Upon treatment with silver perchlorate (0.1–0.15 *M*) in benzene, bicyclobutane (**1**)[3] (0.3–0.5 *M*) itself was rearranged to afford butadiene (**2**). This conversion proceeded smoothly at room temperature and the yield of **2** was more than 90% at any stage of the reaction, based on the consumed amount of **1**.[4] *exo,exo*- and *endo,exo*-2,4-dimethylbicyclobutanes (**3**, **4**)[5] under the same conditions underwent largely stereospecific conversion into *trans,trans*- and *cis,trans*-2,4-hexadienes (**5**, **6**), respectively, and the results are tabulated below (Table I). No other C_6 products were observed during the course of reaction. Both *cis*- and *trans*-dimethylcyclobutanes (**7**, **8**)[6] as well as **5**, **6**, and *cis,cis*-2,4-hexadiene (**9**) were recovered unchanged under the above conditions with silver perchlorate. Therefore, **5**, **7**, **8**, and **9** and their silver complex are eliminated as intermediates during the conversion of **4** to **6**.

Table I. Product Distribution (%) of Ag(I)-Catalyzed Reaction of 2,4-Dimethylbicyclobutane[a]

Compd	5	6	Total yield, %	Temp, °C
3	78	22	89	26
3	77	23	95	5
4	5	95	99	26
4	1	99	99	5

[a] See ref 4.

The above results show that the silver(I)-catalyzed reaction of **3** and **4**, the former to the lesser extent, chooses a discrete stereochemical pathway and stereochemistries of the products are virtually the reverse of those obtained by thermolysis.[5] A prediction can be easily made that readily available tricyclo[4.1.0.0^{2,7}]heptane (**10**)[7] will provide *cis,cis*-cycloheptadiene (**11**). This was found to be the case (97% yield) and the intermediacy of *cis*-bicyclo[3.2.0]heptene-6 can be disregarded since it was shown to be stable under the reaction conditions.[8]

Numerous experiments have been reported to show at least superficially that metal catalysts remove the symmetry restriction on thermally disallowed processes. However, we believe that this communication is the first to demonstrate that the metal ion affects stereospecific reactions in systems with stereochemical alternatives and reverses the stereochemical course of the thermolysis. Because strong extrasymmetric factors[9] which could influence the stereochemistry of the products are not obvious at the present moment, it is suggested that this bicyclobutane–silver(I) reaction is to a large measure governed *at some stage* by the orbital symmetry of the whole system undergoing skeletal changes.[10,11] However, obviously the data presently available preclude further analysis of the reaction. Questions concerning the intermediacy of the bicyclobutane–silver(I) complex, its structure, the possibility of rearrangement of the ligand, and the timing (stage) of removal of silver from the systems must be answered before one can propose the manner in which the observed stereospecificity is controlled.

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(3) Prepared according to the procedure reported by J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, 87, 661 (1965).

(4) The yields reported herein are based on the integration of nmr signals and/or that of glpc peaks and are corrected to the relative sensitivity of the detector in the latter method. In both cases, cyclohexane was used as reference. The rate of rearrangement of **1**, **3**, **4**, and **10** at 40.7° varied directly with the initial Ag(I) concentration, being given by the expression $-d[\text{bicyclobutane}]/dt = k[\text{bicyclobutane}] \times [\text{AgClO}_4]_0$, and unaffected by the addition of the corresponding products, butadiene or its derivatives: **1**, $k = 5.2 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$; **3**, 3.2×10^{-3}; **4**, 1.4×10^{-2}; **10**, 1.9×10^{-3}. A referee, apparently having attempted to repeat our experiments, informed us of the irreproducibility of our results in his laboratory. We earlier had similar experiences, but soon discovered that a trace of acid and possibly moisture are responsible for undesired side reactions. All the glassware including nmr tubes must be washed with dilute ammonia before drying and the reagent and solvent must be handled in a dry nitrogen atomosphere. The yields reported herein are the average of, at least, three runs and the absence of high molecular weight products (if present, presumably less than 5%) was confirmed by heating the glpc column (UC-W98) to 200°. The acid sensitivity of the bicyclobutane–Ag reaction was again confirmed after the referee's report.

