

less photosubstitution active (as expected, since the MLCT* configuration can be represented as a substitution inert Ru(III) coordinated to a reduced ligand center, i.e., Ru^{III}-L).² In addition, the photolability observed is sensitive to the irradiation wavelength with quantum yield rising markedly at lower λ_{irr} . This behavior is interpreted as reflecting the population and reactivity of some higher energy LF* states. These reactivity differences plus the proximity of the lower energy LF and MLCT states allow the use of ligand substituents in the "tuning" of photoreaction behavior. Notably, this model has now been used successfully to explain the quantitative photosubstitution behavior of several other types of metal complexes.^{3,15}

For the Ru(NH₃)₅py-x²⁺ complexes, the crossover from "reactive" to "unreactive" behavior comes when the λ_{max} of the MLCT absorption band falls below ~ 460 nm. Although the data set given in Table IV is limited, a similar pattern is seen for the *trans*-Ru(NH₃)₄LL'²⁺ ions. The bis(pyridine)-complex (λ_{max} 423) is "reactive" with Φ_{tot} independent of λ_{irr} . In contrast, both *trans*-Ru(NH₃)₄(py)(pz)²⁺ (λ_{max} (MLCT-1) = 474 nm) and *trans*-Ru(NH₃)₄(py)(4-ac-py)²⁺ (λ_{max} = 508 nm) display much smaller quantum yields when irradiated at the MLCT-1 maxima and higher quantum yields at shorter wavelengths. Qualitative studies utilizing the spectral changes only (Φ_{spec}) for the latter ions indicate the photoaquation quantum yields follow a smooth gradation for wavelengths between the λ_{irr} values indicated in Table IV. For example, the Φ_{spec} value for *trans*-Ru(NH₃)₄(py)(4-ac-py)²⁺ at λ_{irr} 405 nm is $\sim 1/4$ the value measured at λ_{irr} 366 nm but about 20 times the value at λ_{irr} 520 nm. Thus, there appears to be no special character assignable to the photochemistry resulting when the MLCT-2 band is irradiated.

In another parallel to the pentaammine analogues, the data in Table IV show that the principal photoreaction for *trans*-Ru(NH₃)₄LL'²⁺ is NH₃ aquation regardless of identities of

L and L'. For the tetraammine complexes, however, NH₃ photoaquation is unambiguously the result of labilization of ligands cis to the L-Ru-L' axis. If one assumes that ligand labilization patterns are reflective of the nature of the lowest energy LF* state,¹⁶ the preference for NH₃ labilization implies that the lowest energy LF* state is one that can be qualitatively represented by the one-electron configuration (d_{xz})²(d_{yz})²(d_{xy})¹(d_{x²-y²)¹(d_z)⁰. Given that pyridine is generally considered a weaker σ donor than NH₃,¹⁷ one might expect greater excited-state population in d_z than in d_{x²-y². This type of behavior is reflected in the photoaquation patterns of the isoelectronic Rh(III) analogues¹⁸ Rh(NH₃)₅(py-x)³⁺ which photoaquate py-x exclusively under ligand field excitation. The explanation of the different behavior for the Ru(II) complexes must lie with the much greater π back-bonding interaction between the Ru(II) center and π -unsaturated organic ligands. Such interaction may not only lower the energy of d_z orbitals with the appropriate symmetry but also synergetically increase the σ -donor strength of that ligand, the π -acceptor ligands.}}

Acknowledgment. This work was supported in part by the National Science Foundation. E. T. thanks the Fundação de Amparo à Pesquisa do Estado de São Paulo (Foundation for the Support of Research in the State of São Paulo) for financial support. The ruthenium used in these studies was provided on loan by Matthey Bishop, Inc.

