

Oxidation of Cobalt(II) Macrocycles by Tris(bipyridyl)ruthenium(III) Ions<sup>1</sup>

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The kinetics of the electron-transfer reactions between Ru(bpy)<sub>3</sub><sup>3+</sup> and selected Co(II) complexes were evaluated by laser flash photolysis. The cobalt(II) complexes investigated were (H<sub>2</sub>O)<sub>2</sub>Co(N<sub>4</sub>mac)<sup>2+</sup>, with N<sub>4</sub>mac = [14]aneN<sub>4</sub>, *C-meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>, tim ([14]tetraeneN<sub>4</sub>), [15]aneN<sub>4</sub>, and tmc (1,4,8,11-tetramethylcyclam). The respective second-order rate constants at 25 °C, μ = 0.10 M, are 3.2 × 10<sup>7</sup>, 7.8 × 10<sup>6</sup>, 2.1 × 10<sup>7</sup>, 1.7 × 10<sup>7</sup>, and 6 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>. The results have been evaluated for their agreement with the Marcus theory. The complex Co(tmc)<sup>2+</sup> also reacts with Ru(phen)<sub>3</sub><sup>3+</sup> (*k* = 1.0 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>) and with Ru(4,7-Me<sub>2</sub>phen)<sub>3</sub><sup>3+</sup> (*k* = 3.2 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>). These cobalt(II) complexes also quench the emission of the excited-state complex \*Cr(bpy)<sub>3</sub><sup>3+</sup>. Quenching occurs by electron transfer, except for Co(tmc)<sup>2+</sup>, which appears to react by energy transfer.

## Introduction

Cobalt macrocycles form a homologous series in which most of the Co(III)/Co(II) self-exchange rate constants and standard reduction potentials are known. Since both parameters span a considerable range along the series, their effects on reaction rates can be examined. Particularly interesting are the oxidations of the cobalt(II) complexes by Ru(bpy)<sub>3</sub><sup>3+</sup>, a reagent that adopts a common outer-sphere electron-transfer mechanism. Ru(bpy)<sub>3</sub><sup>3+</sup> is a strong oxidant (*E*<sub>3/2</sub><sup>o</sup> = 1.26 V vs NHE)<sup>2</sup> with large self-exchange rate constant (*k*<sub>RuRu</sub> = 4.2 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>3</sup> The combination is quite favorable, and the oxidation of two mildly reducing cobalt(II) complexes with low self-exchange rate constants is fast<sup>4</sup> and barely measurable by the stopped-flow technique.<sup>5</sup> In this work the Ru(III) complex was therefore generated by flash photolysis,<sup>6-12</sup> which allows the determination of large rate constants and avoids the handling of micromolar concentrations of Ru(bpy)<sub>3</sub><sup>3+</sup> and air-sensitive cobalt(II) complexes in the stopped-flow instrument. A smaller number of measurements were also made with Ru(III) phenanthroline analogues. Additionally, some data were obtained for the quenching of the <sup>2</sup>E excited state of Cr(bpy)<sub>3</sub><sup>3+</sup> by some of the same cobalt(II) macrocycles.

## Experimental Section

The cobalt(II) complexes shown in Figure 1 are known materials. Samples were prepared by procedures in the literature<sup>13-18</sup> and characterized by their UV-visible spectra.<sup>11,13</sup> Details are given in the thesis referenced.<sup>1</sup> Commercial samples of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> were used, and the phenanthroline analogues were prepared by standard methods.<sup>19,20</sup> The

