eluant was evaporated to near dryness in a rotatory evaporator at ca. 40 °C, in the dark. The orange residue was dissolved in 1.5 mL of 0.1 M HCl and chromatographed on a column of Biogel P-300 (100-200 mesh). Elution with 0.1 M HCl gave a partial separation and only the very last portion of orange solution to move from the column was used. The concentration of the last fraction was estimated from its electronic absorption spectrum and a twofold excess of a concentrated solution of $Na_2S_2O_6 \cdot 2H_2O$ was added. Orange crystals formed upon cooling to 0 °C. These were filtered, washed with water at 0 °C and ethanol, and dried under vacuum, yield 10%. Anal. Calcd for $[Co(NH_3)_5NC_5H_4CH_2C_5H_4NH](S_2O_6)_2 \cdot 2H_2O$: C, 19.67; H, 4.50; N, 14.60; S, 19.10; Co, 8.78. Found: C, 19.47; H, 4.56; N, 14.49; S, 18.92; Co, 8.94.

Sodium pentacyanoammineferrate(II) trihydrate was prepared and recrystallized as described previously.[11] Solutions of $Fe(CN)_5OH_2^{3-}$ were prepared by aquation of $Fe(CN)_5NH_3^{3-}$ ($<10^{-4}$ M concentration) in a degassed, pH 7.2, 10^{-4} M Tris buffer solution for 5 min at 25 °C. The concentrations of these solutions were checked by diluting an aliquot with excess pyridine ($\sim 10^{-2}$ M) and measuring the absorbance of the $Fe(CN)_5py^{3-}$ produced (molar absorbance = 3.74×10^3 M^{-1} cm^{-1} at 365 nm).

Analytical Methods. Perchlorate analyses were carried out gravimetrically using tetraphenylarsonium chloride as the precipitating agent.[12] Cobalt analyses were performed spectrophotometrically using nitroso-R salt.[13] pH measurements were carried out with an Orion Model 801 pH meter.

Kinetic Measurements. Slow reactions were studied by measuring absorbance changes at the desired wavelength as a function of time in a thermostated, water-filled cell holder of a Cary 118 spectrophotometer.[14] Absorbances were fitted to time, $A_t = A_\infty + A_0 \exp(-k_{obsd}t)$, by means of a nonlinear least-squares program. Fast reactions were measured using a Durrum D-110 stopped-flow apparatus interfaced to an 1800 IBM computer. The data were treated as described previously.[11] The rate of disappearance of the desired binuclear complex in the presence of pyridine or pyrazine and ascorbic acid was fitted to the two-exponential function $A_t = A_\infty + f\exp[-(k_d + k_{el}^{is})t] + g\exp(-k_{-L}t)$ by means of a nonlinear least-squares program.[11] Stoichiometric measurements of product solutions were carried out spectrophotometrically as described in detail below.

Results

Absorption Spectra. Stable bipyridine complexes of pentacyanoferrate(II) were formed in solution via the reaction of an excess of ligand ($>5 \times 10^{-4}$ M) with dilute $Fe(CN)_5OH_2^{3-}$ ($1-2 \times 10^{-5}$ M) according to the equation

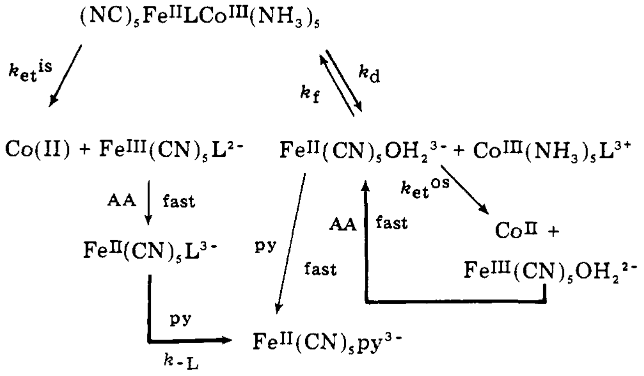
$$Fe(CN)_5OH_2^{3-} + L \underset{k_{-L}}{\overset{k_L}{\rightleftharpoons}} Fe(CN)_5L^{3-} + H_2O \qquad (3)$$

Table I. Metal to Ligand Charge Transfer Spectra of Bipyridine Complexes of Pentacyanoferrate(II)[a]

complex	λ, nm[b]	$10^{-3}A$, M^{-1} cm^{-1} [c]
$Fe(CN)_5py^{3-}$	362	3.7
$Fe(CN)_5BPM^{3-}$	370	4.3
$Fe(CN)_5BPA^{3-}$	365	4.7
$Fe(CN)_5BPP^{3-}$	360	4.3
$Fe(CN)_5BPE^{3-}$	460	7.2
$Fe(CN)_5BPK^{3-}$	520	4.4
$Fe(CN)_5BPMCo(NH_3)_5$	370	4.2
$Fe(CN)_5BPACo(NH_3)_5$	365	4.5
$Fe(CN)_5BPPCo(NH_3)_5$	360	3.3
$Fe(CN)_5BPECo(NH_3)_5$	500	7.5
$Fe(CN)_5BPKCo(NH_3)_5$	555	3.2

[a] In aqueous solution, [Fe(II)] = 1-2 × 10^{-5} M, [ligand] ≥ 5 × 10^{-4} M. [b] Wavelength for absorption maximum. [c] Molar absorbance at absorption maximum.

Scheme I[a]



[a] AA = ascorbic acid; py = pyridine or pyrazine.

Table II. Rate Constants for Formation of Binuclear Complexes $(NC)_5FeLCo(NH_3)_5$[a]

L	$10^4[Co(NH_3)_5L^{3+}]$, M	$10^5[Fe(CN)_5OH_2^{3-}]$, M	$10^{-3}k_f$, M^{-1} s^{-1}
BPM	1.0	1.1	3.90 ± 0.13
BPA	1.0	1.0	4.54 ± 0.17
BPP	1.0-2.3	0.8-1.0	2.16 ± 0.16
BPE	1.0	1.0	2.05 ± 0.04
BPK	1.1-2.1	1.2-2.1	5.23 ± 0.25

[a] At 25 °C, pH 8.0 (Tris buffer), ionic strength = 0.10 M ($LiClO_4$), [ascorbic acid] = 2 × 10^{-4} M, [EDTA] = 1-2 × 10^{-4} M.

(L = BPM, BPA, BPP, BPE, and BPK). The complexes exhibit the broad, intense absorption in the visible or near-UV characteristic[15] of metal to ligand charge transfer (MLCT) ($t_{2g} \rightarrow \pi^*$). The wavelengths for the MLCT bands and their corresponding molar absorbances are presented in Table I. Included in Table I are the appropriate values for the pyridine (py) complex.[15] It will be seen that the complexes of BPM, BPA, and BPP, where the electron-withdrawing effect of the remote pyridine ring is transmitted through a σ framework, display their maxima very near that of pyridine. In contrast, the complexes of BPE and BPK, where the electron-withdrawing effect is transmitted through the π system, exhibit their maxima at considerably lower energies.

Similar, but transient, absorption spectra were displayed by solutions obtained by mixing $Co(NH_3)_5L^{3+}$ complexes (1-2 × 10^{-4} M) with $Fe(CN)_5OH_2^{3-}$ (1-2 × 10^{-5} M). Repetitive scanning of these solutions and extrapolation to the time of mixing yielded the absorption spectra of the precursor binuclear complexes formed via the equation

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5L^{3+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (NC)_5FeLCo(NH_3)_5 + H_2O \quad (4)$$

The wavelengths for the MLCT bands and their corresponding molar absorbances are included in Table I. It will be seen that the absorption maxima for the binuclear complexes bridged by BPM, BPA, and BPP occur at the same wavelengths as those of the corresponding mononuclear iron complexes, whereas the binuclear complexes with BPE and BPK exhibit their MLCT bands at wavelengths 35-40 nm longer than those of the mononuclear iron complexes. Evidently, the strong electron-withdrawing effect of the tripositive cobalt(III) center is not transmitted via the σ framework, but comes into play when there are groups which can interact with the π system of the iron-bound pyridine group.

