J. Am. Chem. Soc. **1980**, *102*, 5519-5526

Oxidation-Reduction Reactions of Complexes with Macrocyclic Ligands. Energetics and Dynamics of Methyl Exchange[1]

John F. Endicott,* K. P. Balakrishnan, and Chung-Lai Wong

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 7, 1979*

Abstract: Intrinsic and thermodynamic components of reactivity have been obtained from rate and equilibrium measurements for the methyl-bridged electron transfer reactions of several $Co(N_4)(OH_2)CH_3^{2+}/Co(N_4)(OH_2)_2^{2+}$ (N_4 a tetraaza macrocyclic ligand) couples, for the $Co(dmgH)_2(OH_2)CH_3/Co^{II}(dmgH)_2$ couple, and for the methylcobalamin/cob(II)alamin couple. The intrinsic (free energy independent) barriers to methyl-bridged electron transfer are smallest in the cobalamin couple and largest for complexes of the most sterically hindered of the neutral macrocyclic ligands. It is proposed that the intrinsic kinetic barrier to these reactions can be represented in terms of a three-center-three-electron ($Co-CH_3-Co$) bonding description of the transition state. Factors which contribute to the intrinsic barrier are those which contribute to bond strength (electron affinity, separation of donor and acceptor centers, etc.); Franck-Condon factors do not appear to play a dominant role in these reactions. Thermodynamic parameters for the various $Co-CH_3/Co(II)$ couples can be related by means of simple thermochemical cycles to differences in reactant and product $Co-CH_3$ bond energies, entropy differences of outer-sphere redox couples, and a collection of relatively small solvation terms. Data from other studies on photohomolysis threshold energies and the temperature dependence of electrode potentials permit the estimation of $Co-CH_3$ bond energies for several complexes. The $Co-CH_3$ bond energies vary from ~48 to ~33 kcal mol^{-1}. The $Co-CH_3$ bond tends to be stabilized by unsaturation of the equatorial ligand and to be very sensitive to stereochemical perturbations.

Introduction

The effectiveness of reagents in group transfer reactions is frequently discussed in thermodynamic rather than mechanistic terms. Thus, the observation of oxidation-reduction or electrophilic displacement accompanying the methylation reactions of methylcorrinoid complexes has been rationalized in terms of the redox potential of the acceptor.[2,3] Similar concerns arise, perhaps in a more subtle way, in the frequent postulation that cobalt-carbon homolysis is the key step in much of the metabolic functioning of coenzyme B_{12}.[4-6] It remains to be demonstrated that the reactivity in even the simplest of these systems is due to thermodynamic rather than intrinsic kinetic factors. Of course this ambiguity is not unique to reactions of enzymic or of organocobalt complexes since the separation of the thermodynamic and "intrinsic" components of reactivity patterns is rarely a simple matter. However, the intrinsic kinetic barriers to many reactions of cobalt complexes are especially large,[6-10] so there is considerable cause to suspect that "purely kinetic" factors may be of great importance in determining reactivity patterns even in cobalt-mediated alkylations. The complexity and variety of these reactions are illustrated by the oxidation of organocobalt complexes by powerful oxidants such as Ce^{IV},[3,11] formally CH_3^- transfer ("electrophilic displacements") to mild oxidants such as Hg^{2+},[2,3] and formally CH_3 transfer to a strong reductant such as Cr^{2+}.[3a,3c,12] In some sense each of these is an oxidation-reduction reaction, subject to the kinetic constraints typical of electron-transfer processes.

The methylation of Cr^{2+} has been described as a "reductive homolytic cleavage", but is formally analogous to the well-known halide-bridged inner-sphere electron-transfer reactions so common in the oxidation-reduction chemistry of cobalt and chromium.[7-10,13,14] In fact a common mechanistic description of the halide and methyl-bridged reactions has been proposed[15] which involves three-center-three-electron bonding descriptions of the transition states. The methyl-bridged electron-transfer reactions have tended to have much smaller rates[12,15] than the analagous halide-bridged reactions.[7-9] This is consistent with the small electron affinity of CH_3 and the consequent relatively "weakly bound" transition state for the methyl-bridged reactions. Nevertheless, an appreciable range of reactivities has been observed in the Cr^{2+} reductions of methylcobalt complexes[12] and in methyl transfer between different cobalt substrates.[16,17] Unfortunately, these previous studies have not been able to distinguish the intrinsic kinetic components of observed reactivity differences from those variations in reactivity which arise only from differences of the driving force of the reactions.

---

(1) (a) Partial support of this research by the National Institutes of Health (AM 14341) is gratefully acknowledged. (b) Presented in part at the 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979, INOR 054.

(2) Ridley, W. P.; Dizikes, L. J.; Wood, J. M. *Science* **1977**, *197*, 329.

(3) (a) Fauchiang, Y.-T.; Ridley, W. P.; Wood, J. M. In "Organometals and Organometalloids", Brinckman, F. E., Bellama, J. M., Eds.; ACS Symposium Series, No. 82; American Chemical Society: Washington, D.C., 1978; Chapter 4, p 54. (b) Thayer, J. S. In ref 3a, Chapter 12, p 188. (c) Kochi, J. K. In ref 3a, Chapter 13, p 205.

(4) (a) Ables, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114. (b) Ables, R. H. In "Biological Aspects of Inorganic Chemistry", Addison A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley-Interscience: New York, 1977.

(5) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376. (b) Krouwer, J. S.; Babior, B. M. *Mol. Cell. Biochem.* **1977**, *15*, 89.

(6) Golding, B. T. In "Comprehensive Organic Chemistry", Haslam, E., Ed.; Pergamon Press: New York, 1978; Vol. 5.

(7) (a) Linck, R. G. *MTP Int. Rev. Sci.: Ser. One* **1972**, *9*, 303. (b) *MTP Int. Rev. Sci.: Ser. Two* **1974**, *9*, 173. *Surv. Prog. Chem.* **1976**, *7*, 89.

(8) Sutin, N. In "Inorganic Biochemistry", Eichhorn, G. L., Ed.; American Elsevier: New York, 1973; Chapter 19, p 161.

(9) (a) Endicott, J. F.; Durham, B. In "Coordination Chemistry of Macrocyclic Compounds", Melson, G. B., Ed.; Plenum Press: New York, 1979; Chapter 6. (b) Glick, M. D.; Kuszaj, J. M.; Endicott, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 5097. (c) Glick, M. D.; Schmonsees, W. G.; Endicott, J. F. *Ibid.* **1974**, *96*, 5661. (d) Durham, B.; Endicott, J. F.; Wong, C. L.; Rillema, D. P. *Ibid.* **1979**, *101*, 847. (e) Wong, C. L.; Endicott, J. F., work in progress.

(10) Durham, B. Ph.D. Dissertation, Wayne State University, 1977.

(11) (a) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S.; Topich, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1606. (b) Halpern, J. A.; Chan, J. S.; Roche, T. S.; Tom, G. M. *Acta Chem. Scand., Ser. A* **1979**, *33*, 141.

(12) (a) Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, 95, 4468. (b) Espenson, J. H.; Sellers, Jr., T. D. *Ibid.* **1974**, *96*, 94.

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

(14) (a) Taube, H. "Electron Transfer of Complex Ions in Solutions"; Academic Press: New York, 1970. (b) Taube, H. *Can. J. Chem.* **1959**, *37*, 129.

(15) Endicott, J. F.; Wong, C. L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.*, in press.

(16) (a) Van Den Bergen, A.; West, B. O. *Chem. Commun.* **1971**, 52. (a) *J. Organomet. Chem.* **1974**, *64*, 1125.

(17) Dodd, D.; Johnson, M. D. *Chem. Commun.* **1971**, 1371.

0002-7863/80/1502-5519$01.00/0

Recent work in this laboratory[9d] has shown that intrinsic and thermodynamic components of reactivity patterns can be separated even for inner-sphere electron-transfer reactions. The present report describes our studies of the methyl-bridged electron-transfer reactions of a series of macrocyclic cobalt complexes. The intrinsic kinetic barriers which we have found for the methyl-bridged electron-transfer reactions span a far greater range than previously found for halide-bridged reactions.[9d,14,18] Since this work necessitated the determination of equilibrium constants for methyl-bridged reactions, the combination of data from the present study with photochemically determined $Co-CH_3$ bond energies[19] has permitted us to establish $Co-CH_3$ bond energies for methylcobalamin and several complexes with synthetic equatorial ligands.

Experimental Section

Preparation of the Complexes. Methylated cobalt complexes containing synthetic equatorial ligands were prepared by means of procedures described in the literature.[19-22] Methylcobalamin was obtained from Sigma Chemical Corp. Spectrophotometric data for all complexes and microanalytical data for the synthetic complexes were in excellent agreement with literature reports.