Table I. Summary of Kinetic Data for the Reactions of Co(N<sub>4</sub>mac)<sup>2+</sup> with Ru(bpy)<sub>3</sub><sup>3+</sup>

macrocycle	quencher	<i>k</i> /M <sup>-1</sup> s <sup>-1</sup> <sup>a</sup>
[14]aneN <sub>4</sub>	[Co(NH <sub>3</sub> ) <sub>3</sub> py](ClO <sub>4</sub> ) <sub>3</sub>	(3.2 ± 0.1) × 10 <sup>7</sup>
<i>C-meso</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	[Co(NH <sub>3</sub> ) <sub>3</sub> Br](ClO <sub>4</sub> ) <sub>2</sub>	(7.8 ± 0.1) × 10 <sup>6</sup>
	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl](ClO <sub>4</sub> ) <sub>2</sub>	(7.6 ± 0.2) × 10 <sup>6</sup>
tim	[Co(tim)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	(1.0 ± 0.2) × 10 <sup>7</sup> <sup>b,c</sup>
	[Co(tim)(H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	(2.1 ± 0.1) × 10 <sup>7</sup>
Me <sub>6</sub> [14]4,11-dieneN <sub>4</sub>	[Co(NH <sub>3</sub> ) <sub>3</sub> Br](ClO <sub>4</sub> ) <sub>2</sub>	(1.7 ± 0.1) × 10 <sup>6</sup> <sup>b,c</sup>
	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl](ClO <sub>4</sub> ) <sub>2</sub>	(1.7 ± 0.2) × 10 <sup>7</sup>
[15]aneN <sub>4</sub>	[Co(NH <sub>3</sub> ) <sub>3</sub> Br](ClO <sub>4</sub> ) <sub>2</sub>	(1.8 ± 0.1) × 10 <sup>7</sup>
	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl](ClO <sub>4</sub> ) <sub>2</sub>	(6.2 ± 0.2) × 10 <sup>5</sup>
	[Co(NH <sub>3</sub> ) <sub>3</sub> Br](ClO <sub>4</sub> ) <sub>2</sub>	(5.2 ± 0.2) × 10 <sup>5</sup>
	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl](ClO <sub>4</sub> ) <sub>2</sub>	(6.4 ± 0.4) × 10 <sup>5</sup>
tmc	[Co(NH <sub>3</sub> ) <sub>3</sub> Br](ClO <sub>4</sub> ) <sub>2</sub>	(5.2 ± 0.2) × 10 <sup>5</sup>
	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(6.4 ± 0.4) × 10 <sup>5</sup>

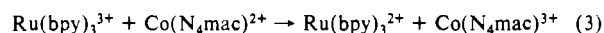
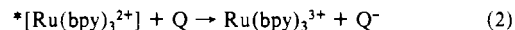
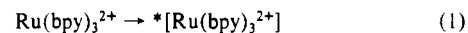
<sup>a</sup> At 25 °C and μ = 0.10 M, except as noted. <sup>b</sup> Reference 4, by stopped-flow methods. <sup>c</sup> 1.0 M H<sub>2</sub>SO<sub>4</sub>.

sample of tris(bipyridine)chromium(III) perchlorate and the phenanthroline analogues were prepared by a literature procedure.<sup>21</sup>

The laser flash photolysis apparatus used to produce the excited-state complex \*[Ru(bpy)<sub>3</sub>]<sup>2+</sup> has been described.<sup>22-24</sup> Oxidative quenching of the excited state by an appropriate reagent yields Ru(bpy)<sub>3</sub><sup>3+</sup>.<sup>25,26</sup> The choice of quencher in a given instance depends on the compatibility of that particular quencher with the given cobalt(II) macrocycles. For example, the quenchers Co(NH<sub>3</sub>)<sub>3</sub>X<sup>2+</sup> (X = Cl, Br) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were used for complexes having N<sub>4</sub>mac = *C-meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>, [15]aneN<sub>4</sub>, and tmc. For others (tim and [14]aneN<sub>4</sub>), (NH<sub>3</sub>)<sub>3</sub>Co(py)<sup>3+</sup> and (H<sub>2</sub>O)<sub>2</sub>Co(tim)<sup>3+</sup> were used. For several of the reactions the results were checked by using several quenchers.