Registry No. [*t*-Ru(NH₃)₄(py)(4-ac-py)](BF₄)₂, 71964-13-1; [*t*-Ru(NH₃)₄(py)(pz)](BF₄)₂, 71964-15-3; [*t*-Ru(NH₃)₄(py)(pzH)](BF₄)₃, 71964-16-4; [*t*-Ru(NH₃)₄(pz)₂](BF₄)₂, 71964-17-5; [*t*-Ru(NH₃)₄(py)₂](BF₄)₂, 71964-18-6; [*t*-Ru(NH₃)₄(pzH)₂](BF₄)₄, 71964-19-7; [Ru(NH₃)₅(4-ac-py)](BF₄)₂, 71964-20-0; [Ru(NH₃)₅pz](BF₄)₂, 41481-91-8; [Ru(NH₃)₅pzH](BF₄)₃, 71964-21-1; [*t*-Ru(NH₃)₄(SO₄)(py)]Cl, 63251-18-3; [*t*-Ru(NH₃)₄Cl₂]Cl, 22327-28-2; *t*-Ru(NH₃)₄(pzH)pz³⁺, 71964-23-3.

(15) (a) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. (b) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1979**, *17*, 3385. (c) Figard, J. E.; Peterson, J. D. *Ibid.* **1978**, *17*, 1059.

(16) (a) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208. (b) Wrighton, M. S.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 165.

(17) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399.
(18) Petersen, J. D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3188.

Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11794

Kinetics and Mechanism of the Forward and Reverse Reactions between (Pyridine)pentaammineruthenium(III) or (4,4'-Bipyridine)pentaammineruthenium(III) and (Ethylenediaminetetraacetato)cobaltate(II)¹

JAMES PHILLIPS and ALBERT HAIM*

Received June 18, 1979

Kinetic measurements of the forward and reverse reactions for Ru(NH₃)₅L³⁺ + CoEDTA²⁻ \rightleftharpoons Ru(NH₃)₅L²⁺ + CoEDTA⁻ have been carried out at 25.0 °C, pH 6.0, and ionic strength 0.10 M. For L = pyridine or 4,4'-bipyridine, the rate constants are 32 ± 1 and 77 ± 4 M⁻¹ s⁻¹ (forward reactions) and 236 ± 5 and 156 ± 3 M⁻¹ s⁻¹ (reverse reactions). The mechanisms of these reactions are discussed in the context of Marcus' cross relation for outer-sphere processes corrected for electrostatic effects.

Introduction

The reduction of the d⁵ low-spin complex Fe(CN)₆³⁻ by the d⁷ high-spin complex CoEDTA²⁻ (EDTA = ethylenediaminetetraacetate) has been studied very extensively.²⁻⁶ The

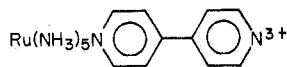
first detectable² product (millisecond time scale) of the reaction is the cyano-bridged binuclear complex (EDTA)-Co^{III}NCFe^{II}(CN)₅⁵⁻ in which both metal centers are inert, d⁶ low-spin systems. In a time scale of the order of minutes at

(1) This work was supported by Grants CHE 7610449 and CHE 79-09253 from the National Science Foundation.
(2) Adamson, A. W.; Gonick, E. *Inorg. Chem.* **1963**, *2*, 129.

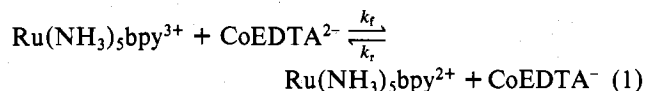
(3) Huchital, D. H.; Wilkins, R. G. *Inorg. Chem.* **1967**, *6*, 1022.
(4) Huchital, D. H.; Hodges, R. J. *Inorg. Chem.* **1973**, *12*, 998.
(5) Rosenheim, L.; Speiser, D.; Haim, A. *Inorg. Chem.* **1974**, *13*, 1571.
(6) Huchital, D. H.; Lepore, J. *Inorg. Chem.* **1978**, *17*, 1134.