Most of the cobalt(II) complexes containing macrocyclic ligands were prepared by standard literature techniques.[9d,23] Owing to the extreme oxygen sensitivity of $Co(dmgH)_2(OH_2)_2$, $Co([14]aneN_4)(OH_2)_2^{2+}$,[24] $Co(Me_2[14]4,11\text{-}dieneN_4)(OH_2)_2^{2+}$,[24] and cob(II)alamin, these complexes were prepared in solution immediately before use. To prepare $Co(dmgH)_2(OH_2)_2$ we mixed stoichiometric amounts of $Co(O_2CCH_3)_2\cdot 6H_2O$ and dimethylglyoxime ($dmgH_2$), each dilute in deaerated 0.1 M NaO_2CCH_3. To prepare solutions containing $Co([14]aneN_4)(OH_2)_2^{2+}$, we mixed carefully deaerated 0.1 M $NaClO_4$ solutions of $Co(ClO_4)_2\cdot 6H_2O$ and $[14]aneN_4$ (in slight stoichiometric excess). Solutions of $Co(Me_2[14]4,11\text{-}dieneN_4)(OH_2)_2^{2+}$ and cob(II)alamin were prepared by reduction of solutions of $Co(Me_2[14]4,11\text{-}dieneN_4)(OH_2)_2^{3+}$ [25,26] and Sigma Chemical Corp. hydroxycobalamin 0.1 M in $NaCF_3SO_3$ with $Ru(NH_3)_6^{2+}$, amalgamated zinc, or Cr^{2+}.

Solutions of $Ru(NH_3)_6^{2+}$ in 0.1 M $NaClO_4$ or 0.1 M $NaCF_3SO_3$ were prepared by reduction of argon-purged solutions of $Ru(NH_3)_6^{3+}$ with amalgamated zinc. The $Ru(NH_3)_6Cl_3$ was obtained from the Matthey-Bishop Co.

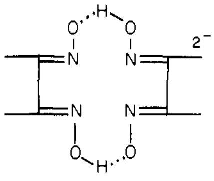
All solutions were prepared with redistilled, deionized water. Reagent-grade chemicals were used throughout.

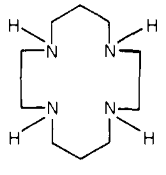
Kinetic Procedures. Rapid reactions were followed by using an Aminco stopped-flow apparatus[9] with either oscilloscopic or recorder readout. The rates of the slower reactions were monitored by using a Gilford 250 spectrophotometer with a thermostated cell compartment and a programmed sampling attachment.

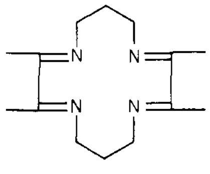
All reactions were run under pseudo-first-order conditions. In most cases the methyl complexes were in more than fivefold excess of the cobalt(II) complexes. Reagent solutions were separately purged with Cr^{2+}-scrubbed N_2 and transferred through serum caps by means of syringes equipped with platinum needles. For the slower reactions, the reaction cell was usually a 1-cm spectrophotometer cell equipped with a serum cap and purged with N_2 prior to transfer of the reactant solutions.

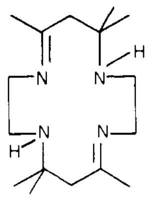
Spectrophotometric Determinations of Equilibrium Constants. Owing to the large differences in absorptivity between methylcobalamin and cob(II)alamin,[27,28] these reagents were used in most of the equilibrium determinations. To maximize sensitivity, reactants were chosen so that the extent of reactions would be small. Reaction solutions were deaerated and thermostated at 25 °C. Absorbance readings were made over a period of 1 day or more, until a constant reading was obtained.

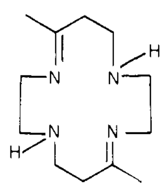
The transfer of the methyl group in several of the macrocyclic systems was demonstrated from ^1H NMR spectra, using a Varian T-60 spectrometer. The chemical shifts of methyl groups on the equatorial ligands and the $Co-CH_3$ group were sufficiently different from complex to complex to permit identification of the methylcobalt complexes present in the equilibrated mixtures. Quantitative NMR measurements were precluded by the limited solubility of most of the complexes.

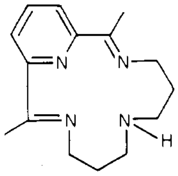

$(dmgH)_2^{2-}$


$[14]aneN_4$


$Me_4[14]tetraeneN_4$


$Me_6[14]4,11\text{-}dieneN_4$


$Me_2[14]4,11\text{-}dieneN_4$


$Me_2pyo[14]trieneN_4$

Results

The results of our kinetic determinations are summarized in Table I and presented in greater detail in Table S-1.[29] That the reactions observed involve methyl transfer between cobalt complexes has been qualitatively demonstrated by ^1H NMR spectroscopy and by the observation of the expected complementary changes in cobalt(II) and methylcobalt complex absorbancies. Since the alkylcobalt complexes tend to be reduced at ~−1 V vs. NHE,[19] outer-sphere reduction of the organocobalt complexes by $Co^{II}(N_4)$ complexes is unfavorable by 1–1.5 V. Most of the reasons for excluding alternative reaction pathways have been discussed in the earlier literature.[11,15]

We have quoted a few kinetic parameters for reactions with quite unfavorable equilibrium constants. Such rate constants are nearly always complicated by the approach of the reacting mixture to equilibrium; however, these approximate numbers are useful as order of magnitude checks on some of the analyses developed below.

Equilibrium constants are summarized in Table II. Greater detail of the experimental determinations can be found in Table S-II.[29]

Discussion

While the methyl-bridged electron-transfer reactions investigated here are generally much slower in rate than the corresponding halide-bridged reactions,[9d,e] the range of reactivity is far greater than previously found for any other single class of electron-transfer reactions of related macrocyclic complexes.[9,10] Thus, rates vary over a 10^6-fold range even for methyl-bridged reactions with $\Delta G^\circ < 0$. When corrections are made for the free-energy contributions, the range of reactivity is found to span some eight orders of magnitude (see below). In an electron-transfer context this large rate variation would be associated with some sort of Franck–Condon reorganizational barrier. However, the large trans influence of the $Co-CH_3$ bond weakens the $X-(Co-CH_3)$ bond[30,31]

---

(18) Endicott, J. F.; Wong, C. L., work in progress.

(19) (a) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 1276. (b) *Ibid.* **1978**, *100*, 123. (c) Ciskowski, J. M.; Endicott, J. F., work in progress.

(20) (a) Roche, T. S.; Endicott, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 8622. (b) *Inorg. Chem.* **1974**, *13*, 1575.

(21) (a) Jackels, S. C.; Framery, K.; Barefield, E. K.; Rose, N. J.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 2893. (b) Farmery, K.; Busch, D. H. *Ibid.* **1972**, *11*, 2901.

(22) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

(23) Endicott, J. F.; Lilie, J.; Kuszak, J. M.; Ramaswany, B. S.; Schmonsees, W. G.; Glick, M. D.; Rillema, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429.

(24) Ligand abbreviations: $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $Me_6[14]4,11\text{-}dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_2[14]4,11\text{-}dieneN_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $Me_2pyo[14]trieneN_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadec-1(17),2,11-13,15-pentaene; bpy = 2,2′-bipyridine; dmgH = 3,4-dimethylglyoximate (1−); sepulchrate = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

(25) (a) Hay, R. W.; Jeragh, B. *J. Chem. Soc., Dalton Trans.* **1977**, 1261. (b) Hay, R. W.; Lawrence, G. A. *Ibid.* **1975**, 1466.

(26) Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.*, in press.

(27) Hogenkamp, H. P. C. In "Cobalamin", Baboir, B. M., Ed.; Wiley-Interscience: New York, 1975; Chapter 1, p 21.

(28) Dunne, C. P. Ph.D. Dissertation, Brandeis University, 1971.

(29) See paragraph at end of paper regarding supplementary material.

(30) Lenhert, P. J. *Chem. Commun.* **1967**, 980.

Table I. Summary of Rate Constants for Methyl-Bridged Electron-Transfer Reactions[a]

$$\mathrm{Co(N_4)(OH_2)CH_3 + Co^{II}(N_4')(OH_2)_2 \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} Co^{II}(N_4)(OH_2)_2 + Co(N_4')(OH_2)CH_3}$$

