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Intramolecular Electron Transfer. 3. Bis(4-pyridyl)methane as Bridging Group

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Abstract: Attention is drawn to an ambiguity in the interpretation of so-called rates of intramolecular electron transfer for species in which Co(III) is the oxidizing agent, an ambiguity which raises questions about the relevance of the results thus far reported to the issue of whether the reactions are adiabatic. Measurements of the rate of intramolecular electron transfer for bis(4-pyridyl)methane bridging Co(III)–Ru(II) show the rate to be a factor of 21 slower than for the analogous system with 4,4′-bipyridine as bridging group. It appears that for this system at least the effects of nonadiabaticity are being felt, and this together with other arguments supports the conclusion that the ambiguity mentioned does not vitiate the inferences based on the related studies which have been done.

A number of recent studies[2-5] have been devoted to measuring rates of intramolecular electron transfer for systems in which the positions of the metal ions involved in the redox process are fixed. The most extensive measurements of this kind deal with species in which 4,4′-byridine and related molecules serve as the bridging groups. A striking result of these studies is that the rates of the so-called intramolecular electron transfer reactions differ only slightly for what would appear to be rather drastic changes in the electronic coupling between the two pyridine rings. The advantages of measuring the rates of reaction in the intramolecular mode have long been appreciated and have repeatedly been referred to. What has not been emphasized is that measurements of this kind themselves can suffer from a serious limitation. Consider the general reaction scheme:

$$(NH_3)_5Co^{III}L\ldots LRu^{II}(NH_3)_4H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NH_3)_3Co^{*II}L\ldots LRu^{III} \quad (1)$$

$$(NH_3)_5Co^{*II}L\ldots LRu^{III}(NH_3)_4H_2O \xrightarrow{k_2} \text{products} \quad (2)$$

In this mechanism, it is postulated that an intermediate species is produced in the net reduction of Co(III) to Co(II), an altogether reasonable possibility considering the fact that there is a spin change, and that substitution accompanies the net change in oxidation state. Reaction 2, in which the net change is consummated, may involve substitution, or a spin change,[16] or both. Should k_{-1} be substantially greater than k_2, the overall reaction rate is governed by the product K_1k_2, where K_1 is the equilibrium quotient for reaction 1. This limiting form of the general rate law would at once explain why the rates reported within the Co(III)–Ru(II) series (or within the Co(III)–Fe(II) series) are so nearly alike—since the immediate environment around the metal ions is the same within each series, both K_1 and k_2 are expected to be nearly constant. If this limit is applicable, the results have no bearing on the issue of whether the reactions are adiabatic.

By contrast, when the reactions are conducted in the intermolecular mode, the form of the rate law which has been observed ensures that the step analogous to (1) in the forward direction is solely rate determining. Cast into the intermolecular form, the mechanism becomes:

$$(NH_3)_5Co^{III}L + (NH_3)_5Ru^{II}L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (NH_3)_5{}^*Co^{II}L + (NH_3)_5Ru^{III}L \quad (3)$$

$$(NH_3)_5{}^*Co^{II}L \xrightarrow{k_4} \text{products} \quad (4)$$

and the general form of the rate law is

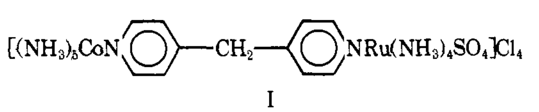
$$\frac{d[(\text{prod})]}{dt} = \frac{k_4k_3[Co(III)][Ru(II)]}{k_4 + k_{-3}[Ru(III)]}$$

Since the rates of reduction are not affected by the accumulation of the product of the oxidation of the reducing agent, it follows that $k_{-3}[Ru(III)] \ll k_4$ and the rate law reduces to $k_3[Co(III)][Ru(II)]$. Unfortunately, this outcome for the intermolecular case does not resolve the ambiguity for the intramolecular one. The specific rate k_{-1} is expected to be considerably greater than $k_{-3}[\mathrm{Ru(III)}]$ and thus, although $k_{-3}[\mathrm{Ru(III)}] < k_4$, k_{-1} may well be greater than k_2. (It should be noted that k_2 and k_4 are expected to have nearly the same values.)