Kinetics of Formation of Binuclear Complexes. Initial rates of formation of the binuclear intermediates[11] were determined by monitoring the increases in absorbance at the wavelengths listed in Table I. The measurements were carried out at 25 °C and pH 8.0 in the presence of 2 × 10^{-4} M ascorbic acid and with the cobalt complex in excess. Under these circumstances, the ratio of k_{obsd} to $[Co(NH_3)_5L^{3+}]$ gives directly values of k_f since any $Fe(CN)_5OH_2^{3-}$ that disappears by the outer-sphere reaction given by eq 5 is rapidly regenerated by the rapid reaction[16] of the iron(III) produced with ascorbic acid. Values of k_f for the complexes studied in the present work are listed in Table II.

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5L^{3+} \xrightarrow{k_{os}} Fe(CN)_5OH_2^{2-} + Co(NH_3)_5L^{2+} \quad (5)$$

Kinetics of Disappearance of Binuclear Complexes. Various methods were utilized in order to obtain the rate constants for intramolecular electron transfer from iron (II) to cobalt(III) in the binuclear complexes $(NC)_5FeLCo(NH_3)_5$. Therefore, for clarity and efficiency of presentation, it is appropriate to introduce at the outset the general mechanistic scheme (Scheme I) that has been adopted, and then to examine, within the framework of the scheme, the physical significance of the measured rate of disappearance of the binuclear complex for each method that was utilized. Since the measurements were carried out after the formation of the binuclear complex was substantially complete, it is taken to be the initial reactant. Three types of measurements were carried out.

A. Spontaneous Disappearance. The iron and cobalt reactants were mixed, and the binuclear complex was allowed to develop. Once formed, it will be seen that the binuclear complex disappears via two parallel paths. An irreversible intramolecular electron transfer (k_{et}^{is}) results in the formation of the ligand transfer product $Fe(CN)_5L^{2-}$. A reversible dissociation (k_d) yields the mononuclear products $Fe(CN)_2OH_2^{3-}$ and $Co(NH_3)_5L^{3+}$. These can regenerate the binuclear reactant (k_f) or undergo an outer-sphere redox reaction (k_{et}^{os}) that produces $Fe(CN)_5OH_2^{2-}$. Under these circumstances, the observed first-order rate constant, $k^A{}_{obsd}$, is equal to k_{et}^{is} + $k_{et}^{os}k_d/(k_f + k_{et}^{os})$. At the end of the reaction, stoichiometric measurements were carried out to determine the concentrations of $Fe(CN)_5L^{2-}$ and $Fe(CN)_5OH_2^{2-}$. For L = BPA and BPP, the product solution was treated with an excess of pyrazine and then with ascorbic acid. Upon addition of ascorbic acid (which is known[16] to reduce rapidly the Fe(III) complexes to the corresponding Fe(II) complexes), a rapid increase in absorbance is observed at 457 nm, the absorption maximum[15] of $Fe(CN)_5pyr^{3-}$, and is followed by a slow increase in absorbance. The rapid absorbance increase is a measure of the

Table III. Kinetics of Dissociation and of Intramolecular Electron Transfer for $(NC)_5FeBPECo(NH_3)_5$[a]

$10^3k^C_{obsd}$, s^{-1}	10^4k_{-L}, s^{-1}	$10^3k_{el}^{is}$, s^{-1}	10^3k_d, s^{-1}
4.59	7.36	1.57	3.02
4.21	6.40	1.26	2.95
3.99	6.65	1.22	2.77
4.17	6.35	1.32	2.85
4.56	6.65	1.54	3.02
2.28[b]	3.43	0.72	1.56
2.09[b]	3.16	0.63	1.46
8.26[c]	14.6	2.74	5.52
8.08[c]	13.7	2.73	5.35
4.66[d]	7.43[d]	1.53	3.13
4.65[d]	7.16[d]	1.63	3.02
3.04[e]	5.84[e]	0.59	2.45
3.22[e]	6.16[e]	0.64	2.58
1.72[f]	5.73[f]	0.30	1.42
1.59[f]	5.25[f]	0.24	1.35

[a] Measurements at 500 nm, pH 8.0, [EDTA] = 1.67×10^{-4} M, [pyridine] = 0.10 M, [ascorbic acid] = 2.0×10^{-4} M, $[Co(NH_3)_5BPE^{3+}] = 1.0 \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{2-}] = (0.83-1.0) \times 10^{-5}$ M, ionic strength = 0.10 M, t = 25.0 °C. [b] At 20.3 °C. [c] At 30.0 °C. [d] Ionic strength = 0.053 M. [e] Ionic strength = 0.21 M. [f] Ionic strength = 0.66 M.

Table IV. Kinetics of Dissociation and of Intramolecular Electron Transfer for $(NC)_5FeBPACo(NH_3)_5$[a]

$10^3k^C_{obsd}$, s^{-1}	10^3k_{-L}, s^{-1}	$10^3k_{el}^{is}$, s^{-1}	10^3k_d, s^{-1}
6.32	1.31	2.02	4.30
6.98	1.27	2.29	4.69
6.45	1.21	2.13	4.32
5.89	1.26	1.84	4.05
6.02	1.08	2.02	4.00

[a] Measurements at 360 nm, pH 8.0, [EDTA] = 1.67×10^{-4}, [pyrazine] = 0.010 M, [ascorbic acid] = 2.0×10^{-4} M, $[Co(NH_3)_5BPA^{3+}] = (1.0-1.5) \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = (1.0-1.5) \times 10^{-5}$ M, ionic strength = 0.10 M, t = 25.0 °C.

$Fe(CN)_5OH_2^{2-}$ produced, while the slow absorbance increase is a measure of the $Fe(CN)_5L^{2-}$ produced. This can be seen from Scheme I, where both steps required to transform $Fe(CN)_5OH_2^{2-}$ into $Fe(CN)_5pyr^{3-}$ are rapid, whereas the rate of transformation of $Fe(CN)_5L^{2-}$ into $Fe(CN)_5pyr^{3-}$ is limited by the slow[15] rate of ligand loss (k_{-L}) from $Fe(CN)_5L^{3-}$. The ratio $[Fe(CN)_5OH_2^{2-}]/[Fe(CN)_5L^{2-}]$ produced in the reaction is given, according to Scheme I, by $k_{el}^{os}(k_{el}^{is} + k_d)/k_{et}^{is}k_f$.[17] The observed first-order rate constant k^A_{obsd} and stoichiometric ratio were combined with the known values of k_f (measured as described above) and of $k_{el}^{is} + k_d$ (measured as described below) and an iterative calculation was carried out in order to obtain individual values of k_{el}^{is}, k_{el}^{os}, and k_d. For the system where L is BPE, the stoichiometric ratio was measured by adding pyridine rather than pyrazine to the product solution.