Once formed, the Ru(bpy)<sub>3</sub><sup>3+</sup> undergoes reduction by Co(N<sub>4</sub>mac)<sup>2+</sup>, a reaction that can be monitored by the buildup of the ruthenium(II) concentration at 443 nm (ε 12 800 M<sup>-1</sup> cm<sup>-1</sup>).<sup>2</sup> The reactions were conducted with a substantial stoichiometric excess of Co(II), and the data in each experiment followed pseudo-first-order kinetics. The transmittance data were converted to absorbance (*D*) and were fit by standard nonlinear least-squares programs to the equation *D*<sub>*t*</sub> = *D*<sub>∞</sub> + (*D*<sub>0</sub> - *D*<sub>∞</sub>)e<sup>-*k**t*</sup>.

The sequence of reactions consists of excitation to the charge-transfer excited state (several Coumarin dyes with emission at 420-460 nm were used), oxidative quenching, and the reaction of interest, as given in eqs 1-3.



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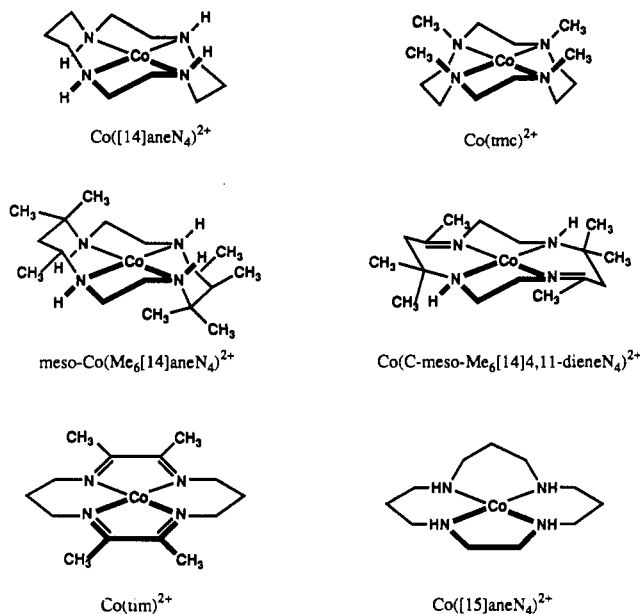


Figure 1. Structural formulas of the cobalt complexes used in this work, showing the abbreviated names used for them.

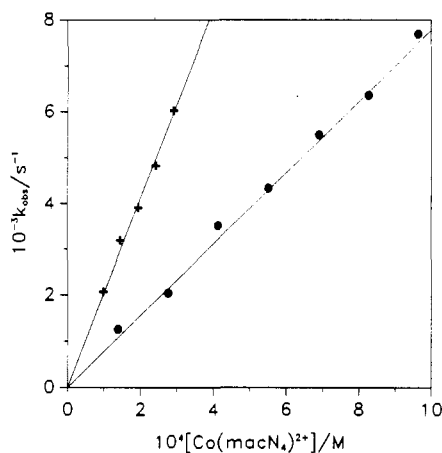


Figure 2. Kinetic data for the oxidation of Co(N<sub>4</sub>mac)<sup>2+</sup> complexes by Ru(bpy)<sub>3</sub><sup>3+</sup>, as shown by plots of pseudo-first-order rate constants against [Co(II)]. Data are shown for (H<sub>2</sub>O)<sub>2</sub>Co(tim)<sup>2+</sup> (pluses) and (H<sub>2</sub>O)<sub>2</sub>Co(C-meso-Me<sub>6</sub>[14]aneN<sub>4</sub>)<sup>2+</sup> (filled circles).

## Results

**Kinetics.** Plots of  $k_{\text{obs}}$  versus [Co(II)] are linear, as shown for a representative set of complexes in Figure 2. The slopes of the lines provide the values of  $k_3$ . Table I summarizes all the kinetic data. The kinetic pattern establishes that reaction 3 follows second-order kinetics and suggests that it occurs by an elementary bimolecular step.