N_2	N_4'	medium[b]	temp, °C	k_{ab}, M^{-1} s^{-1} [c]	k_{ba}, M^{-1} s^{-1} [c]
corrin[d]	Me_4[14]tetraeneN_4		19.8	0.51 ± 0.01 (2)	
			25	1.07 ± 0.06 (11)	0.25 ± 0.02 (6)
			33.4	5.03 ± 0.06 (2)	1.02 ± 0.02 (2)
			38.5	10.9 ± 0.3 (2)	1.82 ± 0.07 (2)
		0.1 M $HClO_4$	19.8		0.46 ± 0.02 (2)
		0.1 M $HClO_4$	25	1.01 ± 0.02 (6)	0.28 ± 0.02 (3)
Me_2pyo[14]trieneN_4	corrin[e]		25	602 ± 30 (4)	
Me_6[14]4,11-dieneN_4	corrin[e]		25	1.55 ± 0.08	
$(dmgH)_2$	corrin[e]		25	~760 ± 55 (3)[f]	$(5.6 \pm 0.2)10^4$ (2)
$(dmgH)_2$	Me_4[14]tetraeneN_4		25	3.96 ± 0.14 (7)	
		0.1 M $HClO_4$	25	9.39 ± 0.13 (9)	
		0.1 M NaO_2CCH_3	25		10.4 ± 0.6 (2)
Me_2pyo[14]trieneN_4	$(dmgH)_2$	0.1 M NaO_2CCH_3	25	4.6 ± 0.5 (3)	
[14]aneN_4	$(dmgH)_2$	0.1 M NaO_2CCH_3	25	2.95 ± 0.06 (2)	
Me_6[14]4,11-dieneN_4	$(dmgH)_2$	0.1 M NaO_2CCH_3	25	0.059	
Me_4[14]tetraeneN_4	Me_2pyo[14]trieneN_4		25	~0.14 ± 0.01 (5)[f]	27.3 (5)
[14]aneN_4	Me_4[14]tetraeneN_4		25	0.13 ± 0.02 (4)	
Me_2pyo[14]trieneN_4	[14]aneN_4		25	0.32 ± 0.01 (4)	
Me_6[14]4,11-dieneN_4	Me_4[14]tetraeneN_4	0.1 M HCF_3SO_3	28.6	0.010	
		0.1 M HCF_3SO_3	35.2	0.022	
		0.1 M HCF_3SO_3	42.8	0.032	
Me_6[14]4,11-dieneN_4	Me_2pyo[14]trieneN_4	0.1 M HCF_3SO_3	28.6	0.017	$\sim 3 \times 10^{-4}$ [f]
			35.2	0.027	$\sim 4 \times 10^{-4}$ [f]
			42.8	0.047	$\sim 5.6 \times 10^{-4}$ [f]
Me_6[14]4,11-dieneN_4	Me_2[14]1,11-dieneN_4-13-one	0.1 M HCF_3SO_3	28.6	4.4×10^{-4}	
			35.2	6.8×10^{-4}	
			42.8	1.4×10^{-3}	
Me_2pyo[14]trieneN_4	Me_2[14]1,11-dieneN_4-13-one	0.1 M HCF_3SO_3	28.6	1.8×10^{-3}	
			35.2	3.1×10^{-3}	
			42.8	5.3×10^{-3}	

[a] Details of concentrations, etc., may be found in Table S-I. [b] 0.1 M $NaClO_4$ except as indicated. [c] Number of determinations in parentheses. [d] Methylcobalamin. In neutral solution the benzimidazole base is coordinated to the trans axial position rather than H_2O. [e] Cob(II)-alamin. [f] Estimated rate constant for a reaction which did not go to completion.

Table II. Kinetic and Thermodynamic Parameters for Methyl-Bridged Electron-Transfer Reactions[a]

N_4-a	N_4-b	K_{ab}(25°C)	$\Delta G^{\ddagger}_{ab}$, kcal mol^{-1} [b]	$\Delta H^{\ddagger}_{ab}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{ab}$, eu
corrin	Me_4[14]tetraeneN_4	4.3 ± 0.6[c,d]	15.2	7.5 ± 0.8	−22 ± 4
		3.6 ± 0.4[d,e]	15.2[e]		
Me_2pyo[14]trieneN_4	corrin	44 ± 17[f]	11.4		
Me_6[14]4,11-dieneN_4	corrin	$(1.7 \pm 0.3)10^3$ [f]	14.9		
corrin	Me_2[14]4,11-dieneN_4	0.25 ± 0.04[f]			
corrin	$(dmgH)_2$	59 ± 10[f]	8.6		
[14]aneN_4	corrin	8 ± 1[f]			
$(dmgH)_2$	Me_4[14]tetraeneN_4	0.38 ± 0.04[d]	14.4		
Me_2pyo[14]trieneN_4	$(dmgH)_2$	(2.9 ± 1.4)10[g]	14.3		
[14]aneN_4	$(dmgH)_2$	$(5.0 \pm 1.5)10^2$ [g]	14.5		
Me_6[14]4,11-dieneN_4	$(dmgH)_2$	$(1.0 \pm 0.3)10^5$ [g]	16.9		
Me_2pyo[14]trieneN_4	Me_4[14]tetraeneN_4	$(1.1 \pm 0.4)10^2$ [f]	13.2		
[14]aneN_4	Me_4[14]tetraeneN_4	34 ± 10[g]	16.4		
Me_2pyo[14]trieneN_4	[14]aneN_4	6 ± 2[g]	15.9		
Me_6[14]4,11-dieneN_4	Me_4[14]tetraeneN_4	$(7 \pm 2)10^3$ [g]	18.1	11 ± 2	−33 ± 4
Me_6[14]4,11-dieneN_4	Me_2pyo[14]trieneN_4	40 ± 5[g]	17.9	13 ± 2	−23 ± 4

[a] The "sense" of the reagents is the same as in Table I. See Tables I and S-I for conditions and details. [b] Based on $k_{ab} = Ze^{-\Delta G^{\ddagger}_{ab}/RT}$; $Z = 10^{11}$ M^{-1} s^{-1}. [c] $\Delta H^{\circ}_{ab} = 1.6 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\circ}_{ab} = 2.9 \pm 2$ eu; benzimidazole coordinated. [d] $K_{ab} = k_{ab}/k_{ba}$. [e] Benzimadazole replaced by H_2O; 0.1 M $HClO_4$. [f] Spectrophotometric determination. [g] Calculated, $K_{ab} = K_{ac}K_{cb}$ or $K_{ab} = K_{ad}/K_{bd}$, from combinations of equilibrium constants in this table.

(in our cases X = H_2O or benzimidazole), so that contributions associated with bond-length changes trans to the briding group must be even smaller than those found for halide-bridged electron transfer.[9d,e] These several different kinds of variation in the activation free energy with the changes in Co–OH_2 bond length are illustrated in Figure 1 for self-exchange electron-transfer reactions. In order to gain insight into the origin and variations of the barriers to methyl-transfer reactions, it is necessary to separate the intrinsic kinetic factors from the contributions of the overall free-energy changes. These components of the free energy of activation are considered in separate sections below.

A. Thermodynamics of Methyl-Bridged Electron Transfer. Co–CH_3 Bond Energies. We have been able to measure equilibrium constants, K_{ab}, for several of the methyl-transfer reactions. Analogous equilibrium constants for outer-sphere electron-transfer reactions can be analyzed in terms of the separate contributions of the redox couples of each of the reactant partners (e.g., in terms of differences in the standard electrode potentials for the two redox couples). Such a linear analysis permits one to calculate equilibrium constants which are especially difficult to measure and

---

(31) Endicott, J. F.; Halko, D. J.; Butler, W. M.; Glick, M. D. Proceedings of the XVII International Conference on Coordination Chemistry, Dublin, Ireland, Aug 1974; Paper 3.43.

Table III. Intrinsic Thermodynamic and Kinetic Parameters for Cobalt-Methyl Complexes

complex	$S_{\mathrm{rc},j}$,[a] eu	rel redox couple free energy δG_j,[b] kcal mol^{-1}	rel Co–CH$_3$ bond energy $\Delta H_{j,\mathrm{CH_3}} - \Delta H_{\mathrm{a,CH_3}}$,[c] kcal mol^{-1}	Co–CH$_3$ bond energy $\Delta H_{j,\mathrm{CH_3}}$,[d] kcal mol^{-1}	intrinsic reorganizational free energy $\Delta G^{\ddagger}_{jj}$, kcal mol^{-1} [e]
methylcobalamin (MeB$_{12}$)	~10[f]	0	0	46	11.7 ± 1.2 (3)
aquomethylcobalamin	~10[f]	~0	~−1.5	~44	~12
$Co(dmgH)(OH_2)CH_3$	~10[f]	1.0	+1	47 ± 2	~11[g]
$Co(Me_2pyo[14]trieneN_4)(OH_2)CH_3^{2+}$	29	−2.3	−4.5 (−7)	41 (38)	12.7 ± 1.5 (3)
$Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$	23	0.9	+0.5 (−2)	46 ± 2 (44)	17.6 ± 1.5 (3)
$Co([14]aneN_4)(OH_2)CH_3^{2+}$	36	−1.3	−6 (−8)	40 (37)	17.8 (1)
$Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$	45	−4.5	−12 (−14)	33 (31)	22.7 ± 1.5 (3)
$Co(Me_2[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$	36	0,8	−3.5 (−6)	42 (40)	

[a] Reference 32 except as indicated. [b] Free-energy change for the reaction $Co(N_4)(OH_2)CH_3^{2+} + B_{12r} \rightleftharpoons Co^{II}(N_4) + MeB_{12}$, except as indicated. [c] Relative to MeB$_{12}$: $\Delta H_{j,\mathrm{CH_3}} - \Delta H_{a,\mathrm{CH_3}} = \Delta G_{ja} + T(S_{\mathrm{rc},j} - S_{\mathrm{rc},a}) + \delta\Delta G_{aj}$, with $\delta\Delta G_{aj} = 3.5$ kcal mol^{-1} (values in parentheses based on $\delta\Delta G_{aj} = 1$ kcal mol^{-1}; see discussion in text). No corrections for solvation are included. [d] Based on photohomolysis threshold energies (corrected by 2 kcal mol^{-1} for $\Delta H^{\ddagger}{}_{r}$[37]) as indicated for $Co(dmgH)_2(OH_2(OH_2)CH_3^{2+}$ and $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$; values in parentheses based on $\delta\Delta G_{aj} = 1$ kcal mol^{-1} (see footnote *c*); uncertainties are estimated at ±3 kcal mol^{-1} except as indicated. Bond energies are with respect to the aqueous medium; there may be a solvation contribution. [e] Mean apparent reorganizational barriers for self-exchange reactions of indicated complexes; values are determined by combinations of three independent rate constants (k_{aj}, k_{jb}, k_{ab}); numbers in parentheses are the number of different combinations of rate constant used in computing the mean values of $\Delta G^{\ddagger}{}_{jj}$. [f] Estimates based on trends in ref 32. [g] Based on Figure 3.

it permits some convenient checks on the reliability and consistency of measured equilibrium constants. A linear analysis of equilibria in inner-sphere electron-transfer reactions is also possible. This is shown by consideration of Scheme I.

