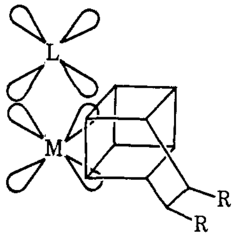
Table II. Solvent Effects of $PdCl_2(Ph_3P)_2$-Catalyzed Rearrangements of 1,1′-Bishomocubane **1**[a]

Solvent	% **2**	% **3**	% **4**
$CDCl_3$	41	23	35.5
CH_2Cl_2	43	20	37
$CH_3C{\equiv}N$	55	13	31.5
$CD_3C({=}O)CD_3$	55.5	13	31.5
$CD_3S({=}O)CD_3$	71	9	19.5
$HOCH_2CH_2OH$	85	4	11
CH_3OH	86	4	9.5

[a] Reactions were performed similarly to those in Table I. There was no rate comparison due to varying solubility of catalysts in solvents.

as shown in Table II, it has been found in the $PdCl_2[P(C_6H_5)_3]_2$-catalyzed rearrangement of **1** that as the solvent was changed the amount of the dicyclopropyl rearrangement product increased with the carbonium ion stabilizing ability of the solvent.

The results from this study of the ligand effect upon the rearrangement of the strained bishomocubane system to the dienes **3** and **4** are in agreement with the suggestion that the rearrangement process proceeds *via* a bidentate interaction of the strained carbon system with the transition metal complex[12,13] (I). The



I

orbital symmetry and the geometry of the metal d orbitals make the d_{xz} orbital an effective π acceptor from the organic substrate and make the d_{yz} orbital an effective donor to the σ^* orbital of the substrate.[12] The bidentate interaction is equivalent to an oxidative addition[14] and the results reported in this study show a good correlation between those ligands which enhance the oxidative addition of a transition metal[14] and those ligands on Pd(II) which favor formation of dienes **3** and **4**. The results of Rh(I) giving only dienes **3** and **4** are also in line with the greater oxidative addition ability of Rh(I) relative to Pd(II).[14,15] It has previously been pointed out that in highly strained ring systems where there is a large energy release upon isomerization, a continuum very likely exists between the stepwise oxidative addition process and a more concerted process.[12]

The present results demonstrate for the first time in the transition metal complex catalyzed rearrangement of a strained cage compound that by variation of the ligand a change in product distribution has resulted. The extent of the two rearrangement courses to **2** and to **3** and **4** followed is controlled by the σ electron acceptor ability of the complex and by the σ donor π acceptor ability, and polarizability, of the ligands in the transition metal complex.

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(12) (a) F. D. Mango, *Tetrahedron Lett.*, 505 (1971); (b) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **93**, 1123 (1971).

(13) An edge-on insertion into one carbon–carbon σ bond is also a possibility to be considered. However, this is comparable to and indistinguishable from the face-on insertion since initially it is a matter of small differences in metal atom positions. In the final stage of the rearrangement for both cases the metal atom would be symmetrically coordinated to the dienes before leaving to give free diene products.

(14) J. P. Collman and W. R. Roper, *Advan. Organometal Chem.*, **7**, 53 (1968); J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); J. Halpern, *ibid.*, **3**, 386 (1970), and references therein.

(15) Preliminary results using $PtCl_2(Ph_3As)_2$ and $PtCl_2(Ph_3Sb)_2$ showed a mixture of **2**, **3**, and **4** were formed also in line with the oxidative addition ability of Pt(II).