B. Disappearance in the Presence of Added Ligand. As in the previous method, the reactants $Co(NH_3)_5L^{3+}$ and $Fe(CN)_5OH_2^{3-}$ were mixed, and the charge-transfer band of the binuclear complex was allowed to develop. At a predetermined time (30 or 40 s, a time sufficiently long for the binuclear complex to reach its maximum concentration), an excess of a ligand (pyridine or pyrazine) was added and the disappearance of the binuclear intermediate or the appearance of $Fe(CN)_5py^{3-}$ was monitored. It will be seen that the binuclear complex disappears by two irreversible parallel paths, namely, intramolecular electron transfer (k_{el}^{is}) to yield $Fe(CN)_5L^{2-}$ and dissociation (k_d) to yield $Fe(CN)_5OH_2^{3-}$ which rapidly reacts with py to yield $Fe(CN)_5py^{3-}$. Under these circumstances, the observed first-order rate constant, k^B_{obsd}, is equal to $k_{et}^{is} + k_d$. At the completion of the reaction, stoichiometric measurements were carried out in order to determine the concentrations of $Fe(CN)_5OH_2^{2-}$ (produced by the outer-sphere pathway during the formation of the binuclear complex), $Fe(CN)_5L^{2-}$, and $Fe(CN)_5py^{3-}$ (produced via the k_{el}^{is} and k_d pathways, respectively). The absorbance of the product solution at the maximum for $Fe(CN)_5py^{3-}$ was measured, and then ascorbic acid was added, whereby a rapid increase in absorbance occurred and was followed by a slower increase. The absorbance of the product solution corrected for the absorbance of the excess $Co(NH_3)_5L^{3+}$ and the small contributions of $Fe(CN)_5L^{2-}$ and $Fe(CN)_5OH_2^{2-}$ is a measure of the $Fe(CN)_5py^{3-}$ produced. The rapid increase in absorbance corresponds to the rapid reduction of $Fe(CN)_5OH_2^{2-}$ followed by rapid complexation by py and is, therefore, a measure of the $Fe(CN)_5OH_2^{2-}$ produced. The slow increase in absorbance corresponds to the formation of $Fe(CN)_5py^{3-}$ by rapid reduction of $Fe(CN)_5L^{2-}$ followed by the rate-determining dissociation of L from $Fe(CN)_5L^{3-}$, and is a measure of the $Fe(CN)_5L^{2-}$ produced. The ratio $[Fe(CN)_5L^{2-}]/[Fe(CN)_5py^{3-}]$, corrected for the amount of $Fe(CN)_5L^{2-}$ produced prior to the addition of py, is equal to k_{el}^{is}/k_d. From the ratio and the sum (equal to k^B_{obsd}), individual values of k_{el}^{is} and k_d were obtained.

C. Disappearance in the Presence of Added Ligand and Ascorbic Acid. These are the conditions used in our previous work[2,11] and the absorbance changes yield two exponentials, $k^C_{obsd}(=k_d + k_{el}^{is})$ and k_{-L}, respectively. The value of k_{et}^{is} was then obtained as described previously.[2,11] Independent measurements of k_{-L} were carried out by allowing $Fe(CN)_5L^{3-}$ to be formed in the presence of low (~10^{-4} M) concentrations of L and then adding a large excess (~0.1 M) of py. Under these conditions, net substitution of L by py takes place, but the loss of L is the rate-determining step.[15]

The measurements by method C for the reactions involving BPE are summarized in Table III. Four experiments under the same conditions as those in Table III except that pyridine and ascorbic acid were omitted (method A) yielded an average value of $k^A_{obsd} = (2.54 \pm 0.22) \times 10^{-3}$ s^{-1} from which we calculate $k_{el}^{os} = (1.21 \pm 0.66) \times 10^3$ M^{-1} s^{-1}. Included in Table III are measurements of the ionic-strength dependence of the rate constants.

The measurements by method C for the reactions involving BPA are summarized in Table IV. The measurements by methods A and B and the ionic strength and temperature dependences of the rates are presented in Table V. Since the values of k^A_{obsd} are equal, within the relatively large experimental error, to the values of k_{el}^{is} derived from method C, it is concluded that the outer-sphere electron-transfer path is slow. An estimate of k_{et}^{os} was obtained by measuring the ratio $S^A = [Fe(CN)_5BPA^{2-}]/[Fe(CN)_5OH_2^{2-}]$ produced in experiments of type A. From measured values of $S^A = 11.7 \pm 0.1$, we estimate $k_{et}^{os} = 130 \pm 20$ M^{-1} s^{-1}.

The results of kinetic and stoichiometric measurements by methods A and B for BPP are summarized in Table VI. The derived values of k_{el}^{is}, k_d, and k_{et}^{os} are $(4.8 \pm 0.3) \times 10^{-3}$ s^{-1}, $(4.0 \pm 0.3) \times 10^{-3}$ s^{-1}, and $(1.4 \pm 0.2) \times 10^2$ M^{-1} s^{-1}, respectively.

As was the case for the preceding ligands, the reaction between $Co(NH_3)_5BPM^{3+}$ and $Fe(CN)_5OH_2^{3-}$ resulted in the rapid formation of the charge-transfer band characteristic of the binuclear complex $(NC)_5FeBPMCo(NH_3)_5$. However, in contrast with the behavior of the binuclear complexes bridged by the other bipyridine ligands, the BPM binuclear complex underwent a very slow reaction which appeared to become increasingly retarded, and after about 1 h the decrease in absorbance amounted to only 5-10%. Addition of pyrazine to the binuclear complex resulted in a nice, first-order disap-

Table V. Ionic Strength and Temperature Dependence of Kinetics of Dissociation and of Intramolecular Electron Transfer for $(NC)_5FeBPACo(NH_3)_5$^{a}

$10^3k^A_{obsd}$, s^{-1} ^{b}	$10^3k^B_{obsd}$, s^{-1}	10^3k_d, s^{-1} ^{c}
2.77^{d}	6.32^{d}	3.55
2.37^{e}	6.25^{e}	3.88
1.99	5.67	3.68
2.03	5.80	3.77
2.01	5.90	3.89
1.46^{f}	4.87^{f}	3.41
1.23^{g}	4.49^{g}	3.26
0.72^{h}	2.74^{h}	2.02
8.66^{i}	19.4^{i}	10.7
4.54^{j}	10.9^{j}	6.35
1.08^{k}	2.92^{k}	1.84
0.52^{l}	1.24^{l}	0.72

[a] Measurements at 360 nm, pH 8.0, [EDTA] = 1.67×10^{-4} M, $[Co(NH_3)_5BPA^{3+}] = 1.0 \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = 1.0 \times 10^{-5}$ M, [pyrazine] = 0.010 M for entries of k^B_{obsd}. Unless specified otherwise, t = 25 °C and ionic strength = 0.10 M. [b] Since the outer-sphere contribution is negligible, these values are also k_{et}^{is}. [c] Calculated as $k^B_{obsd} - k^A_{obsd}$. [d] Ionic strength = 0.026 M. [e] Ionic strength = 0.053 M. [f] Ionic strength = 0.26 M. [g] Ionic strength = 0.40 M. [h] Ionic strength = 0.91 M. [i] t = 34.7 °C. [j] t = 30.0 °C. [k] t = 20.2 °C. [l] t = 15.2 °C.

Table VI. Kinetics of Dissociation and of Intramolecular Electron Transfer for $(NC)_5FeBPPCo(NH_3)_5$^{a}

t, °C	$10^3k^A_{obsd}$, s^{-1}	S^{A} ^{b}	$10^3k^B_{obsd}$, s^{-1} ^{c}	S^{B} ^{c,d}
30.0	8.21 ± 0.22^{e}		15.6 ± 0.2^{f}	
25.0	5.05 ± 0.42^{g}	8.43 ± 0.02^{f}	8.84 ± 0.18^{g}	1.42 ± 0.13^{f}
20.0	2.34 ± 0.28^{h}		3.56 ± 0.06^{g}	
15.0	1.23 ± 0.23^{h}	10.1 ± 0.1^{f}	2.14 ± 0.02^{f}	

[a] Measurements at 360 nm, pH 8.0, [EDTA] = $(1.0\text{-}2.0) \times 10^{-4}$ M, $[Co(NH_3)_5BPP^{3+}] = (0.96\text{-}1.5) \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = (0.85\text{-}1.0) \times 10^{-5}$ M, ionic strength = 0.01 M. [b] This is the ratio $[Fe(CN)_5BPP^{2-}]/[Fe(CN)_5OH_2^{2-}]$ produced. [c] In the presence of 0.010 M pyrazine. [d] This is the ratio $[Fe(CN)_5BPP^{2-}]/[Fe(CN)_5pyr^{3-}]$ produced. [e] Average of six runs. [f] Average of two runs. [g] Average of four runs. [h] Average of five runs.