Returning now to the intramolecular case, if a substantial rate decrease is observed for a system related to the 4,4′-bipyridine one, there is some certainty that at least for the slow reaction we are not dealing with the rather trivial case of measuring the product K_1k_2. Such a system has been encountered when the bridging ligand is bis(4-pyridyl)methane. The results obtained for it and for some related molecules are described in this paper.

Experimental Section

Synthesis of I. Synthesis of bis(4-pyridyl)methane was carried out following the description in the literature.[6] In every case, an oil was produced and we failed to obtain the desired product in following the published procedure. Thin layer chromatography showed that the oil contained at least three species and that the reactants had been consumed. Of the three products, only one had a strong absorption at 260 nm. The oil was placed on a silica gel column and was extracted with benzene. The fraction with the strong band at 260 nm, which comprised about 10% of the total, was collected and the benzene evaporated. The substance is still a pale yellow oil, and is very hygroscopic. On treatment with concentrated HBr, the material solidifies. The solid was recrystallized from benzene and the product was washed with cooled solvent. Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; N, 16.45; H, 5.92. Found: C, 76.93; N, 16.35; H, 5.83. Calcd for $C_{11}H_{10}N_2 \cdot 2HBr$: C, 39.79; N, 8.43; H, 3.64. Found: C, 39.59; N, 8.41; H, 3.62. The material was characterized by absorption, mass, and NMR spectroscopy. Dissolved in 0.02 M $NaHCO_3$, bands were found at 263, 256.5, 252, and ~207 nm (sh) with values of ϵ ($M^{-1}\ cm^{-1}$) of 3.53×10^3, 4.65×10^3, 4.17×10^3, and 14.9×10^3, respectively. Mass spectrometric analysis gave the following masses (intensity): 171 (13), 170 (100), 169 (46), 168 (7), 143 (4), 142 (6), 141 (3), 118 (4), 116 (5) 106 (5), 92 (4), 89 (3), 84 (4), 78 (4), 65 (5), 63 (5), 51 (12). NMR spectra were run in $CDCl_3$ with the results summarized below.


$[(NH_3)_5CoNC_5H_4-CH_2-C_5H_4NRu(NH_3)_4SO_4]Cl_4$

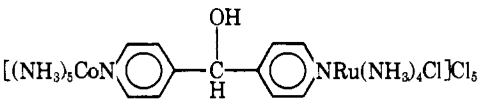
I

δ (Me_4Si)	Intensity	Description
8.43	2	Doublet of doublets
7.00	2	Doublet of doublets
3.83	1	Singlet

The ligand has since been synthesized by Haim and co-workers using an alternative and superior method.[7] The properties observed are the same for material prepared by the two routes. The compound $[Co(NH_3)_5(NC_5H_4CH_2C_5H_4NH)]Cl_4$ was prepared following the procedure described by Dockal and Gould[8] and using $[Co(NH_3)_5N_3][ClO_4]_2$ as the source of Co(III). The pentaamminecobalt(III) product was purified by chromatography (Bio-Gel P2 (Bio-Rad) using 0.2 M HCl as eluting agent), and the Co(III) complex was converted to compound I following the procedure described by Isied.[2] Again, a Bio-Gel column was used for purification prior to precipitation.

Anal. (for the binuclear compound) Calcd: C, 16.4; H, 5.6; Cl, 18.2; Co, 6.9; N, 18.5; Ru, 12.3; S, 3.72. Found: C, 16.3; H, 5.8; Cl, 17.7; Co, 7.2; N, 19.0; Ru, 12.4; S, 4.95.

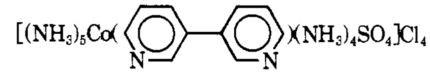
Synthesis of II. The bridging ligand was synthesized following the procedure described by Minn et al.[9] and the synthesis of the metal complexes according to the general procedures already described. For reasons that are obscure, in this case the sulfate on Ru(III) is replaced rather rapidly by Cl^- during the column purification, and the chloro complex comprises the major band of the material being eluted.


$[(NH_3)_5CoNC_5H_4-CH(OH)-C_5H_4NRu(NH_3)_4Cl]Cl_5$

II

Anal. Calcd: C, 17.7; H, 5.1; Cl, 33.2; Co, 7.9; N, 20.9; Ru, 13.5; S, 0. Found: C, 17.5; H, 5.3; Cl, 34.1; Co, 8.2; N, 20.2; Ru, 12.9; S, <0.5.