(5) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, 90, 2452 (1968). We are grateful to Professor Closs for providing us with experimental details of the preparation of **3** and **4**.

(6) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965).

(7) W. R. Moore, H. R. Ward, and R. T. Merritt, *J. Amer. Chem. Soc.*, 83, 2019 (1961). For thermolysis of **10**, see K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(8) After submission of this paper, this particular reaction (**10** to **11**) was reported by L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, 92, 7002 (1970). Clearly this example by itself provides no answer to the question raised in the text because of the expected thermodynamic instability of as yet unknown *cis,trans*-cycloheptadiene compared with **11** (see ref 2). These authors incorrectly viewed the reaction, if concerted, as $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ which leads to *trans,-trans*-cyclohepta-1,3-diene. Obviously $[{}_{\sigma}2_a + {}_{\sigma}2_a]$ represents the net change of **10** in the orbital symmetry sense.

(9) J. A. Berson and S. S. Olin, *ibid.*, 92, 1086 (1970).

(10) Theoretical arguments pertinent to this subject have already appeared (see ref 1a and 1b) and repetition is avoided.

(11) The degree of nonspecificity in the case of **3** demands special attention. It is also likely that the stereospecificity varies with the kind of metals employed and we have no intention of generalizing the present results to other metal-catalyzed reactions.

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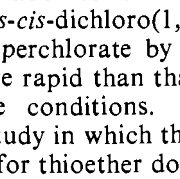
Effect of Thioether Donor Atoms as Nonbridging Ligands in the Reduction of Cobalt(III) Complexes by Iron(II)

Sir:

In a recent paper, Lane and Bennett reported a rate enhancement for the reduction of mercaptoacetatobis(ethylenediamine)cobalt(III) by chromium(II).[1] Recent work in our laboratories has demonstrated that the reduction of *s-cis*-dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate by iron(II) occurs at a rate 10^3 times more rapid than that for *cis*-$\text{Co(en)}_2\text{Cl}_2^+$ under comparable conditions. This represents the first quantitative study in which the nonbridging-ligand effect is evaluated for thioether donors positioned trans to a chloride–cobalt(III) bridge for reduction by iron(II).

Previous stereochemical studies have established the geometry of *s-cis*-Co(eee)Cl_2^+ as that shown below.[2]



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(1) (a) R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, **92**, 1089 (1970). (b) k_{S_2} has been more recently determined to be in the order of $\sim 5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$: L. E. Bennett, private communication.

(2) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).

The ion is relatively inert to isomerization and aquation in dilute aqueous acid solution.[3] It is structurally significant that the ion possesses two cis-coordinated thioether functions which are both mutually trans to the coordinated chloride atoms.

$[Co(eee)Cl_2]ClO_4$ was prepared by literature procedures[2] and twice recrystallized from water. Its purity was established from analyses and reported electronic (ϵ_{610} 309 ± 4) spectra.[2,4] Reaction rates were determined at 15.0, 25.1, and 35.0° and 1.0 M total perchlorate in the presence of excess iron(II) using a Cary-14 recording spectrophotometer and accessory temperature-control equipment. Plots of $\ln (D_t - D_\infty)$ *vs.* time were found to be linear over 95% reaction. The observed pseudo-first-order rate constants were determined from the slopes of such plots as evaluated by a computer least-squares program based on input of t, D_t, D_∞, and first-order rate equations.

Table I. Kinetics for the $Co(eee)Cl_2^+$–Fe^{2+} Reaction[a]

$10^4[Co(III)]$, M	$[Fe^{2+}]$, M	$[H^+]$, M	Temp, °C	k_t, M^{-1} sec^{-1}
7.84	0.005	0.10	25.1	1.29 ± 0.04
	0.010	0.10	15.0	0.680
	0.010	0.10	25.1	1.40
	0.010	0.10	35.0	2.14
	0.015	0.10	25.1	1.34
	0.020	0.10	25.1	1.39
	0.025	0.10	25.1	1.35
	0.030	0.10	25.1	1.30
7.84	0.020	0.05	25.1	1.34 ± 0.03
	0.020	0.10	25.1	1.39
	0.020	0.20	25.1	1.38
	0.020	0.40	25.1	1.34
	0.020	0.60	25.1	1.29
	0.020	0.80	25.1	1.33
3.9	0.010	0.10	25.1	1.36

[a] $[ClO_4^-] = 1.00$ M, maintained with $HClO_4$–$NaClO_4$.