Table VII. Kinetics of Dissociation of $Fe(CN)_5L^{3-}$ ^{a}

L	10^3k_{-L}, s^{-1}
BPA^{b}	1.39, 1.44, 0.59,^{c} 0.60,^{c} 2.67,^{d} 2.67^{d}
BPE^{e}	0.72, 0.73, 0.76, 0.33,^{c} 0.32^{c} 1.62,^{d}
BPP^{f}	1.59, 1.49^{g}
BPK^{h}	0.59, 0.63, 0.60, 0.60
BPM^{f}	1.25, 1.36, 1.38

[a] Measurements at 25 °C, ionic strength 0.10 M, [L] = 1.0×10^{-4} M, $[EDTA^{2-}] = 1.0 \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = 1.0 \times 10^{-5}$ M, [pyridine] = 0.10 M or [pyrazine] = 0.010 M. [b] Measurements at 360 nm with pyrazine. [c] At 20 °C. [d] At 30 °C. [e] Measurements at 460 nm with pyridine. [f] Measurements at 360 nm with pyrazine. [g] Measurement at 457 nm. [h] Measurements at 525 nm with pyridine.

pearance of the latter. Three measurements with $[Co(NH_3)_5BPM^{3+}] = (1.0\text{-}1.5) \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = (1.1\text{-}2.1) \times 10^{-5}$ M, pH 8.0, [EDTA] = 2.0×10^{-4} M, [pyrazine] = 0.010 M, ionic strength = 0.10 M, and t = 25 °C yielded values of $k^B_{obsd} = 7.79 \times 10^{-3}$, 7.93×10^{-3}, and 7.85×10^{-3} s^{-1}. At the end of the reaction, the nature and concentration of the iron(III) products were determined by addition of ascorbic acid and subsequent spectrophotometric examination of the resulting iron(II) complexes at 457 nm, the absorption maximum of $Fe(CN)_5pyr^{3-}$. Upon addition of ascorbic acid, two absorbance increases were observed. The first, very small and complete within 10 s, was a measure of the $Fe(CN)_5OH_2^{2-}$ produced by the outer-sphere path (see k_{et}^{os} in Scheme I) prior to the addition of pyrazine.[18] This accounted for approximately 6% of the total iron, from which we estimate a value of $k_{et}^{os} \sim 2 \times 10^2$ M^{-1} s^{-1}. The second absorbance increase was slow and obeyed first-order kinetics with an average rate constant of $(6.4 \pm 2.6) \times 10^{-3}$ s^{-1}. This accounted for approximately 10% of the total iron. The origin of this fraction will be discussed below. The remaining iron was present as $Fe(CN)_5pyr^{3-}$ (in the reduced form even before adding ascorbic acid) which is produced by the k_d path in Scheme I. Using the measured value of k^B_{obsd} and the fraction of $Fe(CN)_5pyr^{3-}$ produced by the dissociation pathway, we calculate $k_d = (6.63 \pm 0.33) \times 10^{-3}$ s^{-1}. The agreement between the latter value and the rate constant for the slow absorbance increase that occurs upon addition of ascorbic acid indicates that the species responsible for the increase is the binuclear complex $(NC)_5FeBPMCo(NH_3)_5$ which is formed by reduction of $(NC)_5FeBPMCo(NH_3)_5^+$. A plausible source of the latter complex is the outer-sphere oxidation[19] of $(NC)_5FeBPMCo(NH_3)_5$ by excess $Co(NH_3)_5BPM^{3+}$.

$$(NC)_5FeBPMCo(NH_3)_5 + Co(NH_3)_5BPM^{3+} \rightarrow (NC)_5FeBPMCo(NH_3)_5^+ + Co(NH_3)_5BPM^{2+}$$

From the magnitude of the slow absorbance increase and the measured value of k^B_{obsd} we estimate the rate constant for reaction 5 to be 10 M^{-1} s^{-1}. Assuming that 10% of $Fe(CN)_5BPM^{2-}$ would have been detected in the stoichiometric measurements, we place an upper limit of $\sim 6 \times 10^{-4}$ s^{-1} for k_{et}^{is}.

The reaction of $Co(NH_3)_5BPK^{3+}$ with $Fe(CN)_5OH_2^{3-}$ resulted in the rapid formation of the binuclear complex $(NC)_5FeBPKCo(NH_3)_5$ which exhibits an absorption maximum at 555 nm. The absorbance at the maximum decreased at first (about 15% in 800 s), but then an increase in absorbance and a shift of the maximum toward smaller wavelengths were observed. After about 4000 s the absorbance was approximately equal to the initial value, and the maximum occurred at 525 nm. Presumably, the binuclear complex dissociates via Co-N bond breaking to yield $Co(NH_3)_5OH_2^{3+}$ and $Fe(CN)_5BPK^{3-}$, and it is apparent that little, if any, intramolecular electron transfer takes place in this system. When the binuclear complex was allowed to develop and then pyridine (0.10 M) was added, a nice, first-order disappearance of $(NC)_5FeBPKCo(NH_3)_5$ was observed. Five measurements at 25 °C, μ = 0.10 M, $[Fe(CN)_5OH_2^{3-}] = (0.01\text{-}1.95) \times 10^{-5}$ M, and $[Co(NH_3)_5BPK^{3+}] = (1.10\text{-}1.19) \times 10^{-4}$ M yielded an average value for k^B_{obsd} of $(4.1 \pm 0.2) \times 10^{-3}$ s^{-1}. Spectrophotometric examination of the product solutions of the kinetic measurements revealed that $Fe(CN)_5py^{3-}$ was produced in ~90% yield, and therefore $k_d = (3.7 \pm 0.2) \times 10^{-3}$ s^{-1}, and we place an upper limit of $\sim 1 \times 10^{-4}$ on the value of k_{et} for intramolecular electron transfer in $(NC)_5FeBPKCo(NH_3)_5$.

Kinetics of Dissociation of Substituted Pyridine Complexes of Pentacyanoferrate(II). The substituted pyridine complexes were allowed to be formed by the reaction of $Fe(CN)_5OH_2^{3-}$ ($\sim 10^{-5}$ M) with the appropriate ligand ($\sim 10^{-4}$ M). Then, an excess of pyridine or pyrazine was added and the disappearance of the complex at its absorption maximum was monitored. The results are summarized in Table VII. The values in Table VII can be compared with those for BPA and BPE in Tables IV and III, respectively. The agreement between the two sets of values is relatively poor. However, it must be recognized that the values of k_{-L} obtained by kinetic method C correspond to the slow, tail ends of reactions for systems that exhibit biphasic kinetics. Taking this fact into consideration, the agreement is viewed as acceptable, but, to be sure, the direct measurements in Table VII are the most reliable.