Direct Measurement of a First-Order Rate Constant for an Elementary Electron Transfer Step[1]

Sir:

Most kinetic studies of oxidation–reduction reactions, whether of the inner-sphere or the outer-sphere class, provide second-order rate constants for the overall reaction. One notable exception is afforded by the $Co(NH_3)_5L{-}Fe^{2+}$ system (L = nitrilotriacetate anion)[2] where the precursor complex was detected and the first-order rate constant for electron transfer within the binuclear inner-sphere unit was determined. In view of the importance of obtaining quantitative information about the elementary steps of redox reactions, we have started an investigation of the reduction of various tripositive cobalt(III) complexes by the hexacyanoferrate(II) anion. The choice of highly oppositely charged reactants was based on the expectation[3] that outer-sphere complex formation by the reactants would be substantial at relatively low concentrations. This expectation has been fulfilled in the $Co(NH_3)_5OH_2{}^{3+}{-}Fe(CN)_6{}^{4-}$ system, and we wish to report what we believe to be the first measurement of a first-order rate constant for an electron-transfer process within a binuclear, outer-sphere complex.

When aqueous solutions of $[Co(NH_3)_5OH_2](ClO_4)_3$ and $Na_4[Fe(CN)_6]$ are mixed at 10^{-4}–10^{-3} *M* concentrations, a precipitate [presumably cobalt(II) hexacyanoferrate(II) and/or cobalt(II) hexacyanoferrate(III)] forms within a few seconds, and therefore homogeneous kinetic measurements are precluded. However, when disodium dihydrogen ethylenediaminetetraacetate is added to the solution to complex the cobalt(II) formed, no precipitate is produced, and therefore all kinetic measurements reported here have been carried out in the presence of H_2EDTA^{2-}, the stoichiometry of the reaction being represented by[4]

$$Fe(CN)_6{}^{4-} + Co(NH_3)_5OH_2{}^{3+} + H_2EDTA^{2-} + 3H^+ = Fe(CN)_6{}^{3-} + CoEDTA^{2-} + 5NH_4{}^+ + H_2O$$

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[1] This work was supported by the National Science Foundation under Grant GP-9669.

[2] R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, **92**, 3800 (1970).

[3] Outer-sphere complex formation between $Co(en)_3{}^{3+}$ and $Fe(CN)_6{}^{4-}$ has been reported by R. Larsson, *Acta Chem. Scand.*, 21, 257 (1967).

[4] The addition of H_2EDTA^{2-} causes a slight complication because of the $CoEDTA^{2-}{-}Fe(CN)_6{}^{3-}$ reaction: D. H. Huchital and R. G. Wilkins, *Inorg. Chem.*, **6**, 1022 (1967). However, under the conditions of our experiments, the $CoEDTA^{2-}{-}Fe(CN)_6{}^{3-}$ reaction proceeds only to a small extent (*ca.* 20%) and is extremely rapid compared to the

Table I. Kinetics of the $Co(NH_3)_5OH_2^{3+}$–$Fe(CN)_6^{4-}$ Reaction[a]

Expt no.	[Fe-(CN)$_6^{4-}$]$_0$, $M \times 10^3$	[Co(NH$_3$)$_5$-OH$_2^{3+}$]$_0$, $M \times 10^4$	[H$_2$EDTA^{2-}], $M \times 10^3$	$10^2 k_{obsd}$,[b] sec^{-1}
1	3.01	2.00	0.200	15.3 ± 0.6
2	1.52	2.00	0.200	13.1 ± 0.5
3	0.829	2.00	0.200	9.4 ± 0.4
4	0.194	0.216	0.200	4.19 ± 0.08[c]
5	0.194	0.216		4.33 ± 0.20[c,d]
6	0.194	0.216	0.020	4.21 ± 0.04[c]
7	1.02	1.98	0.500	9.7 ± 0.3
8	1.01	2.03	1.00	9.6 ± 0.2
9	1.00	1.98	1.50	8.7 ± 0.2
10	1.00	2.20	5.50	6.0 ± 0.1
11	3.02	2.03	1.00	13.9 ± 0.5[e]
12	1.51	2.03	1.00	11.0 ± 0.4[e]
13	0.795	2.03	1.00	8.1 ± 0.2[e]
14	0.406	2.03	1.00	5.2 ± 0.1[e]
15	0.393	0.195	1.00	5.1 ± 0.1[c]
16	0.994	0.196	1.00	17.0 ± 0.1[f]