The results of the kinetic measurements are summarized in Table I. The values of the second-order rate constants which appear in the last column of Table I were calculated from the relation $k_t = k_m/[Fe^{2+}]$, where k_m is the measured pseudo-first-order rate constant. It is seen that k_t is independent of [Co(III)], [Fe(II)], and $[H^+]$. Under these conditions, the reduction process obeys the mixed second-order rate law

$$-d[Co(eee)Cl_2^+]/dt = k_t[Co(III)][Fe(II)] \qquad (1)$$

and corresponds to the chemical process

$$Co(eee)Cl_2^+ + Fe(II) \xrightarrow{H^+} Co(II) + Fe(III) + eeeH_2^{2+} + 2Cl^- \qquad (2)$$

The enthalpy of activation, $\Delta H^\ddagger$, was determined from a plot of $\log k_t/T$ *vs.* $1/T$, which gave a computer-evaluated least-squares slope corresponding to $\Delta H^\ddagger = 9.25$ kcal/mol. The entropy of activation, $\Delta S^\ddagger$, calculated from transition-state theory is −34.9 eu.

Inner-sphere mechanisms with chloride as the bridging function have been established for comparable cobalt(III)–iron(II) reactions through the detection of the metastable $FeCl^{2+}$ intermediate.[5] In the case of $Co(H \cdot EDTA)Cl^-$, *trans*-$Co(en)_2OH_2Cl^{2+}$, and $Co(NH_3)_5Cl^{2+}$, a chloride-bridged inner-sphere mechanism was demonstrated.[5,6] Reasoning by analogy, and in view of the tendency of iron(II) to react by an inner-sphere mechanism whenever a potential bridging ligand is present in the coordination sphere of the oxidant, it seems reasonable to assume an inner-sphere mechanism for the present reaction as well.[7]

Treatment of $Co(eee)(1,10\text{-phen})^{3+}$, $Co(eee)(acac)^{2+}$, or $Co(eee)(\alpha,\alpha'\text{-dipy})^{3+}$ with 0.02 M iron(II) shows no reaction after 24 hr at 25°, lending further support to the assumption of an inner-sphere mechanism in the present work. This demonstrates that electron transfer proceeds through a chloride bridge and not through a sulfur bridge. Chloride being a better electron-transfer bridge than thioether is especially significant in view of Lane and Bennett's results, where a thiol function was shown to be a much better bridge than chloride.[1b] Thus, tying up one of the free electron pairs on a thiol function with a carbon linkage seems to significantly reduce the effectiveness of sulfur to function as an electron-transfer bridge.

Early arguments presented by Orgel[8] and later extended and supported by the researches of Taube[9] show that an important barrier to activation for the type complexes under consideration is the apparent necessity to stretch the cobalt-bridging bond prior to electron transfer.

A crude indication of the relative ease of chloride–cobalt(III) bond stretching might possibly be estimated by considering the relative ease of chloride removal from the cobalt(III)-activated complex by making a comparison of the known aquation rates, since aquation involves stretching of the chloride–metal bond. When the aquation rate of *cis*-$Co(en)_2Cl_2^+$ ($k_{aq} = 24.4 \times 10^{-5}$ sec^{-1} at 25°) is compared to that of *s-cis*-$Co(eee)Cl_2^+$, having $k_{aq} = 1.2 \times 10^{-5}$ sec^{-1}, one might be inclined to suggest that the chloride–metal bond associated with the *cis*-$Co(en)_2Cl_2^+$ ion stretches more easily than the corresponding bond in *s-cis*-$Co(eee)Cl_2^+$. That the reduction rate for *s-cis*-$Co(eee)Cl_2^+$ is 10^3 times faster than the reduction of the *cis*-$Co(en)_2Cl_2^+$ analog suggests that factors other than the ease of chloride removal from the oxidant coordination sphere dominate the reduction process.