Discussion

General Mechanistic Considerations. There is no question that for the ligands that lead to rapid, net redox chemistry (BP, BPA, BPP, and BPE) the major pathway for the reactions of $Co(NH_3)_5L^{3+}$ with $Fe(CN)_5OH_2^{3-}$ is via an inner-sphere mechanism. The supportive evidence includes the detection and identification of the precursor binuclear complexes and of the mononuclear iron(III) products resulting from ligand transfer. The intermediacy of Fe(II)-Co(III) binuclear complexes bridged by the nitrogen heterocycle is demonstrated by the formation, at a rate characteristic of the substitution of the water in the coordination sphere of $Fe(CN)_5OH_2^{3-}$ (see discussion of rates of substitution below), of the metal to ligand charge transfer bands of pentacyanoferrate(II) bound to a π-accepting, aromatic nitrogen heterocycle. The evidence for the formation of the ligand-transfer products is the spectroscopic detection of the complexes $Fe(CN)_5L^{2-}$ and of their reduction products, $Fe(CN)_5L^{3-}$, formed rapidly by reaction of the iron(III) product complexes with ascorbic acid. Thus, the complete reaction path via the inner-sphere mechanism involves the classic[4] three-step scheme: formation of the precursor complex (eq 6), intramolecular electron transfer (eq 7), and dissociation of the successor complex (eq 8).

$$Fe^{II}(CN)_5OH_2^{3-} + Co^{III}(NH_3)_5L^{3+} \underset{k_{dp}}{\overset{k_{fp}}{\rightleftharpoons}} (NC)_5Fe^{II}LCo^{III}(NH_3)_5 + H_2O \tag{6}$$

$$(NC)_5Fe^{II}LCo^{III}(NH_3)_5 \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} (NC)_5Fe^{III}LCo^{II}(NH_3)_5 \tag{7}$$

$$(NC)_5Fe^{III}LCo^{II}(NH_3)_5 \underset{k_{fs}}{\overset{k_{ds}}{\rightleftharpoons}} Fe(CN)_5L^{2-} + Co(NH_3)_5^{2+} \tag{8}$$

In previous contributions to the subject of intramolecular electron transfer,[3,6,11,20] it had been assumed tacitly that the slow, rate-determining step was given by the electron-transfer step (eq 7), and therefore that the measured rate constants for the disappearance of the precursor, binuclear complexes were an effective measure of k_{el}. However, this assumption has been questioned recently,[21] and it was argued that, if $k_{et} \gg k_{ds}$, then the disappearance of the precursor complex would be a measure of $k_{el}k_{ds}/k_{-el}$ and, therefore, that the studies reported would yield no information about the factors that govern the rates of intramolecular electron transfer. Although the suggestion that eq 8 may be rate determining cannot be ruled out conclusively, the following argument[22] renders this proposal unlikely. Assuming that the product of the electron-transfer step is ground-state, high-spin cobalt(II), and using ~ 0.5[15] and ~ 0.1 V[23,24] for the reduction potentials of the $Fe^{III/II}$ and $Co^{III/II}$ couples, respectively, the calculated equilibrium constant, k_{el}/k_{-el}, for reaction 7 is $\sim 1.7 \times 10^{-7}$. Since the measured rate constants for the disappearance of the binuclear complexes are in the vicinity of 2×10^{-3} s^{-1}, assuming that eq 8 is rate determining we obtain $k_{el}k_{ds}/k_{-el} \sim 2 \times 10^{-3}$ s^{-1} and therefore, $k_{ds} \sim 10^4$ s^{-1}. However, the rate constant for ligand detachment from $Co(NH_3)_6^{2+}$ has been measured by a pulse radiolytic technique[25] and found to be $>10^6$ s^{-1}. The latter value is at least two orders of magnitude faster than the value of k_{ds} calculated on the *assumption* of rate-determining successor complex dissociation, and therefore we tend to rule out the mechanism which postulates eq 8 as the rate-controlling step. However, it might be argued that the primary cobalt(II) product of the intramolecular electron-transfer step is not the ground-state, high-spin Co(II) complex, but a low-spin, unstable intermediate. Under these circumstances, eq 7 of the mechanism represented by eq 6–8 must be replaced by eq 9 and 10.

$$(NC)_5Fe^{II}LCo^{III}(NH_3)_5 \underset{k'_{-el}}{\overset{k'_{et}}{\rightleftharpoons}} (NC)_5Fe^{III}LCo_{LS}{}^{II}(NH_3)_5 \tag{9}$$

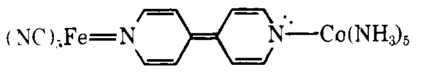
$$(NC)_5Fe^{III}LCo_{LS}{}^{II}(NH_3)_5 \underset{k_{-sp}}{\overset{k_{sp}}{\rightleftharpoons}} (NC)_5Fe^{II}LCo_{HS}{}^{II}(NH_3)_5 \tag{10}$$

We are not concerned with *both* eq 9 and 10 being rapid equilibria since, under these circumstances, eq 8 would still be rate controlling, and we have already shown that a mechanism with such a stipulation is unlikely. The concern is that eq 10 may become rate determining. Under these conditions, the measured rate for the disappearance of the precursor complex would be given by $k'_{el}k_{sp}/k'_{-el}$. A value of k'_{el}/k'_{-el} can be estimated from the value of k_{el}/k_{-el} calculated above and the difference in energy between low-spin and high-spin $Co(NH_3)_6^{2+}$. The latter value has been estimated at 13.4 kcal/mol[26] and thus we obtain $k'_{el}/k'_{-el} \sim 2 \times 10^{-17}$ and $k_{sp} \sim 10^{14}$ s^{-1}. The latter value is seven to eight orders of magnitude larger than measured[27] rate constants for low-spin–high-spin interconversion rates of cobalt(II) complexes, and therefore we tend to rule out the mechanism represented by eq 6, 8–10 with eq 10 being rate controlling. Admittedly, the above calculations are approximate, and, therefore, the basis for ruling out eq 8 or 10 as the rate-determining step is somewhat tenuous. However, these arguments add to those presented earlier,[21] and consequently, in the remainder of the discussion, the observed disappearance of the precursor complexes is interpreted as the result of rate-determining intramolecular electron transfer and the corresponding measured rate constants are taken to represent k_{el} in eq 7.

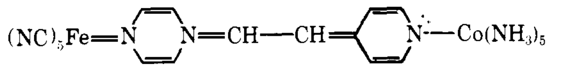
Metal to Ligand Charge Transfer Spectra. The 4,4′-bipyridine ligand used in our previous work[2] and the substituted 4,4′-bipyridine ligands used in the present work can be classified into two classes depending on whether the electron-withdrawing effect of a cobalt(III) center attached to the remote nitrogen of $Fe(CN)_5L^{3-}$ is transmitted to the pentacyanoferrate(II) moiety. The criterion used is based on a comparison between the energy of the iron(II) to pyridine charge transfer transition in the binuclear complexes $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ and the energy of the corresponding transition in the parent mononuclear complex $Fe(CN)_5L^{3-}$. On this basis, BP, BPE, and BPK fall into one group and BPM, BPA, and BPP fall into another. Thus, for BP, BPE, and BPK substantial bathochromic shifts in the absorption maximum of $Fe(CN)_5L^{3-}$ obtain when the $Co(NH_3)_5^{3+}$ moiety is attached to the remote N: BP, 432 to 505 nm; BPE, 460 to 500 nm; BPK, 520 to 555 nm. In contrast, for BPM, BPA, and BPP, the mononuclear iron(II) complexes and the binuclear iron(II)-cobalt(III) complexes exhibit their maxima at exactly the same wavelengths: BPM, 370 and 370 nm; BPA, 365 and 365 nm; BPP, 360 and 360 nm. An identical pattern is obtained by examining the effects of electron-withdrawing substituents such as H^+ or $Co(NH_3)_5^{3+}$ on the metal to ligand charge transfer transitions of $Ru(NH_3)_5^{2+}$ complexes with the bipyridines. Thus, the 478-nm MLCT of $Ru(NH_3)_5BP^{2+}$ [28] is shifted to 563 or 555 nm by attaching H^+ [28] or $Co(NH_3)_5^{3+}$ [6] to the remote N.[29] Similarly, the 508-nm maximum of $Ru(NH_3)_5BPE^{2+}$ [28] is shifted to 570 or 564 nm by attaching H^+ or $Co(NH_3)_5^{3+}$ [6] to the remote N. In contrast, there is a negligible shift in the 407-nm MLCT band of $Ru(NH_3)_5BPA^{2+}$ upon protonation (411 nm) or attachment of