**Co(tmc)<sup>2+</sup>.** This complex differs considerably from the others. It has an unusual visible spectrum, with a long wavelength absorption ( $\lambda_{\text{max}}$  725 nm,  $\epsilon$  12 M<sup>-1</sup> cm<sup>-1</sup>)<sup>18</sup> that suggests the predominant species in solution is a five-coordinate complex, analogous to *R,S,R,S*-(H<sub>2</sub>O)M(tmc)<sup>2+</sup> for M = Ni and Zn.<sup>27-34</sup> In

addition, Co(tmc)<sup>2+</sup> does not bind O<sub>2</sub> and is not oxidized by it; only small, linear ligands (e.g., NCS<sup>-</sup>) coordinate appreciably.<sup>35</sup>

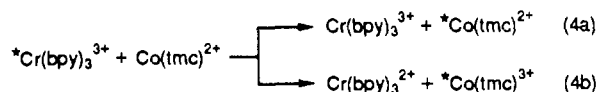
Co(tmc)<sup>2+</sup> is not readily oxidized chemically; no reactions occurred with Br<sub>2</sub> or Cl<sub>2</sub>. The cobalt(II) complex catalytically decomposes hydrogen peroxide, during which it is eventually converted irreversibly to a species with a 540-nm absorption maximum. This is not Co(tmc)<sup>3+</sup> and cannot be reduced to the parent Co(tmc)<sup>2+</sup>; evidently ligand oxidation or degradation occurs.

The cyclic voltammogram of Co(tmc)<sup>2+</sup> was completely irreversible even at the scan rate of 250 mV/s. An oxidation wave was seen at 1.05 V vs SCE. This implies that Co(tmc)<sup>3+</sup> is very unstable, perhaps due to the difficulty in attaining the six-coordinate structure that would best stabilize the low-spin d<sup>6</sup> configuration. The lack of reversibility implies that demetalation or ligand oxidation occurs rapidly.

The complex Co(tmc)<sup>2+</sup> reacts not only with Ru(bpy)<sub>3</sub><sup>3+</sup> ( $E^{\circ}_{3/2} = 1.26$  V),<sup>2</sup> but also with Ru(phen)<sub>3</sub><sup>3+</sup> ( $E^{\circ}_{3/2} = 1.26$  V)<sup>2</sup> and with Ru(4,7-Me<sub>2</sub>phen)<sub>3</sub><sup>3+</sup> ( $E^{\circ}_{3/2} = 1.09$  V).<sup>2</sup> The second-order rate constants for the three are respectively  $(6.2 \pm 0.2) \times 10^5$ ,  $(9.7 \pm 0.7) \times 10^5$ , and  $(3.5 \pm 0.2) \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C and  $\mu = 0.10$  M.

**Quenching of \*Cr(bpy)<sub>3</sub><sup>3+</sup>.** To explore this chemistry further, quenching of the emission from the <sup>2</sup>E excited state of Cr(bpy)<sub>3</sub><sup>3+</sup> by Co(tmc)<sup>2+</sup> was examined. The excited state is a powerful oxidant ( $E^{\circ}_{3/2} = +1.46$  V)<sup>36-40</sup> and as such could provide useful information about the electron-transfer reactions of Co(tmc)<sup>2+</sup>, if such occur.

Indeed, Co(tmc)<sup>2+</sup> quenches the excited state with  $k_4 = 3 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>. This value, being somewhat higher than those for the reactions of Co(tmc)<sup>2+</sup> with the ruthenium(III) complexes discussed above, is quite reasonable for electron-transfer quenching. However, the reaction produces no Cr(bpy)<sub>3</sub><sup>2+</sup>, and it thus appears that the quenching takes place by energy transfer (eq 4a) and not electron transfer (eq 4b).