Since $-RT \ln K_{ab} = \Delta G^{\circ}{}_{ab}(\mathrm{IS}) = \Delta H^{\circ}{}_{ab} - T\Delta S^{\circ}{}_{ab}$, the components of the free-energy change may be analyzed in terms of the different entropy and enthalpy cycles. Thus

$$\Delta G^{\circ}{}_{ab}(\mathrm{IS}) = (\Delta H_{a,\mathrm{x}} - \Delta H_{b,\mathrm{x}}) + (\Delta H_{b,\mathrm{s}} - \Delta H_{a,\mathrm{s}}) - T\Delta S^{\circ}{}_{ab}(\mathrm{OS}) - T(\Delta S_{a,\mathrm{x,s}} - \Delta S_{b,\mathrm{x,s}}) \quad (1)$$

The only "cross term" in eq 1 is the entropy change associated with outer-sphere electron transfer, $\Delta S^{\circ}{}_{ab}(\mathrm{OS})$. This term is simply the difference in the entropy change associated with the outer-sphere redox couples of the respective diaquo complexes: $\Delta S^{\circ}{}_{ab}(\mathrm{OS}) = S_{\mathrm{rc},b} - S_{\mathrm{rc},a}$. Values of $S_{\mathrm{rc},j}$ have been determined by Weaver and co-workers[32,33] for most of the macrocyclic complexes used in this study.

Obviously it is possible to group the terms of eq 1 in such a way that $\Delta G^{\circ}{}_{ab}(\mathrm{IS}) = \Delta G_a - \Delta G_b$, separating the contributions of reactants *a* and *b*. As a consequence it is valid to assume that the reactants contribute linearly to $\Delta G_{ab}(\mathrm{IS})$, and equilibrium constants may be estimated for all the reactions we have investigated in this study. Such quantities are included in Table II and used below.

Several of the terms in eq 1 merit further comment. For reactions symmetrical with respect to charge (e.g., for the synthetic tetraazamacrocyclic ligands which we have used), the last term is expected to be very small since the entropies of solvolysis of similarly charged cobalt(III) complexes are expected to be similar ($\Delta S_{a,\mathrm{x,s}} \simeq \Delta S_{b,\mathrm{x,s}}$); consequently the last term should be the smallest in eq 1. The values of $\Delta H_{a,\mathrm{s}}$ and $\Delta H_{b,\mathrm{s}}$ (the second term in eq 1; enthalpy changes associated with formation of five-coordinate cobalt(II) species) could in principle be estimated from values of enthalpies of activation for axial substitution into the very labile, low-spin cobalt(II) complexes. Unfortunately, little such information is available. However, these cobalt(II) complexes are so labile[20,23,34,35] that the activation parameters are all likely to be small. Assuming that substitutions on the low-spin cobalt(II) species are largely determined by enthalpies of activation, we would estimate $\Delta H_{i,\mathrm{s}} \simeq 5$ kcal mol^{-1} for the complexes with N$_4$ = neutral synthetic macrocycle ($k_{\mathrm{H_2O}} \sim 10^9$ s^{-1})[9d,23] and $\Delta H_{j,\mathrm{s}} \sim 4$ kcal mol^{-1} for cob(II)alamin and Co$^{\mathrm{II}}$(dmgH)$_2$ ($k_{\mathrm{H_2O}} \sim 10^{10}$ s^{-1}).[35]

The first and third terms clearly make the largest contributions to eq 1. With values of the smaller contributions as noted above, and the measured values of K_{ab} and $S_{\mathrm{rc},j}$, we could readily obtain a *relative* series of cobalt–methyl homolysis bond energies ($\Delta H_{j,\mathrm{CH_3}}$

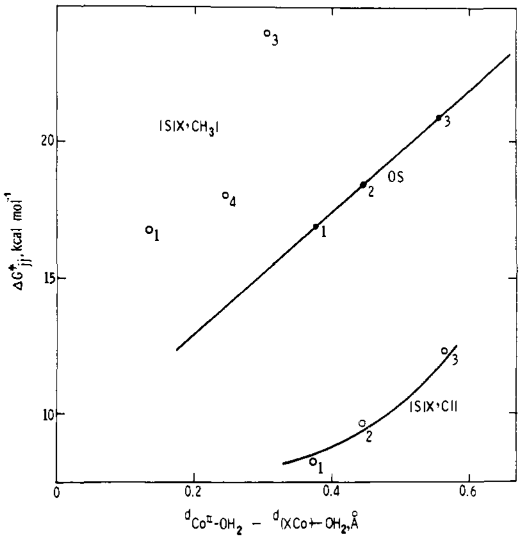


Figure 1. Correlation of free energy independent activation free energy ($\Delta G^{\ddagger}{}_{jj}$ in kcal mol^{-1}) with bond-length changes (Å) for different classes of electron-transfer reactions. Middle curve (closed circles) is for $Co(N_4)(OH_2)_2^{3+,2+}$ outer-sphere self-exchange reactions; kinetic data based on ref 10; X-ray structural parameters based on ref 9b,c, 23, and Durham, B.; Anderson, T. J.; Switzer, J. A.; Endicott, J. F.; Glick, M. D. *Inorg. Chem.* **1977**, *16*, 271. Lower curve (open circles) is for $Co(N_4)(OH_2)Cl^{2+}/Co(N_4)(OH_2)_2^{2+}$ chloride-mediated inner-sphere self-exchange reaction: kinetic data based on ref 9d,e; structural data as for outer-sphere reactions, assuming "normal cobalt(III)" bond lengths in the trans aquochloro complexes. The open circles at the top of the figure are for methyl-mediated inner-sphere self-exchange reactions: kinetic data from Table III; X-ray structural data for N$_4$ = Me$_4$[14] tetraeneN$_4$ from ref 23 and 31, $Co([14]aneN_4)(OH_2)_2^{2+}$ from ref 23. A Co-OH$_2$ bond length of 2.4 Å has been assumed for $Co([14]aneN_4)(OH_2)_2^{2+}$ based on the $Co([14]aneN_4)(OH_2)_2^{3+,2+}$ outer-sphere self-exchange and the correlation noted. A Co-OH$_2$ bond length of ~2.1 Å has been assumed for $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$ based on the lability of the water molecule in this complex. Note that the only bond-length change occurs for the axial coordination positions in these reactions. Reactions represented for N$_4$ = Me$_4$[14]tetraeneN$_4$ (1), Me$_2$[14]1,11-dieneN$_4$-13-one (2), Me$_6$[14]4,11-dieneN$_4$ (3), and [14]aneN$_4$ (4).

---

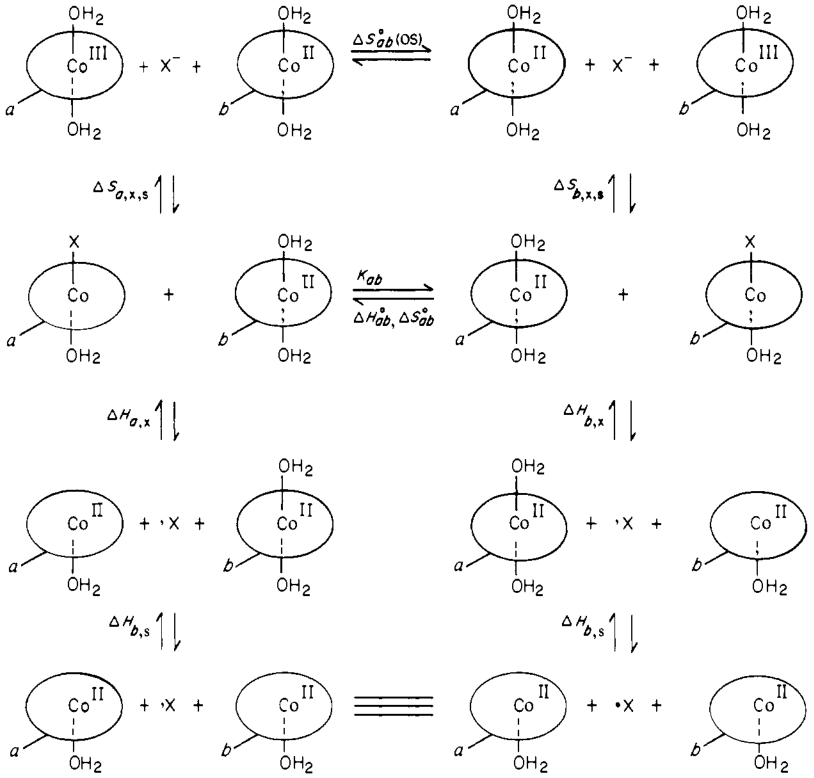
(32) (a) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem.* Soc. **1979**, *101*, 1131. (b) Weaver, M. J., private communication.

