bond dissociation enthalpy (BDE) estimate of 37 ± 3 kcal/mol. This is the highest[3,37] Co–C BDE yet measured,[38] slightly above Toscano's 33 ± 2 kcal/mol BDE for Me–Co(DH)$_2$py in bromoform.[39]

The activation parameters allow computation of a MeCbl Co–CH_3 homolysis rate constant at −30 °C of $k_{h,on} = 10^{-19\pm4}$ s^{-1}. This is the highest temperature at which the rate for (MeCbl)$^{\bullet-}$ homolysis is sufficiently slow[40] to be measurable electrochemically (rate constant = 1200 s^{-1} at −30 °C in DMF/1-propanol).[16] Comparing these two rate constants quantifies the *$10^{22\pm4}$ homolysis rate enhancement at −30 °C* due to the extra, Co−−CH_3 antibonding electron in (MeCbl)$^{\bullet-}$.

Informative rate comparisons at higher temperatures can be made if one compares MeCbl to methylcobinamide,[9] MeCbi$^+$ (the benzimidazole-base-free form of MeCbl; the lack of the axial base in MeCbi$^+$/MeCbi$^\bullet$ slows the Co–C cleavage rates enough to make them measurable electrochemically at 25 °C). Rigorously, the MeCbi$^+$/MeCbi$^\bullet$ electrochemical data[16] serve as a *lower limit*[40] to the rates for MeCbl$^{\bullet-}$ Co–CH_3 cleavage at other temperatures. That is, the rate enhancements that follow are *lower limits* to the true values. (If desired, the Co–C cleavage rates from MeCbi$^\bullet$ and MeCbl$^{\bullet-}$ can be taken as equivalent[40] within the estimated $\pm10^{2-3}$ error bars, and given the large rate enhancements observed.)

The electrochemically derived,[16] temperature-dependent MeCbi$^\bullet$ Co–CH_3 homolysis rates, k_h,[41] provide the activation parameters $\Delta H^\ddagger = 19$ (±1) kcal/mol and $\Delta S^\ddagger = 21$ (±3) eu. Hence at 25 °C the MeCbi$^\bullet$ k_h is 4400 s^{-1}, which, compared to our MeCbl $k_{h,on} = 10^{-12\pm3}$ s^{-1}, demonstrates a *rate enhancement of $>10^{15\pm3}$ at 25 °C*. The rate enhancement is still $>10^{13}$ or $>10^{11}$ at even 90 or 135 °C, respectively.

Comparing activation parameters for reduced $(\sigma)^2(\sigma^*)^1$ MeCbi$^\bullet$ and $(\sigma)^2$ MeCbl suggests that *an antibonding electron lowers the Co–C bond strength by more than half* (i.e., from 37 kcal mol^{-1} down to approximately[42-44] 12 kcal mol^{-1}). The effect of the M−−C antibonding electron—the first such measurement for any M–C/M–C$^{\bullet-}$ pair—is impressive.[42]

It is of interest to consider the possible biological relevance of this mechanism for greatly enhancing M–C cleavage. Extremely labile M–alkyls are hereby predicted for systems isoelectronic to d^7 Co(II)−−CH_3, notably any d^7 Ni(III)–alkyls related to cofactor F_{430}.[45] On the other hand, rather stable Co–methyl bonds (BDE = 37 kcal/mol) that *are not reducible by biological reductants*[46] are the apparent rule for d^6 Co–CH_3 corrinoids. This latter statement is supported by the work of Ragsdale and co-workers, who have recently tested for, but found no evidence of, reductive cleavage of a d^6 Co(III)–CH_3 bond in the corrinoid/4Fe-4S-containing protein which serves as the methyl carrier protein in the acetyl-CoA pathway of *Clostridium thermoaceticum*.[47] Perhaps it is the enormous stability difference between a d^7 Ni(III)–CH_3 and a d^6 Co(III)–CH_3 that Nature is exploiting.

Consistent with the above, the mechanism responsible for the observed enzymatic rate enhancement[1] of Co–C homolysis in AdoCbl probably does *not* involve (AdoCbl)$^{\bullet-}$.[6,46] Our reasoning behind this statement, and a parallel analysis of the rate enhancement following AdoCbl reduction, is presented elsewhere.[46]

Acknowledgment. We thank Prof. Stephen Ragsdale for a preprint,[47] Prof. Kenneth L. Brown for giving us his corrin purification procedures[22] prior to publication and for a gift of MeCbi$^+$, and Prof. Thomas W. Koenig at Oregon for helpful discussions. Financial support was provided by the NIH (Grant DK-26214).

Registry No. MeCbl, 13422-55-4; MeCbl$^{\bullet-}$, 67087-21-2; Co$^{II}B_{12r}$, 14463-33-3; TEMPO, 2564-83-2; TEMPO-Me, 34672-84-9.

(35) (a) An efficient cage ($F_c \simeq 1$) and BDE $\simeq \Delta H^\ddagger_{obsd}$(soln) − $F_c\Delta H^\ddagger_\eta$ are assumed.[2] (b) For this 0.96–1.5 cP viscosity[36] solvent (at 120–150 °C), the cage-escape diffusion barrier is approximated as $\Delta H^\ddagger_\eta$ (4.0 kcal mol^{-1}; calculated via the Frenkel form[35c] of Guzman's "Andrade" equation[2]). (c) Frenkel, J. *Nature (London)* **1930**, *125*, 581–582.

(36) Thomas, L. H.; Meatyard, R.; Smith, H.; Davis, G. H. *J. Chem. Eng. Data* **1979**, *24*, 161–164.

(37) The second highest Co–C BDE, that for AdoCbi$^+$,[3] is 34.5 ± 1.8 kcal mol^{-1}.