$Co(NH_3)_5^{3+}$ (409 nm).[6] Similarly, the CT band of $Ru(NH_3)_5BPM^{2+}$ is hardly affected by protonation (423 nm) or attachment of $Co(NH_3)_5^{3+}$ (420 nm).[21]

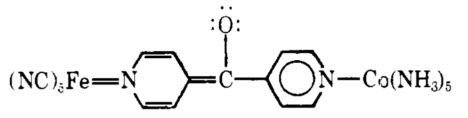
The difference between the two classes of ligands is undoubtedly[30] related to the possibility of delocalization of negative charge from the iron(II) t_{2g} orbitals into the π framework of the pyridine ligands. Adopting resonance language, the attachment of the electron-withdrawing moiety $Co(NH_3)_5^{3+}$ to the remote N of $Fe(CN)_5BP^{3-}$, $Fe(CN)_5BPE^{3-}$, or $Fe(CN)_5BPK^{3-}$ increases the relative contributions of resonance forms I, II, and III as compared to their contributions in the absence of $Co(NH_3)_5^{3+}$, and the MLCT bands move to lower energy. In contrast, for BPM, BPA, and BPP, the electron-withdrawing effect of the $Co(NH_3)_5^{3+}$ moiety is not transmitted through the σ framework connecting the two pyridine rings and no shift in the MLCT bands obtains. It is noteworthy that, although the electron-withdrawing effect of the $Co(NH_3)_5^{3+}$ group increases the extent of metal to ligand π bonding in the BPK complex, the iron t_{2g} electrons are delocalized only in the adjacent pyridine ring, and there appears to be no obvious mechanism for the delocalization of the electrons into the remote ring. In contrast, for BP and BPE, the delocalization of iron d electrons through the π system places negative charge on the N remote to iron.



I



II



III

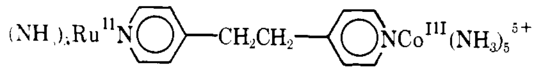
Intramolecular Electron Transfer. The rate constants for intramolecular electron transfer in $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ and, for comparison purposes, those for $(NH_3)_4(OH_2)Ru^{II}LCo^{III}(NH_3)_5$ are presented in Table VIII. It will be seen that, with regard to mediation of electron transfer in the Fe(II)–Co(III) systems, the ligands studied fall into two groups. BP, BPA, BPP, and BPE form one group for which the internal redox reaction proceeds at a measurable rate. BPM and BPK constitute another group for which internal electron transfer is very slow, and dissociation and/or outer-sphere reactions dominate the fates of the binuclear complexes. At first glance, it seems surprising that the BPA and BPP complexes react as fast as or faster than the BP and BPE complexes. The first two ligands feature a saturated chain of carbon atoms between the two pyridine rings whereas the planar conformations of the latter two ligands are conjugated. However, it is apparent that there is free rotation between the C–C bonds connecting the two pyridine rings in the BPA and BPP complexes, and therefore a conformation can be adopted whereby the two metal ions come in close proximity. Thus, we adopt the previous suggestion[3,6] that "outer-sphere" electron transfer obtains in such conformations, the bridging ligands serving to keep the two metal ions together, but not being utilized for orbital coupling. There is ample precedent for the interaction of aromatic rings connected by flexible hydrocarbon chains.[31-34] From studies of excimer formation in diphenyl-[31] and dinaphthylalkanes,[34] of intramolecular association in pyridinyl diradicals of the type $\cdot py(CH_2)_n py \cdot$,[32] and of base–base interactions in dinucleotide analogues[33] it has been shown that the trimethylene group provides a uniquely favored situation for the interaction of aromatic rings. But it has also been shown in some cases[31,32] that a $-CH_2CH_2-$ chain does not lead to any interaction between aromatic groups. This result is in contrast with the one obtained in the present study where both BPA and BPP lead to facile electron transfer. However, it must be recognized that in the examples cited[31-34] maximal interaction between the aromatic rings may necessitate a parallel plane conformation, whereas no such requirement obtains for the outer-sphere electron transfer. Here, what is needed is a sufficient flexibility of the hydrocarbon chain to provide for a close approach between the metal centers, and the $-CH_2CH_2-$ already meets the requirement.

Table VIII. Rate Constants for Intramolecular Electron Transfer of $(NC)_5FeLCo(NH_3)_5$ and $(NH_3)_4(OH_2)RuLCo(NH_3)_5^{3+}$ [a]

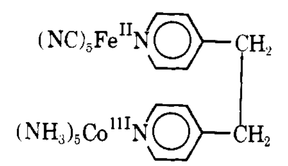
L	10^3k for Fe, s^{-1}	10^3k for Ru, s^{-1}
BP	2.6	44
BPE	1.4	18.7
BPP	4.8	
BPK	<0.1	

[a] At 25 °C, 0.10 M $LiClO_4$ for Fe, 0.40 M CF_3COOH for Ru. Fe data from this work; Ru data from ref 6 and 21.

Two additional findings provide further, albeit indirect, support for the suggestion that outer-sphere electron transfer obtains in the BPA and BPP systems. First, when BPM is the bridge, intramolecular electron transfer becomes too slow to be detected. Molecular models and calculations using a C_1–Fe or C_1–Co distance of 6.1×10^{-8} cm (C_1 is the methylene carbon of BPM) and a 109° Fe–C_1–Co angle indicate that the metal centers cannot come closer than $\sim 10 \times 10^{-8}$ cm, too large a distance for direct electron transfer. Second, there is a substantial decrease in k_{el} when going from BP or BPE to BPA in the Ru–Co system, whereas no such decrease is recorded for the Fe–Co system. The rationale we offer for those trends is that, in the RuBPACo system, the two metal moieties are positively charged and therefore the preferred conformation is the one that results in the open structure IV. However, for the FeBPACo system, the reducing and oxidizing metal centers have charges of −3 and +3, respectively, and therefore the closed structure V is preferred.[35] Thus, for the Ru system the dominant and the reactive forms are not the same and the unfavorable equilibrium, open form ⇌ closed form, is reflected in the rate of electron transfer. In contrast, for the iron system the dominant and reactive forms are the same and no rate limitations obtain because of unfavorable conformations. We sought to obtain information about the question of open vs. closed structures by measuring the effects of ionic strength on the rates of reactions of the BPE (necessarily open) and BPA (presumably closed) complexes. It had been pointed out previously[6] that the rate of reaction of the RuBPACo complex is more sensitive[36] to ionic strength than it is for systems where the open conformation is obligatory. Unfortunately, for the iron systems, both the BPA and BPE complexes showed a substantial decrease in rate with increasing ionic strength and

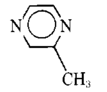


IV



V

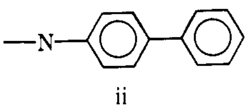
Table IX. Rate Constants for Formation and Dissociation of $(NC)_5FeLCo(NH_3)_5$ at 25 °C, $[LiClO_4] = 0.10$ M[a]