It is significant to note that the cobalt–sulfur bond system in this complex shows no specific trans-labilizing effect as is observed in S-bonded sulfito–Co(III) complexes.[10]

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(3) J. H. Worrell and C. F. Fortune, *Inorg. Chem.*, submitted for publication. The reaction $Co(eee)Cl_2^+ + H_2O \rightarrow Co(eee)H_2OCl^{2+} + Cl^-$ at 25° and 0.10 M H^+ has a pseudo-first-order rate constant $k = 1.20 \times 10^{-5}$ sec^{-1}, with thermodynamic activation parameters $\Delta H^\ddagger = 20.4$ kcal/mol and $\Delta S^\ddagger = -36$ eu.

(4) B. Bosnich, W. R. Kneen, and A. T. Phillip, *ibid.*, **8**, 2567 (1969). Contrary to this report, $[Co(eee)Cl_2]ClO_4$ does not have a shoulder at 645 nm on the low-energy side of the electronic transition centered at ~607 nm.

(5) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

(6) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(7) Our present work with $Co(eee)Cl_2^+$ and related $Co(NSSN)X_2^{n+}$ complexes shows that the rate of reduction is sufficiently rapid to allow detection of FeX^{2+} intermediates. Our inability to provide definitive evidence of mechanism at this time stems from the fact that our laboratories are not yet equipped with a stopped-flow spectrophotometer.

(8) L. Orgel, Report of the Tenth Solvoy Conference, Brussels, 1956, p 289.

(9) (a) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965); (b) H. Diebler, P. H. Dodel, and H. Taube, *ibid.*, **5**, 1688 (1966); (c) R. K. Murmann, H. Taube, and F. A. Posey, *J. Amer. Chem. Soc.*, **79**, 262 (1957).

(10) (a) H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, **7**, 2535 (1968); (b) J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Amer. Chem. Soc.*, **88**, 2877 (1966); (c) P. H. Tweari, R. H. Gaver, H. K. Wilcox, and

For a series of complexes having a common bridging group but different ligands in the trans position, the stronger the crystal-field influence of the trans ligand the farther away it must be moved to lower the energy of the e_g acceptor orbital the necessary extent.[11] The ligand-field strengths of the groups trans to the bridged chloride in the complexes of Table II are en ~ NH_3 $\gg H_2O >$ R–S–R.[12,13] The observed general trend in increased rate of reduction parallels the decrease in field strength of the donor ligand positioned trans to the bridging atom.[14]

Table II. The Reduction of Several Cobalt(III) Complexes by Iron(II) (25°, $\Sigma ClO_4^- = 1.0\ M$)

Complex	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Co(NH_3)_5Cl^{2+}$	0.00135	+12.5	−30
cis-$Co(en)_2Cl_2^+$	0.0016		
trans-$Co(en)_2ClH_2O^{2+}$	0.24		
cis-$Co(eee)Cl_2^+$	1.35	+9.25	−36.6

A comparison of the rate constants for reduction of a series of related complex ions is presented in Table II. The $Co(eee)Cl_2^+$–Fe^{2+} reaction proceeds at a rate which is extremely rapid compared to the corresponding reduction of *trans*-$Co(en)_2ClH_2O^{2+}$, the most reactive member of that class of oxidants. Arguments using molecular models, entropy considerations relative to solvation, and/or successive chelation tend to indicate that steric effects cannot account for the observed rate enhancement.

A similar rate enhancement factor of 10^3 for reduction of $Co(eee)Br_2^+$ and $Co(eee)C_2O_4^+$ compared to the reduction of ethylenediamine analogs by iron(II) has been observed.[15] This suggests that the contributions of these bridging and nonbridging functions to $\Delta G^{\ddagger}$ may be partitioned separately.[16] Three possibilities for the free energies of precursor complex formation are consistent with this: (a) they contribute rather negligibly, (b) they are unaffected by this particular nonbridging ligand variation,[17] and (c) they are affected similarly, which, admittedly, seems unlikely.