Synthesis of III. In synthesizing the bridging ligand, 3,3′-bipyridine, the procedure as described by Smith[10] was adopted. Again, the synthesis of the metal complex followed the usual procedures.



III

Anal. Calcd: C, 15.4; H. 5.6; Co, 7.6; N, 19.8; Cl, 18.2, Ru, 13.0; S, 4.1. Found: C, 15.6; H, 5.0; Co, 8.4; N, 19.3; Cl, 18.5; Ru, 12.6; S, 4.0.

Preparation of Ru(II)–Ru(III) Mixed Valence Species. The preparations were made in solution by mixing $Ru(NH_3)_5H_2O^{2+}$ and the ligand in the concentration ratio 2:1 (concentration level 5×10^{-3}:2.5×10^{-3}; reaction time 30 min). To produce the mixed valence species, a solution containing $(NH_4)_2Ce(NO_3)_6$ was used as the oxidant with 0.1 M HCF_3CO_2 as reaction medium. In each of the two cases, the near IR band develops only when oxidant is added, and disappears when oxidant is in excess.

Kinetic Measurements. The measurements were done using procedures described elsewhere.[5] In the case of compounds I and II, the difference in absorption between Ru(II) as contained in the binuclear complex and when Co(III) is replaced by H^+ is so small that we were obliged to do the measurements using the binuclear complex in excess of the external reducing agents. In these circumstances, the putative pseudo-first-order plots show curvatures,[2] and specific rates are based on the initial slopes. This limitation reduces the precision of the measurements significantly.

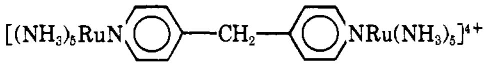
In all cases, intramolecular electron transfer is so slow that loss of SO_4^{2-} or Cl^- takes place on a much shorter time scale, so that rates for aquotetraammine Ru(II) rather than sulfato or chlorotetraammine Ru(II) are being observed.

Results

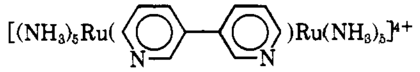
Absorption Spectra for the Binuclear Species. For I dissolved in 0.4 M CF_3COOH, the following absorption characteristics were measured (wavelengths followed by extinction coefficients ($M^{-1}\ cm^{-1}$)): 470 sh (65), 329 (3.7×10^3), 280 sh (1.34×10^4), 260 sh (1.34×10^4). For II spectra were obtained in 0.2 M HCl, and only the band positions were recorded: 470 sh, 345, 253 nm. For III, spectra were also obtained for the compound dissolved in 0.2 M HCl. The band maxima appeared at 470 (sh), 320, 265 (sh), 238 nm (sh).

On reducing the Co(III)–Ru(III) species, the most prominent feature of the spectra is the strong $\pi^* \leftarrow \pi d$ absorption in the visible. The band maxima and extinction coefficients for the species $[(NH_3)_5Co^{III}L \ldots LRu^{II}(NH_3)_4H_2O]^{5+}$ are compared below to those obtained for the ruthenium products $[HL \ldots LRu^{II}(NH_3)_4H_2O]^{3+}$ which result when reducing agent is in excess: For I, 423 (9.4×10^3), 420 (9.8×10^3); for II, 436 (5.7×10^3), 432 (6.0×10^3); for III, 425 (6.8×10^3), 426 nm (6.6×10^3).

The near infrared region was scanned on oxidizing solutions containing IV and V. Absorption bands were observed at 820 nm (ϵ ~5 $M^{-1}\ cm^{-1}$) for the mixed valence species derived from the former and at 830 nm (ϵ ~$6 \times 10\ M^{-1}\ cm^{-1}$) for that derived from the latter.


$[(NH_3)_5RuNC_5H_4-CH_2-C_5H_4NRu(NH_3)_5]^{4+}$

IV



V

Rates of Intramolecular Electron Transfer. Extensive rate measurements were done only with compound I. The results obtained for it are summarized in Table I.