[a] Unless specified otherwise, $t = 25°$, $[Na^+] = 0.10$–0.11 M (adjusted with $NaClO_4$), $[CH_3COO^-] + [CH_3COOH] = 5 \times 10^{-3}$ M, initial pH 4.70, final pH ~4.9. [b] Each entry is the average of four replicate stop-flow measurements with the same pair of solutions. [c] Measured in Cary spectrophotometer. Average of two measurements. [d] From initial rate measurements. A precipitate formed after 2 half-lives. [e] No buffer. 10^{-3} M $HClO_4$ added. pH varies from 3.4 to 4.5 from beginning to end of reaction. [f] No $NaClO_4$ added. $[Na^+] = 8.50 \times 10^{-3}$ M.

The kinetic measurements were carried out under pseudo-first-order conditions with $Fe(CN)_6^{4-}$ in excess[5] by following the increase in absorption at 420 nm. Conventional mixing techniques were used for half-lives longer than 10 sec, and the stop–flow apparatus was used for faster reactions. First-order rate constants, k_{obsd}, were calculated by nonlinear least-squares fitting of absorbance *vs.* time data to the equation $(A_\infty - A) = (A_\infty - A_0)e^{-k_{obsd}t}$. The results are summarized in Table I. We were concerned about the possible effect of H_2EDTA^{2-} on the reaction rate, and it is seen (*cf.* expt 7–10) that k_{obsd} decreases with increasing H_2EDTA^{2-} concentration, presumably because of ion-pair formation with $Co(NH_3)_5OH_2^{3+}$. However, at the low (2.00×10^{-4} M) H_2EDTA^{2-} concentration used in expt 1–6, its effect on the rate is essentially negligible. Additional evidence for the validity of the measurements at low H_2EDTA^{2-} is obtained from an experiment in which H_2EDTA^{2-} was not added, and the rate constant was estimated from initial rates (prior to the formation of the precipitate). It will be seen that the rate constant with no added H_2EDTA^{2-} (expt 5) is in excellent agreement with the rate constants measured in the presence of 2.00×10^{-4} or 2.00×10^{-5} M H_2EDTA^{2-} (expt 4 and 6). The possible dependence of rate on pH was not investigated extensively. However, it will be seen that k_{obsd} is independent of pH in the region 3.4–4.9, where protonation[6] of $Fe(CN)_6^{4-}$ or deprotonation[7] of $Co(NH_3)_5OH_2^{3+}$ are unimportant, and that the buffer does not affect the rate (*cf.* expt 1–3 and 11–15).[8] The dependence of k_{obsd} on $[Fe(CN)_6^{4-}]$ is less than first order and conforms to the equation

$$k_{obsd} = kQ[Fe(CN_6^{4-}]/(1 + Q[Fe(CN)_6^{4-}]) \quad (1)$$

which can be derived from the reaction sequence

$$Co(NH_3)_5OH_2^{3+} + Fe(CN)_6^{4-} \rightleftharpoons CO(NH_3)_5OH_2^{3+}\cdot Fe(CN)_6^{4-} \quad \text{rapid, } Q \quad (2)$$

$$Co(NH_3)_5OH_2^{3+}\cdot Fe(CN)_6^{4-} \longrightarrow \text{products} \quad \text{slow, } k \quad (3)$$