A most important feature of the present investigation has been the demonstration that dramatic rate enhancement is observed when two mutually cis thioether functions are positioned *trans* to a bridging atom. The scope, versatility, and stereochemical factors influencing the reduction process for this new class of compounds is currently being investigated in detail.

Acknowledgment. We wish to acknowledge financial support for this work from a Research Corporation, Frederic Gardner Cottrell Project Grant and National Science Foundation Undergraduate Research Participation Program No. GY-7621. The referees' comments and suggestions have been very helpful and are gratefully acknowledged.

W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967); (d) D. R. Stranks and J. K. Yandell, *ibid.*, **9**, 751 (1970).

(11) A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1084 (1958).

(12) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1572 (1969).

(13) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 709 (1965).

(14) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

(15) The general range of reactivity observed for other *s-cis*-Co(eee)-X_2^{n+} complexes reduced by iron(II) at conditions similar to those reported here gives $k_t \approx$ 1-3 M^{-1} sec^{-1}.

(16) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966, p 74.

(17) For an example where this is not observed, see M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 3982 (1969).

(18) NSF-URP participant, summer 1970.

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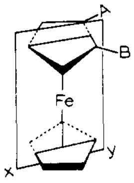
Pseudochirality in Ferrocenes

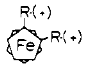
Sir:

Optical activity in recent years has been demonstrated for a number of 1,2-disubstituted ferrocenes, corresponding to the generalized representation I.[1] These molecules do not possess a chirality center or a chirality axis. They do, however, possess a chirality plane (XY), and an interesting situation, which has heretofore gone unnoticed, develops when the different achiral substituents (A and B) are replaced by two constitutionally identical, but chiral, groups.

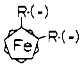


I

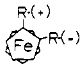
When the two identical groups are also of the same chirality, the plane (XY) is still chiral, and two enantiomers, IIa and IIb, are generated. On the other hand, the substituents may also be of opposite chirality. In this situation, two *achiral diastereomers*, IIc and IId, are generated, and the XY plane, which is no longer an element of chirality, may be cited as a plane of pseudochirality or pseudoasymmetry.[2] The two optically inactive forms may be designated as pseudochiral or pseudoasymmetric isomers.



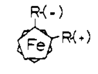
IIa



IIb



IIc



IId

We wish to report the synthesis of each member of two such stereoisomeric sets, the properties of which provide clear experimental demonstration of the stereorelationships discussed above.

The two chiral members (enantiomers) of one set were individually prepared *via* modified Knoevenagel condensations of 1,2-diformylferrocene (III)[3] and (−)-carbomenthoxyacetic acid[4] (IVa) ([α]^{20}D −69.6 ± 0.8° (*c* 2.5, ethanol)) to give (−)-1,2-bis(2-carbomenthoxy-*trans*-ethenyl)ferrocene[5] (Va) (mp 144–146°, [α]^{22}D −72.3 ± 2.0° (*c* 0.250, ethanol)), and with (+)-carbomenthoxyacetic acid[4] (IVb) ([α]D 68.5 ± 1.0° (*c* 2.5, ethanol)) to give the dextrorotatory enantiomer (Vb)[5] (mp 144–146°, undepressed when melted in admixture with (−)-Va, [α]^{22}D 70.0 ± 1.2° (*c* 2.50, ethanol)).

Synthesis of the achiral, pseudoasymmetric isomers

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(1) For an account of much of this work, see: K. Schlögl, *Top. Stereochem.*, **1**, 39 (1967).

(2) For a fuller account of these relationships, see: V. Prelog, *Proc. Kon. Ned. Akad. Wetensch., Ser. B*, **71**, 108 (1968).

(3) G. Marr, B. W. Rockett, and A. Rushworth, *J. Organometal. Chem.*, **16**, 141 (1969).

(4) E. B. Abbot, E. W. Christie, and A. McKenzie, *Chem. Ber.*, **71**, 9 (1938).

(5) Combustion and analyses and the usual set of spectral data were satisfactory and consistent with the assigned structure.