Table I. Kinetics of Electron Transfer in I[a]

[Co-L-Ru], M × 10^4	[Ru^{II}-$(NH_3)_6^{2+}$], M × 10^5	Ionic media	Temp, °C	$k \times 10^3$, s^{-1}
2.42	1.18	0.4 M CF_3COOH	41.0	10.6
1.19	1.04		38.4	8.01
2.58	1.19		36.7	7.32
1.71	1.21		34.5	5.71
1.81	1.21		32.9	4.84
1.99	1.20		29.0	3.09
2.15	1.20		26.6	2.70
2.42	1.20		21.4	1.35
2.06	1.18	0.4 M $HClO_4$	26.5	3.80
2.01	1.15	0.008 M $HClO_4$ 0.392 M $NaClO_4$	26.8	3.66
2.23	2.34	0.200 M $HClO_4$ 0.200 M NaI	26.9	7.85
2.66	4.27	0.008 M $HClO_4$ 0.392 M NaI	26.8	13.6

[a] Spectrophotometer: Beckman Acta VII. Cell: 10 cm. Wavelengths 420 nm.

The data on the specific rates as a function of temperature were treated according to the method described by Cramer.[11] The specific rate at 25 °C is 2.10 × 10^{-3} s^{-1}; $\Delta H^{\ddagger} = 18.4 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger} = 9.0 \pm 1.7$ cal mol^{-1} deg^{-1}.

A single experiment was done with compound II, in 0.4 M CF_3COOH and at 25.0 °C, with [Co(III) . . . Ru(III)] at 2.1 × 10^{-5} M and using $Ru(NH_3)_6^{2+}$ as the external reducing agent at 6.8 × 10^{-6} M. The specific rate measured was 3.2 × 10^{-3} s^{-1}.

For compound III, the reaction conditions were the same, except that in this case $Ru(NH_3)_6^{2+}$ was used in excess (6.1 × 10^{-4} M). The specific rate was measured as 4.2 × 10^{-3} s^{-1}.

Discussion

The rate decrease registered in comparing 4,4′-bipyridine as the bridging group, which is the system among those described earlier[5] showing the fastest rate of intramolecular electron transfer, and that with bis(4-pyridyl)methane as the bridging group is a factor of 21. The entropy difference—that for reaction of the bis(4-pyridyl)methane being recorded as 11.6 cal deg^{-1} mol^{-1} more negative than registered in the other case—seems quite outside the limits covered by the combined errors of the measurements. The rate decrease is observed despite the fact that Ru(II) in the complex featured in this study is somewhat more strongly reducing, by 0.04 V, than when 4,4-bipyridine is the bridging group. Even assuming that in the 4,4-bipyridine case the product K_1k_2 is being measured, it seems certain that when the bis(4-pyridyl)methane is the bridging group, a property of the electron transfer act itself is being measured so that the standard free energy profile for the system takes the form of the solid curve in Figure 1a.

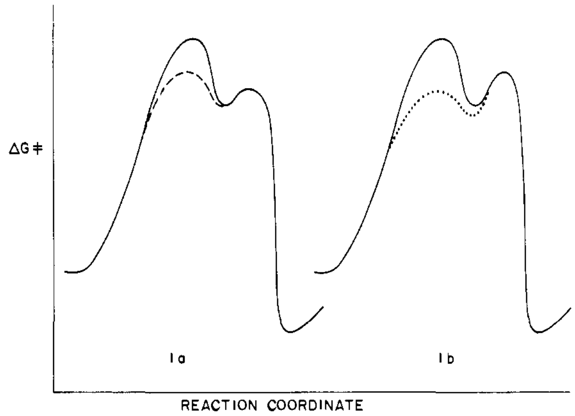
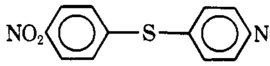


Figure 1. Reaction profiles. Solid curve in each case represents the profile for bis(4-pyridyl)methane as bridging group. For the comparison system (4,4′-bipyridine): in 1b, the rate is given by K_1k_2. and in 1a, by k_1.