25 °C, the metastable binuclear complex disappears with the concomitant production of CoEDTA⁻ and Fe(CN)₆⁴⁻. It was first thought that the binuclear species was a successor complex along the inner-sphere pathway that led from CoEDTA²⁻ and Fe(CN)₆³⁻ to the mononuclear products.²⁻⁴ However, in recent work^{5,6} it has been shown that the binuclear complex represents a dead end as far as direct formation of mononuclear products is concerned and that an alternate outer-sphere reaction between CoEDTA²⁻ and Fe(CN)₆³⁻ is the source of CoEDTA⁻ and Fe(CN)₆⁴⁻.

The present work was started with the purpose of exploring the scope of the mechanistic pattern exhibited by the Fe(CN)₆³⁻-CoEDTA²⁻ system, Fe(CN)₆³⁻ being replaced by



(hereinafter abbreviated as Ru(NH₃)₅bpy³⁺), another d⁵ low-spin complex with a potential bridging ligand. In contrast with the Fe(CN)₆³⁻-CoEDTA²⁻ reaction which proceeds predominantly by an inner-sphere mechanism, the Ru(NH₃)₅bpy³⁺-CoEDTA²⁻ reaction, eq 1, is shown to proceed predominantly, if not exclusively, by an outer-sphere mechanism.



Experimental Section

Materials. Lithium perchlorate and 4,4'-bipyridine were recrystallized from water. The water used in all experiments was distilled water passed through a Barnstead ion-exchange demineralizer and then distilled in a modified (all-glass) Corning Model AG-1b apparatus. [Ru(NH₃)₅bpyH](ClO₄)₄, [Ru(NH₃)₅py]Br₃, and K[CoEDTA]·2H₂O were synthesized as described before.^{5,7,8} Solutions of CoEDTA²⁻ were prepared by the addition of a 10% excess of Na₂H₂EDTA to the appropriate amount of a solution of Co(ClO₄)₂. All other chemicals were reagent grade and used as received.

Analyses. The cobalt(II) perchlorate stock solutions were analyzed spectrophotometrically.⁹ The lithium perchlorate stock solutions were standardized by passing aliquots through a column of Dowex 50-X8 in the hydrogen form and then titrating the HClO₄ in the eluate. pH measurements were carried out with an Orion Model 801 pH meter.

Measurements. The equilibrium constant for eq 1 was determined by a spectrophotometric method. Separate solutions of Ru(NH₃)₅bpy³⁺ and of CoEDTA²⁻ of the desired concentrations, pH, and ionic strength were prepared and deaerated with argon. The desired volumes of these solutions were mixed anaerobically and then transferred to a spectrophotometric cell which was placed in the thermostated cell compartment of a Cary 118 or Cary 17 spectrophotometer. After temperature equilibration (30 min) the absorbance at 490 nm was measured.

Cyclic voltammetry measurements were performed on a Princeton Applied Research Corp. Model 170 electrochemical system. Reversible cyclic voltammograms were obtained at sweep rates from 20 to 200 mV/s with platinum wires as auxiliary and working electrodes vs. a saturated calomel electrode.

All kinetic measurements were carried out with a Durrum D-110 stopped-flow apparatus interfaced⁹ to an 1800 IBM computer. Separate solutions of the oxidant and reductant were prepared at the desired concentration, ionic strength, and pH and then deaerated by flushing the solutions with argon. The solutions were transferred anaerobically to the reservoir syringes of the stopped-flow apparatus, and then four replicate measurements were carried out for each pair of solutions. The Ru(NH₃)₅bpy³⁺-CoEDTA²⁻ and Ru(NH₃)₅py³⁺-CoEDTA²⁻ reactions were followed by observing the increase in absorbance (formation of the Ru(II) complexes) at 482

Table I. Kinetic Data for the Ru(NH₃)₅bpy³⁺-CoEDTA²⁻ and Ru(NH₃)₅py²⁺-CoEDTA⁻ Reactions^a

10 ⁴ × [CoEDTA ^{2-/-}], ^b M	10 ⁵ × [Ru(NH ₃) ₅ bpy ^{3+/2+}], ^b M	k _{obsd} , ^c s ⁻¹
3.87	1.55	0.031
8.71	1.55	0.069
9.68	3.24	0.073
9.68	2.10	0.079
14.5	1.55	0.126
19.4	2.10	0.150
29.0	1.55	0.214
5.24	1.40	0.088
7.86	1.40	0.128
13.1	1.40	0.207
26.2	1.40	0.403