The existence of an energy-transfer pathway is not surprising, given the overlap of the 725-nm absorption band of Co(tmc)<sup>2+</sup> with the emission of \*Cr(bpy)<sub>3</sub><sup>3+</sup> at 727 nm. What is surprising is the apparent slowness of the electron-transfer quenching for which one would predict a rate constant of  $5 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>, on the basis of the data for the Ru(bpy)<sub>3</sub><sup>3+</sup> reaction and the known self-exchange rate constants and reduction potentials for the two oxidants. In an attempt to understand these reactions better we also studied the quenching of the excited states of two other chromium complexes, \*Cr(5-Cl-phen)<sub>3</sub><sup>3+</sup> ( $E^{\circ}_{3/2} = 1.44$  V) and \*Cr(4,4'-Me<sub>2</sub>bpy)<sub>3</sub><sup>3+</sup> ( $E^{\circ}_{3/2} = 1.25$  V), by Co(tmc)<sup>2+</sup>. The quenching rate constants are  $1 \times 10^7$  and  $7 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>, respectively. CrL<sub>3</sub><sup>2+</sup> was not formed in either case, but the kinetics again show some dependence on the potential of the complexes. The possibility still remains, of course, that the reactions take place by energy transfer and that the electron-transfer path is somehow suppressed (or that it is unusually fast for the Ru(III) complexes). Indeed, it should be noted that  $E^{\circ}_{3/2}$  for Co(tmc)<sup>3+/2+</sup> is unknown. On the other hand, we cannot rule out electron-transfer quenching whereby the forward and reverse electron transfers occur within the same collision complex. This would be similar to the quenching

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of  $^*Cr(bpy)_3^{3+}$  by  $I^-$ , a reaction that presumably occurs by electron transfer, but does not yield the expected products.<sup>36</sup> Unlike  $I^-$ , the  $Co(tmc)^{2+}$  cannot effectively ion-pair with the cationic chromium complex, but the driving force for back-electron-transfer is quite large, so that it might take place before the initial products of the quenching reaction diffuse apart.

Quenching experiments were also carried out with several of the other cobalt(II) macrocycles. The quenching rate constants for  $Co([14]aneN_4)^{2+}$ ,  $Co(C-meso-Me_6[14]aneN_4)^{2+}$ ,  $meso-Co(Me_6[14]4,11-dieneN_4)^{2+}$ , and  $Co([15]aneN_4)^{2+}$  are  $(1.4 \pm 0.2) \times 10^8$ ,  $(5.1 \pm 0.4) \times 10^7$ ,  $(2.85 \pm 0.05) \times 10^7$ , and  $(1.55 \pm 0.06) \times 10^8 M^{-1} s^{-1}$ , respectively. Plots of  $k_{obs}$  versus  $[Co(II)]$  are linear. In each of these cases, quenching is accompanied by buildup of  $Cr(bpy)_3^{3+}$  as monitored at 560 nm. We conclude, therefore, that electron-transfer quenching occurs in all of these cases.

### Discussion

Application of the Marcus equation for outer-sphere electron transfer to this series of reactions is useful, since all of the partners (except  $Co(tmc)^{2+}$ ) have known electrode potentials and self-exchange rate constants. The equations used are<sup>41</sup>

$$k_{CoRu(cal)} = (k_{CoCo}k_{RuRu}K_{CoRu})^{1/2} \quad (5)$$

$$\log f = [\log(K_{CoRu})]^2 / 4 \log [k_{CoCo}k_{RuRu} / Z^2] \quad (6)$$

(41) The Marcus equation is used in the simple form given by eqs 5 and 6, using  $Z$  as the gas-phase collision frequency of  $10^{11} M^{-1} s^{-1}$ , without allowance for work terms, since each pair of reactants,  $RuL^{3+}$  and  $Co(N_4mac)^{2+}$ , have the same ionic charges.