L	$10^{-3}k_f$, $M^{-1}\ s^{-1}$	10^3k_d
BPM	3.9	6.63
BPA	4.5	4.27
BPP	2.2	4.0
BP	5.5	4.5
BPE	2.1	2.92
BPK	5.2	3.7
	3.7	1.1×10^4

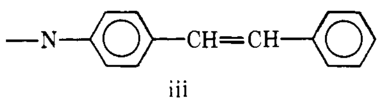
[a] All measurements from the present work except for pyrazine, ref 20, and BP, ref 2.

therefore no unique interpretations can be inferred from these observations.[37]

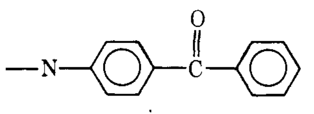
It is noteworthy that there is no exact coincidence between the groupings of the ligands into the two categories based on the kinetic vs. spectroscopic criterion. From electron-transfer rates, we deduced that the transmitting ligands are BP, BPE, BPA, and BPP, whereas BPM and BPK are nontransmitting. From a consideration of bathochromic shifts, BP, BPE, and BPK are transmitting whereas BPM, BPA, and BPP are not. Clearly the extent and mechanisms of communication between the iron and cobalt centers implied by the two criteria are different. However, the two classifications can be reconciled by accepting the above suggestion that electron transfer in the BPA and BPP complexes bypasses the ligands. Thus, for BPM, BPA, and BPP, both criteria suggest that there is no coupling of the metal centers as long as only *through* the ligand communication is considered. For BP and BPE, again the two criteria yield the same result, namely, both electron transfer and electron-withdrawing effects are transmitted through these ligands. The BPK complex, then, appears to represent an anomaly. The spectroscopic criterion suggests communication between the metal centers through the ligand, whereas electron transfer does not obtain. We already noted that the two pyridine rings of BPK are not conjugated. Therefore, although the attachment of $Co(NH_3)_5^{3+}$ to the remote N of $Fe(CN)_5BPK^{3-}$ increases the contribution of resonance from III and produces a bathochromic shift, there is no mechanism for the delocalization of iron electrons into the pyridine ring attached to the Co(III) center and electron transfer is slow. Interestingly, from spin distribution studies[38] in Ni(II) aminotroponeiminate complexes, it was concluded that spin density can be propagated through the systems ii and iii into the para positions of the second benzene rings, but no such transmission obtains in the case of the system iv. Apparently, the conjugative effects necessary for the transmission of spin densities[38] are also operative in ligand-mediated electron transfer. However, it must be pointed out that through σ bond interactions[39,40] or some unspecified mechanism[21] may also provide a pathway for electron transfer as was found[21] in the RuBPMCo system.



ii



iii



iv

Formation and Dissociation of Binuclear Complexes. The rate constants for the formation and dissociation of the binuclear complexes $(NC)_5FeLCo(NH_3)_5$ (eq 4) are listed in Table IX. The values of k_f are approximately ten times larger than the corresponding values measured for neutral ligands.[15,16,41] A dissociative mechanism has been suggested for the replacement of H_2O in $Fe(CN)_5OH_2^{3-}$ by various neutral ligands such as pyridines,[15,41] nitriles,[16] and cyanopyridines.[16] A plot of log k_d vs. log K ($K = k_f/k_d$) for 16 neutral ligands yielded a straight line of slope -0.98 ± 0.03.[16] The data in Table IX also obey an excellent linear free energy relationship, the slope of log k_d vs. log K being -1.00 ± 0.05. The dissociative mechanism is undoubtedly operative in all these substitution reactions, the increased rate of formation for 3+ ligands as compared to the neutral ligands being consistent with rapid ion pair formation preceding the rate-determining loss of water.[42] From the intercepts of the log k_d vs. log K plots

$$Fe(CN)_5OH_2^{3-} + L^{n+} \rightleftharpoons Fe(CN)_5OH_2^{3-} \cdot L^{n+} \quad (11)$$

rapid, outer-sphere complexation

$$Fe(CN)_5OH_2^{3-} \cdot L^{n+} \rightarrow Fe(CN)_5L^{(3-n)-} + H_2O \quad (12)$$

slow, inner-sphere complexation

for neutral and for 3+ charged ligands, it is possible[43] to obtain the ratio of $K_{os}{}^{P}$ to $K_{os}{}^{0}$. $K_{os}{}^{P}$ and $K_{os}{}^{0}$ are the equilibrium constants for reaction 11 when $n = +3$ and 0, respectively. The calculation yields a ratio of 12.9, in excellent agreement with the value of 15 estimated from an electrostatic model[35] for $n = +3$ and a diffusion model[44] for $n = 0$ using a distance of closest approach of 11×10^{-8} cm.[45]

Acknowledgments. One of the authors (A.H.) is grateful to Professors R. C. Kerber, J. Lauher, C. S. Springer, Jr., and A. Wishnia for discussions that helped clarify many of the issues raised in the manuscript.

References and Notes

(1) (a) This work was supported by Grant CHE 7610449 from the National Science Foundation; presented in part at the Centennial Meeting of the American Chemical Society, New York, April 1976, No. INOR-15. (b) Cheng Kung National University, Tainan, Taiwan.
(2) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).
(3) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
(4) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
(5) J. K. Hurst, *J. Am. Chem. Soc.*, **98**, 4001 (1976).
(6) H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).
(7) P. L. Gaus, F. Johnson, and A. Haim, *J. Org. Chem.*, **42**, 564 (1977).
(8) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).
(9) F. Basolo and R. K. Murmann, *Inorg. Synth.*, **2**, 171 (1946).
(10) C. R. Piriz MacColl and L. Beyer, *Inorg. Chem.*, **12**, 7 (1973).
(11) J. J. Jwo and A. Haim, *J. Am. Chem. Soc.*, **98**, 1172 (1976).
(12) E. Deutsch and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).
(13) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Vol. 2, Part II, Interscience, New York, 1962.
(14) The entrance and exit slits of the cell holder were sealed with Suprasil windows.
(15) H. E. Toma and J. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
(16) A. Szecsy and A. Haim, *Inorg. Chim. Acta*, **28**, 189 (1978).
(17) If the initial reactant is the binuclear complex, then the stoichiometric ratio is equal to $k_{el}{}^{os}k_d/k_{el}{}^{is}(k_f + k_{el}{}^{os})$. However, while the binuclear complex is formed, $Fe(CN)_5OH_2^{2-}$ is also formed by the competitive outer-sphere pathway, and the combination of rate constants given in the text is equal to the stoichiometric ratio.
(18) The pyrazine was usually added 30 s after the iron(II) and cobalt(III) reactants were mixed.
(19) Some support for the plausibility of eq 5 comes from observations of the outer-sphere oxidation of $Fe(CN)_5pyr^{3-}$ by $Co(NH_3)_5BPM^{3+}$ in a time scale similar to that observed for eq 5.
(20) J. M. Malin, D. A. Ryan, and T. V. O'Halloran, *J. Am. Chem. Soc.*, **100**, 2097 (1978).
(21) K. Rieder and H. Taube, *J. Am. Chem. Soc.*, **99**, 7891 (1977).
(22) See footnote 16 of ref 21.
(23) P. A. Rock, *Inorg. Chem.*, 7, 837 (1968).
(24) The value ~0.3 V given in ref 22 is appropriate for the $Co(NH_3)_5OH_2^{3+/2+}$ couple. However, since the pyridine ligands have a ligand field strength essentially equal to that of ammonia, the ~0.1 V value applicable to the $Co(NH_3)_6^{3+/2+}$ couple is preferred.
(25) J. Lilie, N. Shinohara, and M. G. Simic, *J. Am. Chem. Soc.*, **98**, 6516 (1976).
269 (1974).
(27) M. G. Simmons and L. J. Wilson, *Inorg. Chem.*, **16**, 126 (1977).
(28) D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, **94**, 2583 (1972).
(29) The values quoted for the effect of $Co(NH_3)_5^{3+}$ are, in fact, the maxima for *trans*-$Ru(NH_3)_5(OH_2)LCo(NH_3)_5^{5+}$. However, the comparisons are still appropriate since the difference in the maxima for $Ru(NH_3)_5L^{2+}$ and Ru-

$(NH_3)_4(OH_2)L^{2+}$ complexes is ≤ 3 nm: R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12,** 1392 (1973); S. S. Isied and H. Taube, *ibid.*, **15,** 3070 (1976). H. Taube, private communication, 1979.