^a Measurements at 25 °C, μ = 0.10 M (LiClO₄), pH 6.0 (phosphate). ^b The first seven entries pertain to the CoEDTA²⁻-Ru(NH₃)₅bpy³⁺ reaction and the last four entries pertain to the CoEDTA⁻-Ru(NH₃)₅py²⁺ reaction. ^c Each entry is the average of four replicate measurements with the same pair of solutions.

and 410 nm, respectively. The reverse reactions, Ru(NH₃)₅bpy²⁺-CoEDTA⁻ and Ru(NH₃)₅py²⁺-CoEDTA⁻, were followed by observing the decrease in absorbance at 470 and 410 nm, respectively. In all cases the Co(II) or Co(III) was in at least tenfold excess over the Ru(III) or Ru(II) complex.

Results

Solutions of Ru(NH₃)₅bpy³⁺ at pH > 7 were found¹⁰ to be unstable and to develop, within a few minutes, the characteristic charge-transfer absorption of Ru(NH₃)₅bpy²⁺. At pH < 5.4, substantial protonation of the ruthenium(II) complex obtains.¹¹ Therefore, all measurements were performed at pH 6.0 (phosphate buffer). This represents a compromise in that protonation of Ru(NH₃)₅bpy²⁺ is relatively unimportant (2.5% protonation) and the Ru(NH₃)₅bpy³⁺ is relatively stable (no change in spectrum during 40 min).

The equilibrium constant for eq 1 was determined by measuring the absorbance at 490 nm of equilibrated solutions at 25 °C, ionic strength 0.10 M and pH 6.0. At this wavelength, the absorbances of CoEDTA²⁻ and Ru(NH₃)₅bpy³⁺ are negligible, and therefore the absorbance of the solution per centimeter is given by (ε₁ + ε₂)x, where x is the equilibrium concentration of Ru(NH₃)₅bpy²⁺ (protonated and unprotonated) or CoEDTA⁻ and ε₁ and ε₂ are the molar absorbances of Ru(NH₃)₅bpy²⁺ (1.16 × 10⁴ M⁻¹ cm⁻¹) and CoEDTA⁻ (148 M⁻¹ cm⁻¹) at pH 6.0. An empirical equilibrium constant, K_{emp}, for reaction 1 can be calculated from the value of x and the initial concentrations of Ru(NH₃)₅bpy³⁺ (a₀) and CoEDTA²⁻ (b₀) by using the expression K_{emp} = x²/(a₀ - x)(b₀ - x). For a₀ = (3.50-3.68) × 10⁻⁵ M and b₀ = (2.32-8.10) × 10⁻⁴ M, measured values (6) of K_{emp} were 0.38 ± 0.09. The empirical equilibrium constant for reaction 1 is related to the actual equilibrium constant K by means of eq 2 where K_a, the acid dissociation constant of Ru-

$$K_{\text{emp}} = K(1 + [\text{H}^+]/K_a) \quad (2)$$

(NH₃)₅bpyH³⁺, is 4.0 × 10⁻⁵.¹¹ The value of K found is 0.37 ± 0.09, in excellent agreement with the value 0.31 calculated from the reduction potentials of Ru(NH₃)₅bpy³⁺ (0.34 V at 25 °C, pH 6.0, μ = 0.10 M, measured in the present work) and CoEDTA⁻ (0.37 V at 25 °C, pH 4.6-5.4, μ = 0.20 M¹²).

The kinetic measurements of the forward and reverse reactions in eq 1 are summarized in Table I. With more than tenfold excess of cobalt over ruthenium, excellent linear plots of ln(A_∞ - A_t) vs. time were obtained. This result may be

(7) Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* **1979**, *33*, 51.

(8) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

(9) Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.