(33) We are very grateful to Professor Weaver for his cooperation in making these determinations.

(34) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86.

(35) Endicott, J. F.; Ferraudi, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 243.

Scheme I



quantities in parentheses in Table III). Alternatively, we have used an empirical approach for obtaining values of $\Delta H_{j,\mathrm{CH}_3}$ in Table III. The two approaches agree to within 3 kcal mol^{-1}.

Studies of photoinduced homolyses have indicated that the minimum excitation energy required to induce homolysis (E_{th}, obtained by extrapolation to zero of the quantum yield for homolysis) is a good measure of the homolysis bond energy.[36-43] Values of the photohomolysis threshold energy for Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$ and Co(dmgH)$_2$(OH$_2$)CH$_3$ are $E_{\mathrm{th}} = 48 \pm 2$ and 49 ± 2 kcal mol^{-1},[44] respectively. For the reaction {Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$ + Co$^{\mathrm{II}}$(dmgH)$_2$} we estimate $\Delta G^\circ_{ab} \simeq -0.6$ kcal mol^{-1}. If we put eq 1 in the form

$$\Delta G^\circ_{ab} = (\Delta H_{a,\mathrm{x}} - \Delta H_{b,\mathrm{x}}) - T\Delta S^\circ_{ab}(\mathrm{OS}) + \delta\Delta G_{ab} \quad (2)$$

then the experimental values of ΔG°_{ab}, $\Delta H_{j,\mathrm{CH}_3} = E_{\mathrm{th},j}$, and $S_{\mathrm{rc},j}$ lead to $\delta\Delta G_{ab} \simeq -3.5$ kcal mol^{-1} for this reaction. As noted above, there is reason to believe that the terms contributing to $\delta\Delta G_{ab}$ are similar for the B$_{12}$ and dimethylglyoxime complexes; larger contributions, similar to one another, are expected for the macrocycle complexes. Thus, for the MeB$_{12}$/Co$^{\mathrm{II}}$(dmgH)$_2$ reaction we have set $\delta\Delta G_{ab} \simeq 0$ and for the MeB$_{12}$/(Co$^{\mathrm{II}}$[macrocycle]) reactions we have set $\delta\Delta G_{ab} \simeq +3.5$ kcal mol^{-1} in order to obtain the relative bond energies in Table III.

We have noted below that there does seem to be some small but systematic inconsistency in our kinetic and/or equilibrium data for reactions of dimethylglyoxime complexes. Thus, there is likely to be some small (≤ 2 kcal mol^{-1}) error involved in our determination of bond energies referenced to the Co(dmgH)$_2$/Co(Me[14]tetraeneN$_4$) system. We have nevertheless used this difference in $\delta\Delta G_{ab}$ in order to have an experimental means for estimating each component of eq 1. Since the error introduced appears to be small, systematic, and consistent, it does not affect major features of the bond-energy differences.

Substitution of the homolysis threshold energies for $\Delta H_{j,\mathrm{CH}_3}$ for Co(dmgH)$_2$(OH$_2$)CH$_3$ and Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)CH$_3$$^{2+}$ results in the set of Co–CH$_3$ bond energies in Table III. The temperature dependence of the MeB$_{12}$/Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$ reaction gives $\Delta H^\circ_{ab} = 1.6 \pm 0.5$ kcal mol^{-1}, consistent with the inferred similarities in Co–CH$_3$ bond energies for the corrin and Me$_4$[14]tetraeneN$_4$ complexes. The nearly 15 kcal mol^{-1} range of Co–CH$_3$ bond energies is discussed further below.

B. Intrinsic Kinetic Barriers. At the present time there is relatively little in the way of precedent to utilize in the separation of the contributions of the free-energy and intrinsic contributions to the rates of inner-sphere electron-transfer reactions. In the limit of weak interaction between donor and acceptor, one would expect the dependence of rate on driving force to be similar in inner-sphere and outer-sphere reactions.[39-41] Halide-bridged electron-transfer reactions have been found to exhibit approximately the expected dependence on ΔG°_{ab}.[9d,e] In reactions of closely related molecules, such as those employed in this study, it is reasonable to assume that k_{ab} and k_{ba} have similar dependence on ΔG°_{ab}. For ΔG°_{ab} small, k_{ab} will be proportional to $K_{ab}^{1/2}$ [45-47] Under such cir-

---

(36) (a) Endicott, J. F. In "Concepts in Inorganic Photochemistry", Adamson, A. W., Fleischauer, P. W., Eds.; Wiley: New York, 1975; Chapter 3, p 83. (b) Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630. (c) Ferraudi, G. J.; Endicott, J. F.; Barber, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 640. (d) Endicott, J. F.; Ferraudi, G. J. *Inorg. Chem.* **1975**, *14*, 3133. (e) Endicott, J. F. *Ibid.* **1977**, *16*, 494.

(37) Values of *E*th are in reasonable agreement with thermochemical estimates of the homolysis bond energy for Co–Cl homolysis (ref 36c) and supplementary material. Since alkyl radical cob(II)alamin cage recombination reactions occur with $k_r \sim 2 \times 10^9$ s^{-1},[38] the recombination apparently has an activation barrier of $\Delta G^\ddagger_r \sim 5$ kcal mol^{-1} (from $k_r = (k_BT/h)\exp[-[\Delta G^\ddagger/RT]]$). Much of this barrier is probably associated with the change in geometry from the planar carbon in the alkyl radical to a nearly tetrahedral geometry around carbon in the cobalt–alkyl complex. Classically, the resulting reorganizational energy would be largely enthalpic.[39,40] However, for the vibrational quanta $>kT$, the barrier is only weakly temperature dependent.[41] The threshold energies should be corrected for $\Delta H^\ddagger_r$ (the enthalpic component of $\Delta G^\ddagger_r$) to obtain a bond dissociation energy.[42] Since $\nu_{\mathrm{CH}_3} \sim 2kT$,[43] $\Delta H^\ddagger_r$ must be small. We have set $\Delta H^\ddagger_r \sim 2$ kcal mol^{-1}.

(38) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000.

(39) (a) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (b) *Prog. Inorg. Chem.* **1967**, *8*, 391. (c) *Electrochim. Acta* **1968**, *13*, 1005.

(40) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) *J. Phys. Chem.* **1963**, *67*, 853. (c) *Discuss. Faraday Soc.* **1960**, *29*, 21.

(41) (a) Jortner, J.; Ulstrup, J. *J. Am. Chem. Soc.* **1979**, *101*, 3744. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148.

(42) For example, see: Brenton. A. G.; Morgan, R. P.; Beynon, J. H. *Annu. Rev. Phys. Chem.* **1979**, *30*, 51.

(43) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(44) Ciskowski, J. C.; Endicott, J. F., work in progress.

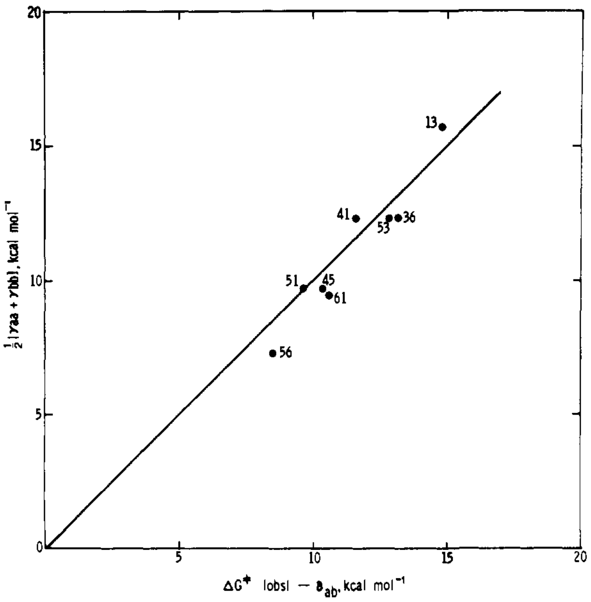


Figure 2. Graphical analysis demonstrating the self-consistency of a linear combination of intrinsic components (γ_{ii}) to the activation free energy in methyl-mediated electron-transfer reactions (eq 3). The line is drawn through zero, with unit slope. Numbers designate combinations of equatorial ligands on the organocobalt and cobalt(II) complexes: N_4 = $Me_4[14]tetraeneN_4$ (1), $Me_6[14]4,11\text{-}dieneN_4$ (3), $[14]aneN_4$ (4), $Me_2pyo[14]trieneN_4$ (5), corrin (6; i.e., methylcobalamin or B_{12r}). δ_{ab} is a combination of work terms as discussed in the text.