(30) It must be recognized that there is an excellent correlation between the positions of the MLCT bands and the extent of metal to ligand π bonding: J. M. Malin, C. F. Schmidt, and H. E. Toma, *Inorg. Chem.*, **14,** 2924 (1975).

(31) F. Hirayama, *J. Chem. Phys.*, **42,** 3163 (1965).

(32) E. M. Kosower and Y. Ikegama, *J. Am. Chem. Soc.*, **89,** 461 (1967); M. Itoh and E. M. Kosower, *ibid.*, **90,** 1843 (1968).

(33) N. J. Leonard, T. G. Scott, and P. C. Huang, *J. Am. Chem. Soc.*, **89,** 7137 (1967); D. T. Browne, J. Eisinger, and N. J. Leonard, *ibid.*, **90,** 7302 (1968).

(34) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92,** 3586 (1970).

(35) An approximate calculation of the relative stabilities of closed vs. open forms can be made by using the equations for estimating outer-sphere association constants: A. J. Miralles, R. E. Armstrong, and A. Haim, *J. Am. Chem. Soc.*, **99,** 1416 (1967). Using distances of closest approach of 7.0 $\times 10^{-8}$ and 13.0 $\times 10^{-8}$ cm for the closed and open forms, respectively, we estimate that the closed form is more stable than the open form by a factor of 4.

(36) However, it must be pointed out that the difference in sensitivity between the two types of systems is less than that claimed.[6] Thus, for the DMPB system at 0.40 and 1.0 M CF_3COOH, $k_{et} = 5.5 \times 10^{-3}$ and 6.1×10^{-3} s^{-1}, respectively. Under the same conditions, values of k_{el} for the BPA system are 1.18×10^{-3} and 1.32×10^{-3} s^{-1}, respectively.

(37) In fact, the ionic strength effects on the rate constants for dissociation are perplexing. For the reactions of the BPA and BPE complexes, k_d *decreases* with increasing ionic strength, whereas an increase would have been anticipated since the activation process for the dissociation reactions involves charge separation.

(38) D. R. Eaton in "NMR Paramagnetic Molecules: Principles and Applications", G. N. LaMar, W. De W. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973, Chapter 5.

(39) R. Hoffman, *Acc. Chem. Res.*, **4,** 1 (1971).

(40) A. J. de Gee, J. W. Verhoeven, W. J. Sep, and T. J. de Boer, *J. Chem. Soc., Perkin Trans. 2*, 579 (1975).

(41) H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, **12,** 2080 (1973).

(42) L. A. Oliveira, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, **22,** 269 (1977).

(43) A. Haim, *Inorg. Chem.*, **9,** 426 (1970).

(44) I. Amdur and G. G. Hammes, "Chemical Kinetics", McGraw-Hill, New York, 1966, p 63.

(45) This is the average of the distances of closest approach on the NH_3 and pyridine sides of $Co(NH_3)_5BP^{3+}$.

Synthesis and Properties of π-Bonded Olefin and Acetylene Complexes of Ruthenium(II). Crystal and Molecular Structure of the Pentaammineruthenium(II) Fumaric Acid Complex, $[(NH_3)_5Ru(C_4H_4O_4)]S_2O_6{\cdot}2H_2O$

H. Lehmann,[1a] K. J. Schenk,[1b] G. Chapuis,[1b] and A. Ludi*[1a]

Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland, and the Institut de Cristallographie, Université de Lausanne, CH-1015 Lausanne, Switzerland. *Received March 16, 1979*

Abstract: Alkenes and alkynes react with the pentaamminemonoaquoruthenium(II) ion to form complexes containing the π-bonded unsaturated organic molecule as a ligand. Syntheses and spectroscopic properties of the complexes with ethylene, isobutene, 1,4-cyclohexadiene, fumaric acid, acetylene, phenylacetylene, and 3-hexyne are reported. The electronic spectra are dominated by an intense band at about 220 nm ascribed to a $\pi(d) \rightarrow \pi^*(L)$ charge transfer. The coordination of the multiple bond to ruthenium is demonstrated by a shift of the C=C and C≡C stretching frequencies by 100–200 cm^{-1} to lower energies. ^1H NMR spectra are consistent with an edge-on bonding arrangement. Formal reduction potentials obtained by cyclic voltammetry are between 0.6 and 1.40 V (vs. NHE) showing the stabilization of the divalent state of ruthenium by the strong back-bonding to the ligand. The crystal and molecular structure of the particular case of the fumaric acid complex has been determined by a single-crystal X-ray study to $R = 0.034$ and $R_w = 0.040$ for 1242 unique reflections. The compound crystallizes in the orthorhombic system with four molecules in space group D_2^5-$C222_1$. Cell dimensions are $a = 9.840$ (3), $b = 10.887$ (4), $c = 15.970$ (4) Å. The five Ru–N distances are between 2.143 (6) and 2.154 (5) Å, the two equivalent Ru–C distances are 2.172 (6) Å, and the C–C bond length of the olefinic group is 1.413 (8) Å.

Introduction

A prominent feature of the pentaammineruthenium(II) moiety is its pronounced affinity for π acids such as pyridine and its many derivatives, nitriles, and sulfur-containing molecules. The bonding and the stability of the resulting complexes have been rationalized in terms of the strong π-back-bonding tendency of the low-spin t_{2g}^6 configuration of octahedrally or pseudooctahedrally coordinated ruthenium(II).[2] Inasmuch as these molecules play an important role in the chemistry of organometallic compounds, it is surprising that this concept has not been extended to include also π acceptors represented by alkenes and alkynes bonded to $Ru(NH_3)_5$. In the case of known olefin complexes of ruthenium the central metal is in low oxidation states and the other ligands are themselves strong π acids, e.g., CO.[3] Some reactions of a few unsaturated hydrocarbons with pentaammineruthenium(II) have been described in a Ph.D. thesis[4] and a few properties of the corresponding complexes have been reported recently in a preliminary publication.[5] It is remarkable that the formation of these complexes proceeds by a very facile substitution of the water molecule of $Ru(NH_3)_5H_2O^{2+}$ by an alkene or alkyne. Complexes $Ru(NH_3)_5L^{2+}$ (L = alkene, alkyne) described in this paper represent a link between classical coordination compounds and organometallic chemistry in much the same way as the well-known Zeise salt, $Cl_3PtC_2H_4^-$. We have studied the reaction of $Ru(NH_3)_5H_2O^{2+}$ with a variety of unsaturated organic molecules in water and acetone as solvents. Some representative examples are described in this report which also comprises the crystal and molecular structure of one particular case, namely, of the complex with fumaric acid. The structures of a number of transition-metal compounds containing olefins in the presence of other π acids have been recently reviewed.[6] No structure, however, appears to have been determined of complexes of the pentaammineruthenium(II) moiety and an alkene representing the sixth ligand.

0002-7863/79/1501-6197$01.00/0 © 1979 American Chemical Society