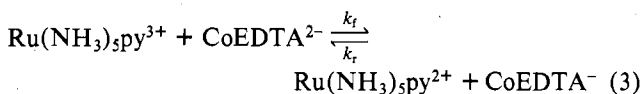
(10) Yeh, A.; Haim, A., unpublished observations.

(11) Lavalley, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583.

(12) Tanaka, N.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1054.

surprising at first glance, since the reactions do not go to completion. However, it has been shown¹³ that reversible reactions of the type $A + B \rightleftharpoons C + D$ which are pseudo first order in one direction and second order in the other may be analyzed by simple first-order kinetics if the reaction proceeds to >90% completion. The conditions used in Table I meet this requirement (>93% completion) and therefore the slopes of the $\ln(A_t - A_\infty)$ vs. t plots give values of $k_{\text{obsd}} = k_f/[\text{Co}^{\text{II}}]$ for the first seven entries and $k_{\text{obsd}} = k_r/[\text{Co}^{\text{III}}]$ for the last four entries. Plots of k_{obsd} vs. $[\text{Co}^{\text{II}}]$ or $[\text{Co}^{\text{III}}]$ were linear, showing that both forward and reverse reactions in eq 1 obey mixed second-order kinetics. Values of k_f and k_r , obtained from a least-squares analysis of the k_{obsd} vs. $[\text{Co}^{\text{II}}]$ or $[\text{Co}^{\text{III}}]$ data are $77 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$ and $156 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The equilibrium constant K , calculated as k_f/k_r , is 0.49 ± 0.04 , within experimental error of the value measured directly 0.37 ± 0.09 .

A cursory kinetic study of the forward and reverse reactions in eq 3 was carried out. With $[\text{Ru}(\text{NH}_3)_5\text{py}^{3+}] = 2.55 \times 10^{-5}$



M and $[\text{CoEDTA}^{2-}] = 1.94 \times 10^{-3}$ and $2.42 \times 10^{-3} \text{ M}$, values of k_{obsd} at 25°C , $\mu = 0.10 \text{ M}$, and $\text{pH} 6.0$ are 0.064 and 0.077 s^{-1} from which we calculate $k_f = 32 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$. With $[\text{Ru}(\text{NH}_3)_5\text{py}^{2+}] = 2.87 \times 10^{-5} \text{ M}$ and $[\text{CoEDTA}^-] = 1.23 \times 10^{-3}$ and $1.96 \times 10^{-3} \text{ M}$, values of k_{obsd} at 25°C , $\mu = 0.10 \text{ M}$, and $\text{pH} 6.0$ are 0.296 and 0.452 s^{-1} from which we calculate $k_r = 236 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$. The equilibrium constant for reaction 3 calculated from k_f/k_r is 0.14 ± 0.01 , in acceptable agreement with the value 0.096 calculated from the reduction potentials of $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ (0.31 V at 25°C , $\text{pH} 6.0$, $\mu = 0.10$, measured in the present work) and CoEDTA^- .

Discussion

Since there is no potential bridging ligand in the coordination sphere of $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$, there is no doubt that the $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ - CoEDTA^{2-} reaction proceeds by an outer-sphere mechanism. For the $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$ - CoEDTA^{2-} system, the presence of the remote N in the 4,4'-bipyridine ligand and the lability of the cobalt(II) reductant makes an inner-sphere mechanism a distinct possibility. In fact, electron transfer mediated by a bridging 4,4'-bipyridine has been clearly demonstrated in the $\text{Co}(\text{NH}_3)_5\text{bpy}^{3+}$ - $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ reaction,¹⁴ and CoEDTA^{2-} is a well-known inner-sphere reductant.^{2-6,15} Nevertheless, it seems certain to us that the $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$ - CoEDTA^{2-} proceeds via an outer-sphere mechanism. First, the binuclear complex $(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{bpy})\text{Co}^{\text{III}}\text{EDTA}^+$, the predicted product of an inner-sphere reaction, would be expected to absorb in the region 530–560 nm.^{16,17} However, rapid spectrophotometric examination of product solutions following the reaction between $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$ and CoEDTA^{2-} revealed only the absorption at 480 nm, characteristic¹¹ of mononuclear ruthenium(II) 4,4'-bipyridine, and no shoulders or peaks could be discerned in the 530–560-nm region. From the absence of detectable (<5%) quantities of the presumed inner-sphere product $(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{bpy})\text{Co}^{\text{III}}\text{EDTA}$, we infer that the inner-sphere mechanism is not operative or, at the most, contributes 5% to the $\text{Ru}(\text{NH}_3)_5(\text{bpy})^{3+}$ - CoEDTA^{2-} redox reaction. However, it might be argued that the binuclear complex is not detected because it