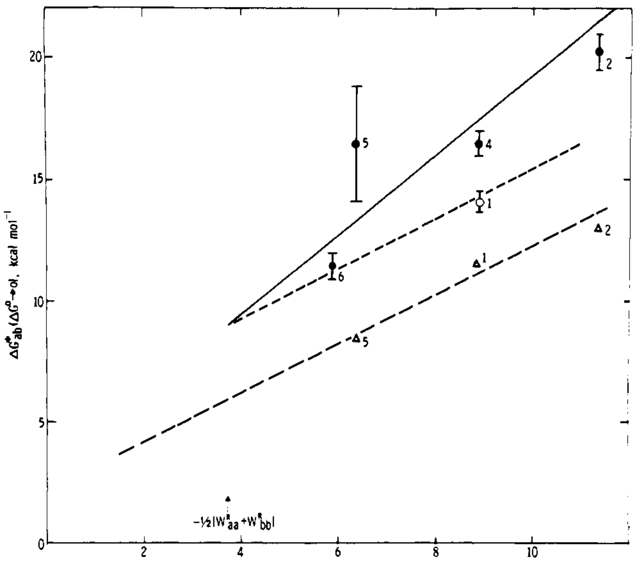


Figure 3. Demonstration of systematic errors in the linear analysis of intrinsic contributions to $\Delta G^{\ddagger}_{ab}$ for reactions of $Co(dmgH)_2(OH_2)CH_3^{2+}$ and $Co^{II}(dmgH)_2$ complexes (open and closed circles). Kinetic data from Tables I and III. Closed circles for $Co(N_4)OH_2CH_3/Co^{II}$ $(dmgH)_2$ reactions; open circle is the geometric mean of the forward and reverse rate constants for $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$ + $Co^{II}(dmgH)_2$. Solid line has slope of 0.82; dashed lines are drawn with a theoretical slope of 0.50 in accord with eq 3. $\Delta G^{\ddagger}_{ab}$ has been corrected for variations in ΔG°_{ab} using values of K_{ab} from Table II and procedures described in the text. The point for the $MeB_{12}/Co^{II}(dmgH)_2$ reaction has been "corrected" for the likely difference in work terms compared to the other reactions (see text). The mean value of the work term for the cross reactions is estimated at 3.75 kcal mol^{-1} and indicated on the figure. Numbering of the equatorial ligands of the counterreagent follows the same convention as in Figure 2. For comparison, similar data for reactions of MeB_{12} and B_{12r} are included (triangles).

cumstances we may "correct" for the free-energy dependence of the inner-sphere electron-transfer rate either by considering the products, $k_{ab}k_{ba} = (k^{\circ}_{ab})^2$, or the differences $\Delta G^{\ddagger}_{ab} - 0.5\Delta G^{\circ}_{ab}$. In the present study, these approaches give identical results. Either approach results in a set of ΔG°-independent activation parameters: $\Delta G^{\ddagger}_{ab}(\mathrm{IS};\ \Delta G^{\circ}_{ab}\to 0)$. In principle these parameters could depend in a very complex manner on the contributions of the individual reactants. Since the individual reactants contribute linearly to the similar ΔG°-independent activation parameters for outer-sphere reactions, a simple means for examining the dependence of k_{ab} on the reorganizational contributions of individual reactants is to compare (1) $\Delta G^{\ddagger}_{ab}(\mathrm{IS};\ \Delta G^{\circ}_{ab}\to 0)$ to $\Delta G^{\ddagger}_{ab}(\mathrm{OS};\ \Delta G^{\circ}_{ab}\to 0)$; (2) $\Delta G^{\ddagger}_{aj}(\mathrm{IS};\ \Delta G^{\circ}_{aj}\to 0)$ to the outer-sphere self-exchange activation parameters $\Delta G^{\ddagger}_{jj}(\mathrm{OS})$ for different reactants *j*. The last comparison has been discussed elsewhere.[9d] Either experimental comparison indicates that $\Delta G^{\ddagger}_{ab}(\mathrm{IS/CH_3};\ \Delta G^{\circ}_{ab}\to 0) \simeq {}^1/_2\Delta G^{\ddagger}_{ab}(\mathrm{OS})$. We conclude that $\Delta G^{\ddagger}_{ab}(\mathrm{IS};\ \Delta G^{\circ}_{ab}\to 0)$ may be represented by the average of the separate contributions of some intrinsic parameters,[48] γ_{ii}, for the respective reactant self-exchange reactions. Thus

$$\Delta G^{\ddagger}_{ab}(\mathrm{IS};\ \Delta G^{\circ}_{ab}\to 0) \simeq \omega^{R}_{ab}(\mathrm{IS}) + (\gamma_{aa}+\gamma_{bb})/2 \quad (3)$$

analogous to the behavior found in outer-sphere electron-transfer reactions. Similar relationships have been found previously for the halide-bridged electron-transfer reactions.[9d,e,49] The work term appropriate to inner-sphere reactions, $\omega^{R}_{ab}(\mathrm{IS})$, has been discussed previously.[9d]

In order to estimate the intrinsic parameters for methyl-bridged electron-transfer reactions we have (1) set $\omega^{R}_{ab} = {}^1/_2(\omega_{aa} + \omega_{bb})$ in eq 3 and used ω_{aa} = 2 kcal mol^{-1} and 5.5 mol^{-1}, respectively, for self-exchange reactions of the neutral (β_{12}) complexes and synthetic macrocycle reactions (choice of values based on arguments similar to those used above for $\delta\Delta G_{ab}$); (2) computed values of γ_{jj} by solving the resulting algebraic equations for all the independent combinations of reactions for which we have obtained the primary kinetic and thermodynamic information; (3) averaged the individual values of γ_{jj}, obtained from different combinations of reactions. The values of $\overline{\Delta G_{jj}}$ in Table III have been computed from $\overline{\Delta G_{jj}} = \gamma_{jj} + \omega_{jj}$. When this procedure was followed for all the pertinent data in Table I, we obtained a reasonable set of intrinsic parameters, but comparison of calculated and observed values of $\Delta G^{\ddagger}_{ab}$, using these parameters, revealed a systematic 1–3 kcal mol^{-1} error in all the data involving dimethylglyoxime complexes. As a consequence all the reactions of dmgH complexes have been omitted in computation of the self-exchange (or intrinsic) parameters in Table III. The self-consistency of this set of parameters is demonstrated by Figures 2 and 3. Clearly, the simple linear partitioning of eq 3 represents very well (to within $\sim\pm 1$ kcal mol^{-1}) the observed reactivity patterns in the methyl-bridged electron-transfer reactions. Cross terms, or other nonlinear terms, do not seem important for the free-energy range investigated.

Our data for reactions of dimethylglyoxime complexes are also presented in Figure 3. The error flags in Figure 3 are based on the error estimates in Tables I and II. There is considerable uncertainty with regard to the $Co(Me_2pyo[14]trienN_4)(OH_2)CH_3^{2+}/Co^{II}(dmgH)_2$ reaction, with most of the uncertainty arising from errors in the calculated equilibrium constant. The data points based on $[Co(N_4)(OH_2)CH_3^{2+} + Co^{II}(dmgH)_2]$ exhibit small systematic deviations from expected behavior. Consistent with this analysis, the point based on the geometric mean of rate

---

(45) Generalized treatments[46,47] of group transfer reactions have shown that $\Delta G^{\ddagger}_{ab} = \alpha\Delta G^{\circ}_{ab} + \Delta G^{\ddagger}_{i,ab}M(\alpha)$, where α is the Brønsted slope, $\Delta G^{\ddagger}_{i,ab}$ is the intrinsic component of reactivity ($\Delta G^{\ddagger}_{ab}$ evaluated at $\Delta G^{\circ}_{ab} = 0$), and $M(\alpha)$ is a function of α. The simple function $\alpha^{-1} = (1 + \exp[\Delta G^{\circ}_{ab}/\Delta G^{\ddagger}_{i,ab}])$ proposed in ref **46** and 47 reduces to the well-known equations of Marcus[40] for $[\Delta G^{\circ}_{ab}/\Delta G^{\ddagger}_{i,ab}] \ll 1$. These treatments[46,47] are very general and do not assume that the potential-energy surfaces are harmonic.

(46) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(47) Levine, R. D. *J. Phys. Chem.* **1979**, *83*, 159.

(48) For convenience we represent the intrinsic component of $\Delta G^{\ddagger}_{ab}(\mathrm{IS})$ by γ_{ab}. As is developed in the ensuing discussion, the intrinsic parameters so evolved are not strictly speaking "reorganizational" parameters in the same sense as for outer-sphere reactions. As usual,[9d,39,40] $\Delta G^{\ddagger}_{aa}(\mathrm{IS}) = \omega^{R}_{aa} + \gamma_{aa}$; ω^{R}_{aa} is a work term.