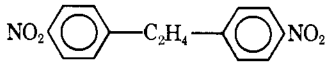
The question next to be considered is whether the reaction profiles for 4,4′-bipyridne in relation to bis(4-pyridyl)methane take the form shown in Figure 1a, in which case k_1 is being measured for the series, or of Figure 1b, in which event the data give the product K_1k_2 for the system showing the more rapid rate. Several arguments support the conclusion that Figure 1a applies. The relationship between specific rate as measured in the Co(III)-Ru(II) system and the intensity of the intervalence band measured for the corresponding Ru(III)-Ru(II) mixed valence complex, as referred to earlier,[5] is upheld by two additional examples—compounds I and III. In making the comparisons, allowance must be made for the fact that the distance separating the metal ions is expected to affect the rate of electron transfer,[12] but does not necessarily affect the intensity of the intervalence transition. Thus the fact that the rate for 4,4′-dipyridylethylene as bridging group is a factor of 2.3 slower than for the 4,4′-bipyridine case, though the intensity of the intervalence band is the same, is not necessarily an exception to the correlation. The barrier to electron transfer by solvent orientation is greater in the case of 4,4′-dipyridylethylene, because of the larger distance separating the metal ions. The trends both in the intensity of the intervalence bands and in rates seem reasonable on the basis of the structures and compositions of the species, strengthening the view that nonadiabaticity accounts for the rate differences. Whatever the quality of the last conclusion, the results obtained with bis(4-pyridyl)methane as bridging group make us optimistic about studying nonadiabatic transfer for still more weakly coupled systems.

Perhaps the most powerful means of diagnosing whether k_1 or k_2K determines the reaction rate is to change the redox potential of the reducing agent. With a group as large as 4,4′-bipyridine separating Co(III) from the reducing agent, it seems likely that if k_2K is rate determining, a change in redox potential should be reflected directly in the rate. Such a comparison is possible using the data of Gaswick and Haim[3] obtained with $Fe(CN)_5^{3-}$ as the reducing agent together with those obtained by Fischer et al. for $Ru(NH_3)_4H_2O^{2+}$.[5] The redox potential in the former case is close to 0.50 V;[13] in the latter case, it is 0.35 V. Thus if k_2K is rate determining, a rate differential for the two systems of approximately 350 would be expected; the measured value is only a factor of 16. Owing to the fact that the values of E_f are not accurately known, and that conditions in other respects may not be identical, the comparison made cannot yet be taken as proof that k_2K is not governing. In applying the approach, it must be kept in mind that while strong deviations from the relation $k_{obsd} \propto K$ prove that k_2K is not rate determining, owing to the idiosyncracies of Co(III) as a reducing agent, if the rates do follow the relation in isolated instances, this would not prove that k_2K is rate determining.

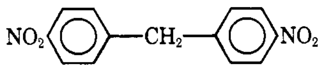
Specific rates were recorded by Harriman and Maki[14] for intramolecular electron transfer in the radical ions obtained by 1 e^- reduction of, among others, VI and VII. These were (25 °C, Me_2SO as solvent) 9 × 10^6 and 2 × 10^6 s^{-1}, respectively, almost precisely the rate ratio recorded for 4,4′-dipyridyl sulfide and 4,4′-dipyridylethane bridging Co(III) and Ru(II). This outcome would be gratifying were it not for the fact that for the radical ion derived from VIII, k is reported as ≥10^8.



VI



VII



VIII

The discrepancy in the effect of inserting CH_2 on the rates in the two series does, however, not vitiate the conclusions which have been reached about the Co(III)-Ru(II) system. In other work it has been observed that breaking conjugation by inserting a CH_2 group diminishes the rate by a factor of only 1.5.[15] While changes in coupling when gross changes in structure occur can probably be predicted qualitatively, the subject is not at all well understood, nor for that matter is the coupling mechanism when a group such as CH_2 separates the pyridine rings known. Is there direct π-π (π-π^*) overlap, or is the effect transmitted through the bond system? The mixed valence species provide an especially convenient approach to illuminating this issue.

Acknowledgments. Fellowship support for Konrad Rieder by the Swiss National Foundation is gratefully acknowledged, as is balance of support of this research by the National Science Foundation (Grant GP24726).

References and Notes

(1) Parts 1 and 2 are comprised by ref 2 and 5.
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(15) S. Zawacky, research in progress. This represents a correction on a conclusion reached on the basis of the results reported in ref. 2. The validity of the correction has been checked by S. Isied.
(16) **Note Added In Proof.** Dr. A. Haim as referee has advanced arguments which make it unlikely that if reaction 1 is maintained as an equilibrium, the intermediate in question is normal high-spin cobalt(II). Using for k_2 a value of 10^6 sec^{-1} [M. Simic and J. Lilie, *J. Am. Chem. Soc.*, **96**, 291 (1974); R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **8**, 554 (1969)] and taking account of the value of E_f for the Ru(III)/Ru(II) couple, it can be shown that the measured value of k_2K_1 would require E_f for the Co(III)/Co(II) couple to be less than −0.15 V. Note that $E°$ for $Co(NH_3)_5H_2O^{3+} + e^- = [Co(NH_3)_5H_2O]^{2+}$ has been estimated at 0.35 V [R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962)].