decomposes rapidly to the products shown in eq 1. A rapid dissociation of $(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{bpy})\text{Co}^{\text{III}}\text{EDTA}$ is highly unlikely since it contains two d^6 low-spin metal centers, and these are well-known to be inert. Moreover, microscopic reversibility would require that the reverse reaction in eq 1 also proceed by an inner-sphere mechanism, and therefore the $156 \text{ M}^{-1} \text{ s}^{-1}$ value measured for the reverse process would represent the substitution of the remote N end of the bound 4,4'-bipyridine into the coordination sphere of CoEDTA^- . Such a high value for a substitution reaction of CoEDTA^- is highly unlikely, most rate constants for such processes falling in the range 10^{-4} – $10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.^{18,19} This argument, previously⁵ presented in support of an outer-sphere mechanism for the CoEDTA^- - $\text{Fe}(\text{CN})_6^{4-}$ reaction and, hence, for the CoEDTA^{2-} - $\text{Fe}(\text{CN})_6^{3-}$ reaction that results in the production of mononuclear products, has been widely accepted.^{6,20,21} Therefore, we conclude that the CoEDTA^{2-} - $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$ proceeds by an outer-sphere mechanism.

Additional details⁸ about the path for electron transfer are obtained by comparing the observed rate constants with those calculated from Marcus' cross relation corrected^{8,22} for electrostatic effects, eq 4–9, where single and double asterisks

$$\Delta G_{12}^* = \Delta G_{12}^{**} + w_{12} \quad (4)$$

$$\Delta G_{12}^{**} = (\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G_{\text{R}}^\circ)/2 \quad (5)$$

$$\Delta G_{11}^{**} = \Delta G_{11}^* - w_{11} \quad (6)$$

$$\Delta G_{22}^{**} = \Delta G_{22}^* - w_{22} \quad (7)$$

$$\Delta G_{\text{R}}^\circ = \Delta G_{12}^\circ + w_{21} - w_{12} \quad (8)$$

$$w = (4.225 \times 10^{-8})z_1z_2/a(1 + (3.285 \times 10^7)\mu^{1/2}a) \quad (9)$$

apply to measured and corrected free energies of activation, respectively, subscripts 1 and 2 pertain to Ru and Co couples, respectively, w 's are the Coulombic terms, calculated for water at 25°C from eq 9, ΔG_{12}° and $\Delta G_{\text{R}}^\circ$ are the measured and corrected standard free energies of reaction, and a is the distance of closest approach. Two different values of the radius of the ruthenium complexes can be used depending on whether electron transfer occurs through the pyridine or ammonia ligands, the values⁸ being 6.4×10^{-8} and $2.7 \times 10^{-8} \text{ cm}$, respectively, for $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ and 9.8×10^{-8} and $2.7 \times 10^{-8} \text{ cm}$, respectively, for $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$. The radius of CoEDTA^{2-} is taken to be $4.0 \times 10^{-8} \text{ cm}$, identical with that²³ of FeEDTA^{2-} . The rate constants for the self-exchange reactions of the ruthenium^{24,25} and cobalt^{26,27} complexes are 1.1×10^5 and $3.5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, respectively. The rate constant calculated for the $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ - CoEDTA^{2-} reaction is 0.75 or $15 \text{ M}^{-1} \text{ s}^{-1}$ depending on whether electron transfer proceeds through pyridine or through ammonia. The corresponding calculated values for the $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$ - CoEDTA^{2-} reaction are 0.74 or $30 \text{ M}^{-1} \text{ s}^{-1}$. Admittedly, calculations based on eq 4–9 may not be sufficiently accurate to obtain geometric details about outer-sphere precursor complexes and the detailed path of electron transfer. However, from the reasonable agreement between the experimental rate constants (32 and $77 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ and $\text{Ru}(\text{NH}_3)_5\text{bpy}^{3+}$, respectively) and the