(49) Patel, R. C.; Endicott, J. F. *J. Chem. Soc.* **1968**, *90*, 6364.

constants for the $Co(dmgH)_2(OH_2)CH_3/Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ and $Co(Me[14]tetraeneN_4)(OH_2)CH_3^{2+}/Co^{II}(dmgH)_2$ reactions appears to be somewhat different from the other data points. These observed discrepancies could indicate some nonlinear contributions to eq 3 for the $Co(dmgH)_2$ reactions; however, we think it more likely that the complications arise from some small differences in ligation of the predominant solution species for $Co^{II}(dmgH)_2$ and $Co^{III}(dmgH)_2$ (e.g., oxime protonation or partial dissociation of the ligand from the labile cobalt(II) complex). Useful comparisons involving the electron-transfer reactions of the $Co(dmgH)_2$ systems must apparantly be deferred until the systems are more rigorously characterized.

A significant part of the variations in the values of $\Delta G^{\ddagger}_{jj}$ in Table III arises from differences in work terms, ω^{R}_{aa}. The work terms associated with the MeB_{12}/B_{12r} and the $Co(dmgH)_2(OH_2)CH_3/Co^{II}(dmgH)_2$ self-exchange reactions are expected to be 2–5 kcal mol^{-1} smaller than the work terms associated with the $Co(N_4)(OH_2)CH_3^{2+}/Co(N_4)(OH_2)_2^{2+}$ self-exchange reactions (owing to the differences in Coulombic repulsion and Co^{II}–OH_2 lability). Consequently, the intrinsic components of reactivity (γ_{jj}) are about the same for the dimethylglyoxine, $Me_4[14]tetraeneN_4$, and $[14]aneN_4$ complexes. Slightly smaller intrinsic factors are found for the corrinoid and $Me_2pyo[14]trieneN_4$ complexes, while the $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}/Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)_2^{2+}$ self-exchange reaction has by far the largest intrinsic activation barrier. For these complexes, variations in $\Delta G^{\ddagger}_{jj}$ cannot be rationalized in terms of Co–OH_2 bond-length changes between precursor and successor complexes. Owing to the large trans influence of CH_3 the H_2O–(Co–CH_3) bond is relatively long, more "cobalt(II)-like" than the H_2O–(Co^{III}–OH_2) or H_2O–(Co^{III}–Cl^-) bonds.[30,31] The weaker trans Co–OH_2 bonds in the methyl complexes would only lead to smaller reorganizational barriers. Furthermore, the largest barrier is found for the $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$ complex, a complex whose ease of dehydration[20] is suggestive of a particularly weak Co–OH_2 bond (see also Figure 1). It is important to note that most of the activation energy difference between Cl- and CH_3-bridged electron-transfer reactions in these systems is enthalpic. This suggests that the small rate constants for the methyl-bridged reactions cannot be entirely attributed to steric or overlap factors.

The magnitude of the activation barrier in an inner-sphere electron-transfer reaction depends on the nature of the unperturbed reactant and product potential energy surfaces and the strength of the donor–acceptor interactions mediated by the bridging ligand. When the bridging ligand is transferred from one metal to another, the pertinent potential-energy surfaces must involve a bond-breaking coordinate.

We have previously proposed[15] that a useful description for inner-sphere electron-transfer reactions involves the following "states" across the reaction coordinate: (1) a "precursor" complex involving the assembled reactants with the cobalt(II) partner coordinatively unsaturated, but involving no donor–acceptor interaction; (2) a "transition" state involving a three-center-three-electron bond {Co^{II}–(·X)–Co^{II}}; (3) a "successor" complex involving the assembled products with the cobalt(II) partner coordinatively unsaturated; (4) a "dissociated" state corresponding to the two cobalt(II) complexes and the radical ·X trapped in a solvent cage. It is then convenient to consider an "unperturbed" potential-energy surface (i.e., a surface on which the donor–acceptor interaction is negligible) as described by Morse potential with $\Delta H_{j,CH_3}$ as the bond dissociation energy. Donor–acceptor interaction in the transition state then results in an activation barrier which decreases as the transition-state binding energy increases. In such a picture, the relatively large activation barriers for methyl-bridged electron-transfer reactions are attributed to the relatively weak binding which would result from the much smaller methyl radical than halogen atom electron affinity.

Any attempt to apply the transition-state binding model to the variations in reorganizational barriers found for methyl-bridged electron-transfer reactions has to be tempered by the observation that there is no simple correlation between $\Delta G^{\ddagger}_{jj}$ and $\Delta H_{j,CH_3}$. However, a very simple correlation is not expected. Within the context of the transition-state binding model, the critical parameters determining $\Delta G^{\ddagger}_{jj}$ are the transition-state bond energy ($BE^{\ddagger}$), $\Delta H_{j,CH_3}$, and the critical distance of separation in the transition state (r_e). Obviously, $BE^{\ddagger}$ and r_e are interrelated. The cobalt(II) complexes employed in this study exhibit a very large range of Co^{II}–OH_2 bond lengths, varying at least from 2.29 Å for $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ to 2.48 Å for $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)_2^{2+}$.[9,23] Factors which weaken the Co^{II}–OH_2 bond might also be expected to weaken the Co^{II}–(·X)–Co^{II} bond and this is substantially the pattern of the larger variations in values of $\Delta G^{\ddagger}_{jj}$ in Table III. A more careful analysis of the trends in $\Delta G^{\ddagger}_{jj}$ must involve corrections for variations in $\Delta H_{j,CH_3}$. This may in principle be done in terms of a Morse potential energy function. For $\Delta G_{jj,int}$, the intersection energy of the unperturbed reactant and product potential-energy surfaces, and δ_{jj}, the splitting energy resulting from the methyl-mediated bonding interactions in the transition state, $\Delta G_{jj,int} = \gamma_{jj} + \delta_{jj}$. Since $\Delta G_{jj,int} = \Delta H_{j,CH_3} - [1 - e^{-re/2a}]^2$, and $a \simeq (1/\pi\nu_e)(\Delta H_{j,CH_3}/2M)^{1/2}$ (r is the distance along the critical configuration coordinate, ν_e is the vibrational mode associated with this coordinate, M is the reduced mass, and the potential-energy minima occur at $r = 0$ and $r = r_e$)

$$\nu_e r_e \simeq (2/\pi)(\Delta H_{j,CH_3}/2M)^{1/2} \ln \left[1 - \left(\frac{\gamma_{jj} + \delta_{jj}}{\Delta H_{j,CH_3}} \right)^{1/2} \right]$$

For $\delta_{jj} = 0$ or 5 kcal/mol^{-1}, data in Table III indicate that $\nu_e r_e = (1.09 \pm 0.09) \times 10^5$ or $(1.57 \pm 0.15) \times 10^5$ cm s^{-1}, respectively, for the methylcobalt corrin, $Me_2pyo[14]trieneN_4$, $Me_4[14]tetraeneN_4$, and $[14]aneN_4$ complexes. The very similar values of $\nu_e r_e$ suggest similar values of ν_e and r_e for methyl-bridged transition states of these four complexes. Since the stereochemistry of the axial coordination site is similar, it appears that the intrinsic barriers for methyl-mediated self-exchange electron transfer in these four systems depend only on the Co–CH_3 bond dissociation energy and a simple geometrical parameter (r_e). Physically plausible values of 250 $cm^{-1} \le \nu_e \le 650$ cm^{-1} and 0.8 Å $\le r_e \le$ 2 Å fit the estimated range of values for $\nu_e r_e$. If r_e is interpreted as the distance the carbon atom moves across the reaction coordinate, the hydrogen and cobalt atoms being considered fixed, then $r_e \sim 1.36$ Å (based on parameteres for methane) and 264 $cm^{-1} \le \nu_e \le 378$ cm^{-1}.

The values of $\nu_e r_e$ obtained for the $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}/Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)_2^{2+}$ self-exchange reaction run between 1.5×10^5 and 2.45×10^5 cm s^{-1} for δ_{jj} = 0 and 5 kcal mol^{-1}, respectively. These values are ~80% larger than those obtained for the less sterically encumbered complexes. The only physically plausible inference is that the presence of geminal methyl groups in the $Me_6[14]4,11\text{-}dieneN_4$ complexes results in a significant increase in r_e.

Naturally, we do not discount the possibility that factors other than Co–CH_3 bond energy and the distance of separation of donor and acceptor centers contribute to the intrinsic barriers to methyl-mediated inner-sphere electron transfer. At present it appears that these are the major factors. The observation of similar rate constants for CH_3- and CD_3-mediated electron transfer is certainly consistent with this picture. These latter observations demonstrate that the Co–C and C–H motions are not coupled across the reaction coordinate.