At 25°, $[H_2EDTA^{2-}] = 2.00 \times 10^{-4}$ M and $[Na^+] = 0.10$–0.11 M, the nonlinear least-squares fitting of the experimental data to eq 1 yields $Q = 1500 \pm 100$ M^{-1} and $k = (1.9 \pm 0.1) \times 10^{-1}$ sec^{-1}.[9] The value of Q seems reasonable for the formation quotient of an outer-sphere complex of this charge type.[10] The calculated value of k finds additional confirmation from the results of expt 16. Under the conditions of low ionic strength, the value of Q would be expected to be considerably larger than 1500, and therefore substantially (>90%) complete formation of the outer-sphere complex would obtain. Under these circumstances, k_{obsd} should approach k, as observed.[11,12] The half-life for electron transfer from Fe(II) to Co(III) within the binuclear outer-sphere complex is ~4 sec. We have carried out preliminary studies with the analogous $Co(phen)_3^{3+}$–$Fe(CN)_6^{4-}$ system, and we find that the half-life for electron transfer within the outer-sphere binuclear complex $Fe(CN)_6^{4-}\cdot Co(phen)_3^{3+}$ is $< 2 \times 10^{-3}$ sec. When this value is compared with the ~4 sec half-life for electron transfer within the binuclear complex $Fe(CN)_6^{4-}\cdot Co(NH_3)_5OH_2^{3+}$ and with the very slow ($t_{1/2} \sim 10^6$ sec) reaction reported[3] for the $Fe(CN)_6^{4-}$–$Co(en)_3^{3+}$ system, it is tempting to speculate that the wide range of rates reflects the varying electron permeability of the ligands in the coordination sphere of the cobalt(III) complex.[13] We are planning to extend these studies to other tripositive cobalt(III) complexes, as well as to pentaammine complexes of lower charge.

$Co(NH_3)_5OH_2^{3+}$–$Fe(CN)_6^{4-}$ reaction. Therefore, there is little interference by the secondary reaction.

(5) If $Co(NH_3)_5OH_2^{3+}$ and H_2EDTA^{2-} are in excess over $Fe(CN)_6^{4-}$, then following the Fe(II)–Co(III) redox reaction, we have observed the $Fe(CN)_6^{4-}$-catalyzed substitution of NH_3 in $Co(NH_3)_5OH_2^{3+}$ by $EDTA^{4-}$.

(6) J. Jordan and G. J. Ewing, *Inorg. Chem.*, 1, 587 (1962).

(7) R. C. Splinter, S. J. Harris, and R. S. Tobias, *ibid.*, 7, 897 (1968).

(8) In comparing expt 1–3 with 11–13, it must be noted that the former were performed in the presence of 2.00×10^{-4} M H_2EDTA^{2-}, whereas the latter were performed in the presence of 1.00×10^{-3} M H_2EDTA^{2-}. The rates at higher $[H_2EDTA^{2-}]$ are somewhat slower.

(9) The values of $[Fe(CN)_6^{4-}]$ used were the average values of *uncomplexed* $Fe(CN)_6^{4-}$.

(10) M. Beck, *Coord. Chem. Rev.*, 3, 91 (1968).

(11) It is assumed that the rate of reaction 3 is rather insensitive to changes in ionic strength.

(12) Additional support for the proposed interpretation and for the validity of the calculated values of k comes from the measurements with $[H_2EDTA^{2-}] = 1.00 \times 10^{-3}$ M. These measurements also conform to eq 1 with $k = (1.9 \pm 0.1) \times 10^{-1}$ sec^{-1} and $Q = 1000 \pm 100$ M^{-1}. The agreement between the calculated values of k at 2.00×10^{-4} and 1.00×10^{-3} M H_2EDTA^{2-} contrasted with the differing values of Q also provides support for the suggestion that the effect of H_2EDTA^{2-} is caused by ion pairing with $Co(NH_3)_5OH_2^{3+}$. At sufficiently high $[Fe(CN)_6^{4-}]$, the $Co(NH_3)_5OH_2^{3+}$ is quantitatively transformed to the ion pair $Co(NH_3)_5OH_2^{3+}\cdot Fe(CN)_6^{4-}$, and, consequently, under these circumstances, H_2EDTA^{2-} has no effect on the rate.

(13) It must be noted, however, that the oxidation of $Fe(CN)_6^{4-}$ by $Co(en)_3^{3+}$ is thermodynamically unfavorable.

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