(13) Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5158.

(14) Gaswick, D.; Haim, A. *J. Am. Chem. Soc.* **1974**, *96*, 7845.

(15) Wilkins, R. G.; Yelin, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 1191.

(16) Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* **1979**, *33*, 51.

(17) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512.

(18) Shimi, I. A. W.; Higginson, W. C. E. *J. Chem. Soc.* **1958**, 260.

(19) Dyke, R.; Higginson, W. C. E. *J. Chem. Soc.* **1960**, 1998.

(20) Huchital, D. H.; Lepore, J. *Inorg. Chem.* **1978**, *17*, 1134.

(21) Taube, H. *Pure Appl. Chem.* **1975**, *44*, 25.

(22) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

(23) Rosenberg, R. C.; Wherland, S.; Holwerda, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 6364.

(24) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(25) The rate constants for self-exchange of various substituted pyridine complexes of $\text{Ru}(\text{NH}_3)_5^{3+/2+}$ are very insensitive to the nature of the pyridine ligand.

(26) Obtained by extrapolation to 25°C from the values reported in ref 27.

(27) Im, Y. A.; Busch, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 3357.

values calculated (15 and 30 M⁻¹ s⁻¹) by assuming electron transfer through ammonia, it is tempting to infer that the actual path of electron transfer is largely through ammonia. On the basis of the insensitivity of the rates of ferrocyanide reduction of substituted pyridine pentaamminecobalt(III) complexes to the nature of the substituent in the pyridine ring,^{28,29} we suggested previously⁸ that electron transfer in these systems involves approach of the Fe(CN)₆⁴⁻ to the ammonia side of the cobalt(III) complexes. However, calculations based on the Marcus cross relation corrected for electrostatics of rate constants for the Fe(CN)₆⁴⁻-Ru(NH₃)₅py³⁺ reaction were taken⁸ to indicate that, in this system, the actual path of electron transfer is through the pyridine ligand. The different mechanism suggested for the Fe(CN)₆⁴⁻-Ru(NH₃)₅py³⁺ re-

action on the one hand and the Fe(CN)₆⁴⁻-Co(NH₃)₅py³⁺ and CoEDTA²⁻-Ru(NH₃)₅py³⁺ reactions on the other can be rationalized on the basis of orbital symmetry considerations.^{8,30} For the former system, acceptor and donor orbitals are of π symmetry and, therefore, a π carrier orbital in the pyridine ligand apparently provides an efficient path for electron transfer. In contrast, for the Fe-Co or Co-Ru systems, donor and acceptor orbitals are of π and σ or σ and π symmetry, respectively. This symmetry mismatch may render the path via pyridine inoperative, and the reactions then proceed with the reductant approaching the oxidant on the ammonia side. We are planning to study the reductions of Ru(NH₃)₅py³⁺ and Co(NH₃)₅py³⁺ by FeEDTA²⁻, a π -donor reducing agent, to inquire into the validity of the orbital symmetry considerations.

Registry No. Ru(NH₃)₅bpy³⁺, 54714-03-3; Ru(NH₃)₅bpy²⁺, 54714-01-1; CoEDTA²⁻, 14931-83-0; CoEDTA⁻, 15136-66-0; Ru(NH₃)₅py³⁺, 33291-25-7; Ru(NH₃)₅py²⁺, 21360-09-8.