C. Implications. 1. Bond Energies. The sequence of bond energies in Table III is quite interesting. That the complexes with the greatest unsaturation in the equatorial ligand should contain the strongest Co–CH_3 bond is very much in accord with theoretical and quasi-theoretical arguments presented some time ago.[50,51] The "destabilization" attributable to ligand saturation does appear to be a bit smaller than inferred in this earlier work. It is interesting, and very likely pertinent to the problem of stabilization of the

---

(50) (a) Green, M.; Smith, J.; Tasker, P. A. *Discuss. Faraday Soc.* **1969**, *47*, 172. (b) Engelhardt, L. N.; Green, M. *J. Chem. Soc., Dalton Trans.* **1972**, 724.

(51) Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. *Adv. Chem. Ser.* **1970**, *No. 100*.

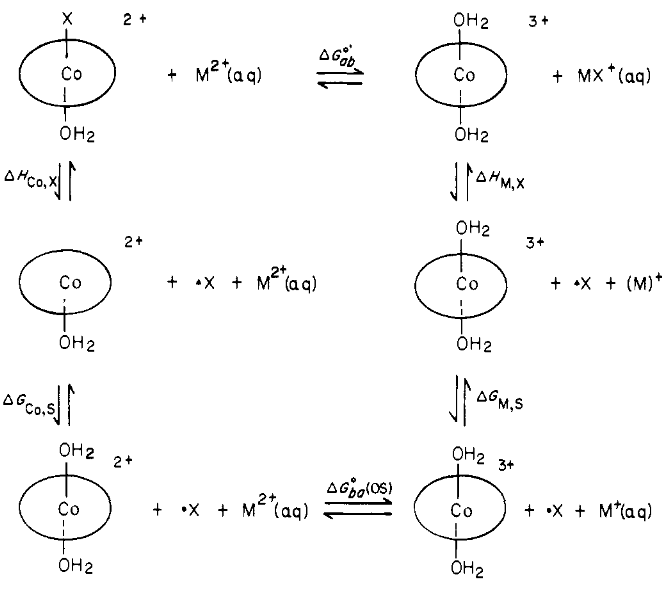
$Co-CH_3$ bond by equatorial ligand unsaturation, that all three tetraimine complexes (corrin, $(dmgH)_2$, and $Me_4[14]tetraeneN_4$) have the same bond energy, while for the other complexes the $Co-CH_3$ bond strength is appreciably smaller, apparently due in part to the presence of amine donor atoms in the equatorial ligand.

The additional instability of the $Co-CH_3$ bond in $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$ is apparently due to nonbonded steric interactions with the geminal methyl groups of the equatorial ligand. From the comparison with the $[14]aneN_4$ and $Me_2[14]4,11\text{-}dieneN_4$ complexes, we would estimate that the geminal methyl groups in $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$ destabilize the $Co-CH_3$ bond by 9 kcal mol^{-1}. Since this complex is also the most easily dehydrated[20] of the aquomethyl complexes we have used, we infer a general weakening of the $H_2O-Co-CH_3$ axial bonding interaction. This is consistent with a component of the axial bonding interaction being attributable to a three-center-four-electron bonding interaction.[19b]

The insensitivity of the $Co-CH_3$ bond energy to replacement of benzimidazole by water in methylcobalamin raises the possibility that in the B_{12} metalloenzymes the role of the axial base is related to binding of the cobalamin complex to the apoenzyme. If cobalt–carbon homolysis is the key mechanistic step in the function of coenzyme B_{12}, then binding of the cobalamin complex to the apoenzyme could sufficiently weaken the cobalt–benzimidazole and/or the cobalt–carbon bond to make thermal Co–C homolysis kinetically feasible. Various mechanisms for appropriate steric interactions have been proposed and discussed elsewhere.[52-54] Any mechanism which weakens the total axial interaction, either through corrin ring buckling[53] or through axial ligand interaction wiith the apoenzyme, could permit a molecular level of control over the homolysis process. We have found[44] a 5 kcal mol^{-1} smaller homolysis threshold energy for $Co(Me_4[14]tetraeneN_4)(OH_2)C_2H_5^{2+}$ than for $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$, in accord with the view[54] that alkyl ligand bulk tends to destabilize the Co–C bond. Additional contributions result from variations in product radical stabilities.[55] The evidence presently at hand indicates that the cobalt–alkyl bond is far more susceptible to stereochemical perturbations than are more classical Co(III)–X (e.g., $Co^{III}-Cl^-$) bonds.[9e,44,56]

2. Intrinsic Barriers to Methyl Transfer. In view of the inferred stereochemical effect on the $Co-CH_3$ bond strength, the observation that the $Co-CH_3$ bond strength is the same for the base-on (Co–benzimidazole) and base-off ($Co-OH_2$) forms of methylcobalamin might be regarded as somewhat surprising. It may be even more surprising that displacement of the axial base in methylcobalamin has almost no effect on the intrinsic barrier to methyl-bridged electron-transfer reactions. However, this last observation is consistent with arguments presented above which show that the predominant contributions to the intrinsic kinetic barrier to methyl-bridged electron-transfer reactions arises from the $Co-CH_3\cdots Co^{II}$ interaction, not from reorganizational contributions of the trans axial ligands.

Scheme II



Information obtained in this study does bear on earlier studies of methyl-transfer reactions of organocobalt complexes. Thus, for example, rate constants of 3.6×10^2, 14.5, and ~ 4 M^{-1} s^{-1} have been reported[12] for the methylations of Cr^{2+} by MeB_{12}, $Co(dmgH)_2(OH_2)CH_3$, and $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$, respectively. Based on eq 2, parameters from Table III, and $\Delta G^{\ddagger}_{ab} \simeq (\Delta G^{\ddagger}_{aa}/2) + (\Delta G^{\ddagger}_{bb}/2) + (\Delta G^{\circ}_{ab}/2)$, we estimate that $^1/_2[-\Delta H_{Cr,CH_3} + \Delta G^{\ddagger}_{Cr,Cr}] \simeq -6$ kcal mol^{-1} for these reactions.[57] Thus, the $Cr-CH_3$ bond energy appears to be only $\sim$12 kcal mol^{-1} larger than the intrinsic activation free energy associated with the $CrCH_3^{2+}/Cr^{2+}$ couple. This is much smaller than the value found for cobalt complexes other than $Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$, and suggests either that $\Delta G^{\ddagger}_{Cr,Cr}$ is very large or $\Delta H_{Cr,CH_3}$ is small.

With some reservations in regard to possible contributions of ΔG°_{ab}, the previously observed decreases (with steric bulk of the alkyl ligand) in the rate of alkyl transfer between cobalt complexes[16,17] can readily be attributed to increases in r_e (the effective separation of metal centers).

3. Electrophilic Methyl Transfer. The methyl-mediated electron-transfer reactions considered in this study will differ from electrophilic methyl transfer reactions at least in regard to the functional form of $\Delta G^{\circ\prime}_{ab}$ and the value of $G^{\ddagger\prime}_{jj}$. From Scheme II we see that

$$\Delta G'_{ab} = (\Delta H_{Co,X} - \Delta H_{M,X}) + \Delta G^{\circ}_{ba}(OS) + (\Delta G_{Co,S} - \Delta G_{M,S}) \quad (4)$$

It is to be noted that (1) and (4) have many similar features: the driving force for both the "electrophilic" and the "reductive" methyl-transfer reactions depends strongly on the difference in reactant and product bond energies, and both kinds of reaction have significant redox components. It is interesting that both classes of reaction have been demonstrated for halide and alkyl bridging groups. The intrinsic barriers to the "electrophilic" methyl transfer reactions may be even larger than those associated with the methyl-bridged electron-transfer reactions owing to contributions of the $H_2O-(CoCH_3) \rightarrow H_2O-Co^{III}$ bond-length changes. Since the axial bonding interactions are relatively strong in normal cobalt(III) complexes, changes in the trans axial ligand should significantly affect the reorganizational barrier for "electrophilic" methyl transfer.

Supplementary Material Available: Estimate of E_{th} from thermochemical data and tables of rate constants and equilibrium constants (9 pages). Ordering information is given on any current masthead page.

---

(52) Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2.

(53) Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601.

(54) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pakor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

(55) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124.

(56) Cobalt(III)–chloride, –water, and/or –ammine bond lengths vary less than 0.02 Å for several different equatorial macrocyclic ligands (Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J.; Schmonsees, W.; Balakrishnan, K. P., submitted for publication in *J. Am. Chem. Soc.*). The variation of the axial bond lengths among $Co(N_4)(OH_2)CH_3^{2+}$ complexes may be of the order of 0.05 Å (ref 31 and Heeg, M. J.; Endicott, J. F.; Glick, M. D., work in progress.) However, the variations in bond energy need not be manifested only in variations in ground-state bond lengths: the very large variations in axial bond lengths of $Co(N_4)(OH_2)_2^{2+}$ complexes[23] are suggestive of a range of stabilities for the $Co(N_4)OH_2^{2+}$ homolysis products.

(57) The individual values are −6.6, −5.2, and −6.7 kcal mol^{-1} for the respective $Co-CH_3$ complexes. We have allowed for the estimated 3.5 kcal mol^{-1} difference in work terms between the neutral and cationic complexes as noted above. We have also used $S_{rc} = 48$ eu for $Cr^{3+,2+}$.