The results for the four complexes for which all of the requisite parameters are known are then as follows:

complex	$E^{\circ}_{3/2}$	$k_{CoCo}/M^{-1} s^{-1}$	$\log k_{CoRu}$	
			obs	calc
$Co([14]aneN_4)^{2+}$	0.42	$8 \times 10^{-4}$	7.5	8.4
$meso-Co(Me_6[14]4,11-dieneN_4)^{2+}$	0.56	$4.5 \times 10^{-5}$	6.2	7.2
$Co(tim)^{2+}$	0.56	$5 \times 10^{-2}$	7.3	8.2
$Co([15]aneN_4)^{2+}$	0.66	$6 \times 10^{-3}$	7.2	7.4

The agreement, although not superb, is within about 1 log unit for each rate constant. The application of the Marcus theory can be reversed to estimate a value for the self-exchange rate constant of the pair  $Co(C-meso-Me_6[14]aneN_4)^{3+/2+}$ ;  $k_{CoCo}$  is estimated to be  $2 \times 10^{-5} M^{-1} s^{-1}$ .

Because the electrode potential and self-exchange rate constant for  $Co(tmc)^{2+}$  are not known, no further analysis is feasible. It is noted, however, that the two ruthenium(III) complexes with nearly the same electrode potentials react at nearly the same rate, whereas the reaction with  $Ru(4,7-Me_2phen)_3^{3+}$ , with a driving force some 0.15 V smaller, occurs about 30 times more slowly, in qualitative agreement with the Marcus theory.

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**Registry No.**  $Ru(bpy)_3^{2+}$ , 18955-01-6;  $(H_2O)_2Co([14]aneN_4)^{2+}$ , 65554-13-4;  $(H_2O)_2Co(C-meso-Me_6[14]aneN_4)^{2+}$ , 68170-27-4;  $(H_2O)_2Co(tim)^{2+}$ , 38337-82-5;  $(H_2O)_2Co([15]aneN_4)^{2+}$ , 74093-13-3;  $(H_2O)_2Co(tmc)^{2+}$ , 126543-79-1;  $Ru(phen)_3^{3+}$ , 23633-32-1;  $Ru(4,7-Me_2phen)_3^{3+}$ , 79747-03-8.

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## Theoretical Study of the Intramolecular Cis-Trans Isomerization Mechanism in $Cr(CO)_5X$ ( $X = CO, PH_3, PPh_3$ )

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The reaction mechanism for intramolecular cis-trans isomerization in  $Cr(CO)_5X$  ( $X = CO, PH_3, PPh_3$ ) was explored. The approximate molecular orbital method PRDDO (partial retention of diatomic differential overlap) was used to optimize the geometries of  $Cr(CO)_6$ ,  $Cr(CO)_5PH_3$ , and  $Cr(CO)_5PPh_3$  and to estimate the transition-state structures resulting from nondissociative cis-trans isomerization mechanisms. The Bailar twist, Ray and Dutt, and bicapped tetrahedron nondissociative mechanisms were investigated. With monodentate ligands, all three mechanisms lead to identical transition states, clearly identifiable as trigonal prisms. Ab initio theory including MP2 perturbation theory was used to evaluate the energy barrier for  $Cr(CO)_6$  and  $Cr(CO)_5PH_3$ . The calculated barrier in both systems is  $\sim 40$  kcal/mol. PRDDO calculations for the same systems yield a slightly higher value of  $\sim 47$  kcal/mol. For  $Cr(CO)_5PPh_3$ , PRDDO predicts a barrier of  $\sim 40$  kcal/mol. Although the predicted energy of activation for a nondissociative mechanism occurring via a trigonal-prism transition state in  $Cr(CO)_5PPh_3$  is 7 kcal/mol lower (at the PRDDO level) than that observed in the two previous systems, the barrier is still slightly higher than the triphenylphosphine ligand dissociation energy of 32 kcal/mol.

### Introduction

Stereomobility of ligands occurring in six-coordinate octahedral complexes has important implications in synthetic organometallic chemistry and has been the focus of numerous experimental studies.<sup>1-7</sup> The mechanisms by which stereochemical rear-

rangements occur provide useful information about the configurational stability of the complex with respect to cis-trans isomerization. Cis-trans isomerization can occur in either of two ways. First, dissociation of a ligand can be followed by rearrangement of the resultant five-coordinate coordinatively unsaturated intermediate. Second, rearrangement may occur via a nondissociative intramolecular mechanism. At least three possible path-

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