(28) For example, the rate constants at 25 °C and ionic strength 0.10 M for the Co(NH₃)₅py³⁺-Fe(CN)₆⁴⁻ and Co(NH₃)₅bpy³⁺-Fe(CN)₆⁴⁻ reactions are 36.2 and 58.3 M⁻¹ s⁻¹, respectively.²⁹

(29) Miralles, A. J. Ph.D. Dissertation, State University of New York, Stony Brook, N.Y., July 1974.

(30) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264.

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Design and Synthesis of New Polydentate Phosphine and Mixed-Donor Phosphine Ligands

RICHARD URIARTE, TERRY J. MAZANEC, KWOLIANG D. TAU, and DEVON W. MEEK*

Received January 26, 1979

By using available vinyl phosphines, allyl compounds, and tertiary phosphines that contain a chloroalkyl group and matching up a synthesis route from among the radical-chain, base-catalyzed, or coupling methods, one can now synthesize a very large number of polydentate phosphine ligands that contain mixed-donor groups, specific types of donors at selected structural sites, and connecting alkyl chains of varying length. Such combinations are illustrated in this paper by the preparations of 16 polydentate ligands, 12 of which are new. The other four ligands or intermediates are made by superior routes compared to the present literature methods. These relatively simple, high-yield-synthesis routes lead to ligands either with a variety of substituents on phosphorus or with a variety of group 5A and 6A donor atoms in the same ligand.

Introduction

The number and diversity of tertiary phosphines used to prepare new coordination and organometallic compounds has increased rapidly during the past 20 years.¹ Compared to monodentate ligands with comparable donor groups, a properly designed polydentate ligand can simultaneously provide (1) more control on the coordination number,² stereochemistry,³ and magnetic properties⁴ of the resulting complex, (2) increased basicity (or nucleophilicity) at the metal,⁵ and (3) higher optical yields in catalytic asymmetric synthesis.^{6,7} Incorporation of other group 5 and/or group 6 donor atoms

to form a "mixed" phosphine readily facilitates controlled variation of the steric and electronic properties of the ligands.

The ability to vary the chelate chain length is an important consideration in the design of polydentate ligands, as important structural differences have been observed in coordination compounds simply by changing the length of the chelate chain. For example, the open-chain triphosphine ligands PhP(CH₂CH₂PPh₂)₂, etp, and PhP(CH₂CH₂CH₂PPh₂)₂, ttp, differ by only one methylene unit in the flexible connecting chains; however, the structures of the five-coordinate cations [Co(etp)L₂]⁺ (L = P(OMe)₃, PR₃, CO) and [Co(ttp)L₂]⁺ are trigonal bipyramidal and square pyramidal, respectively.^{3,8}

Meek and Li⁹ prepared a series of palladium thiocyanate complexes containing the homologous series of chelating diphosphine ligands Ph₂P(CH₂)_nPPh₂ (n = 1, 2, 3). All three ligands contain equivalent donor groups, but remarkable control on the mode of thiocyanate bonding was observed in the structures; namely, both thiocyanate groups were S bonded for n = 1, one was S bonded and one was N bonded for n =

(1) R. Mason and D. W. Meek, *Angew. Chem.*, **90**, 195-206 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 183-94 (1978).

(2) D. W. Meek, *Strem Chem.*, **5**, 3-11 (1977).

(3) D. L. DuBois and D. W. Meek, *Inorg. Chem.*, **15**, 3076 (1976).

(4) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).

(5) T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4194 (1973).

(6) W. S. Knowles, M. Sabacky, B. Vineland, and D. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975).

(7) (a) T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975); (b) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977); (c) M. D. Fryzuk and B. Bosnick, *ibid.*, **99**, 6262 (1977).

(8) R. Mason and G. R. Scollary, *Aust. J. Chem.*, **30**, 2395 (1977).

(9) (a) M. Li, B.S. Thesis, The Ohio State University, 1972; (b) G. J. Palenik, W. L. Steffen, M. Mathew, M. Li, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, **10**, 125 (1974).