The Pentacyanocobaltate(II)-Catalyzed Reactions of μ-Cyano- and μ-Isocyano-pentacyanopentaamminedicobalt(III,III) with Cyanide Ion[1]

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Abstract: The $Co(CN)_5^{3-}$-catalyzed reactions of $(NC)_5CoCNCo(NH_3)_5$ and $(NC)_5CoNCCo(NH_3)_5$ with cyanide ion yield 2 mol of $Co(CN)_6^{3-}$ per mol of binuclear complex. The rate law for the reactions has the form $k_{OS}[Co_2(NH_3)_5(CN)_6]\cdot[Co(CN)_5^{3-}][CN^-]$ with $k_{OS} = (1.82 \pm 0.04) \times 10^4$ and $(3.22 \pm 0.17) \times 10^3$ M^{-2} s^{-1} at 25 °C and ionic strength 0.50 M for $(NC)_5CoCNCo(NH_3)_5$ and $(NC)_5CoNCCo(NH_3)_5$, respectively. The rate-determining step involves the outer sphere reaction of $Co(CN)_6^{4-}$ with the binuclear reactant. By comparing the observed rate constants with those for the corresponding reactions of mononuclear pentaamminecobalt(III) and pentacyanocobaltate(III) complexes, it is suggested that an electron is transferred from $Co(CN)_6^{4-}$ to the $Co(NH_3)_5^{3+}$ moiety to yield the mixed valence intermediates $(NC)_5Co^{III}CNCo^{II}(NH_3)_5^-$ and $(NC)_5Co^{III}NCCo^{II}(NH_3)_5^-$. It is postulated that dissociation of these intermediates by bond rupture at the cobalt(II) site produces $Co(CN)_6^{3-}$ and $Co(CN)_5NC^{3-}$, respectively. The previously studied $Co(CN)_5^{3-}$-catalyzed reaction of $Co(NH_3)_5CN^{2+}$ with CN^- was reexamined. In agreement with previous work, the rate law was found to be $k_{IS} + k_{OS}\cdot[CN^-])([Co(NH_3)_5CN^{2+}][Co(CN)_5^{3-}])$, with $k_{IS} = (2.6 \pm 0.3) \times 10^2$ M^{-1} s^{-1} and $k_{OS} = (4.8 \pm 0.4) \times 10^3$ M^{-2} s^{-1}. However, an experiment used previously to postulate the intermediacy of $Co(CN)_5NC^{3-}$ in the k_{IS} path could not be reproduced, and it is concluded that, if $Co(CN)_5NC^{3-}$ is formed, its rate of isomerization is considerably higher than the 1.6-s half-life reported previously.

The syntheses of the title compounds, $(NH_3)_5CoNC$-$Co(CN)_5$ and $(NH_3)_5CoCNCo(CN)_5$,[2,3] were designed to yield binuclear complexes containing two oxidizing metal centers in different ligand environments of controlled kinetic and thermodynamic properties with respect to one-electron reduction. The $Co(CN)_5^{2-}$ moiety is conducive to facile inner-sphere electron transfer, but the metal center is thermodynamically a poor oxidant, whereas the $Co(NH_3)_5^{3+}$ moiety is reduced very slowly by inner-sphere oxidants, but the metal center has a higher reduction potential. In this manner, it was thought that addition of a good inner-sphere reductant would bring an electron into the $Co(CN)_5^{2-}$ moiety, but the electron would ultimately go to the $Co(NH_3)_5^{3+}$ moiety. If the rate of electron transfer from external reductant to $Co(CN)_5^{2-}$ is fast compared to the rate of electron transfer from one metal center to the other in the binuclear complex, the measurement of intramolecular electron transfer rates becomes feasible.[4]

We have applied this approach, alas unsuccessfully, to the reactions of $(NH_3)_5CoNCCo(CN)_5$ and $(NH_3)_5CoCN$-$Co(CN)_5$ with chromium(II) and with pentacyanobaltate(II).