(38) (a) A previous estimate placed the MeCbl BDE at 46 ± 3 kcal mol^{-1}, based upon photohomolysis threshold energies and estimating $\Delta H^\ddagger_r$ as 2 kcal mol^{-1}. (b) Endicott, J. F.; Balakrishnan, K. P.; Wong, C.-L. *J. Am. Chem. Soc.* **1980**, *102*, 5519–5526.

(39) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166–168.

(40) (a) Axial-base-on alkylcobalamins undergo Co–C homolysis faster than the corresponding base-off alkylcobalamins or benzimidazole-base-free alkylcobinamides.[1,3,4,40b] For example, AdoCbl[4,5] homolyzes 10^2 times faster than[3] AdoCbi$^+$ at room temperature. Furthermore, MeCbl$^{\bullet-}$ homolyzes 440 times faster than MeCbi$^\bullet$ at −30 °C (1200 s^{-1} and 2.7 s^{-1}, respectively).[16] (b) Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 541–546.

(41) (a) The Co–CH_3 cleavage mechanism we expect for reduced alkylcorrins differs from that presented in the electrochemical literature[14-16] by incorporating *reversible* Co(II)−−CH_3 cleavage[41b] followed by $CH_3^\bullet$ trapping, Me[Co(II)corrin]$^{\bullet-}$ ⇌ Co(I)$^-$ + $CH_3^\bullet$, then $CH_3^\bullet$ + trap → CH_3–trap, k_{obsd} = $k_{h,apparent}$ = a composite (with the reverse of the first step probably favored by the preferred, base-off form[41c] of Co(I)). Fortunately, the solvent mixture DMF/1-propanol is apparently serving as a trap (a H$^\bullet$ source as previously noted),[16] thereby preventing Co(I) + Me$^\bullet$ recombination (and thus $k_{h,apparent} \approx k_{h,true} = k_h$ in DMF/1-propanol, but not in H_2O[14]). This mechanism, the evidence for it, and its implications will be discussed in a full paper.[8a] (b) The trapping of a R$^\bullet$ by a diamagnetic metal has precedent: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 314–315. Finke, R. G.; Keenan, S. R.; Watson, P. L. *Organometallics* **1989**, *8*, 263–277, especially p 269 and footnote 26. (c) Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 2652.

(42) Radical-cage effects,[2] although undoubtedly present in $k_{h,on}$ (F_c assumed $\simeq 1$)[35] and possibly $k_{h,apparent}$ (F_c assumed[43] $\simeq 1$, but arguably as small as $\simeq 0$),[41a,43] will not influence the conclusions in this paper (that are based on $>10^{15}$ rate differences) and are most likely negligible compared to the indicated $\pm10^{2-3}$ error bars.

(43) $\Delta H^\ddagger_h = 18.9$ kcal mol^{-1} for (MeCbi$^+$)$^{\bullet-}$ homolysis. Subtracting both 4.5 kcal mol^{-1} for the axial-base contribution[3,4] and $\Delta H^\ddagger_\eta$ (<2.3 kcal mol^{-1}; i.e., assuming $F_c \simeq 1$)[35] yields an *estimated* BDE for (MeCbl)$^{\bullet-}$ of 12 kcal mol^{-1}.

(44) Riddick, J. A.; Bunger, W. B. Organic Solvents. In *Techniques of Chemistry*, 3rd ed.; Weissberger, A., Ed.; Wiley: New York, 1970; Vol. 2.

(45) Leading references: (a) Andrews, R. K.; Blakeley, R. L.; Zerner, B. Nickel and Its Role in Biology. In *Metal Ions in Biological Systems*; Sigel, H., Sigel, A., Eds.; Marcel Dekker: New York, 1988; pp 243–256. (b) Pfaltz, A.; Jaun, B.; Fässler, A.; Eschenmoser, A.; Jaenchen, R.; Gilles, H. H.; Diekert, G.; Thauer, R. K. *Helv. Chim. Acta* **1982**, *65*, 828–865.

(46) Finke, R. G.; Martin, B. D. *J. Inorg. Biochem.*, in press.

(47) Harder, S. R.; Liu, W.-P.; Feinberg, B. A.; Ragsdale, S. W. *Biochemistry* **1989**, *28*, 9080–9087.

Long-Range Electron Transfer in Ruthenium-Modified Cytochrome *c*: Evaluation of Porphyrin–Ruthenium Electronic Couplings in the *Candida krusei* and Horse Heart Proteins

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Received October 2, 1989

Experiments in several laboratories have shown that electron transfer (ET) can take place at appreciable rates over long distances (>10 Å) in organic and inorganic molecules[1-6] and in

(1) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vols. A–D.

(2) Closs, G. L.; Miller, J. R. *Science (Washington, D.C.)* **1988**, *240*, 440–447.

(3) (a) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366–373. (b) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258–3269.

0002-7863/90/1512-2420$02.50/0

Table I. Rate Constants and Activation Parameters for Ru(His-33)-Zn-cyt *c* and Ru(His-39)-Zn-cyt *c* ET Reactions

	Ru(His-33)-Zn-cyt *c*[a]				Ru(His-39)-Zn-cyt *c*[c]		
reactn[b]	$-\Delta G°$, eV	k_{ET}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k_{ET}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$Ru_4(isn)(His)^{2+} \rightarrow ZnP^{+}(ET^b)$	0.66	2.0×10^5	<0.5	−35	6.5×10^5	−1.7	−39
$ZnP^* \rightarrow Ru_5(His)^{3+}$ (ET*)	0.70	7.7×10^5	1.7	−27	1.5×10^6	1.3	−27
$Ru_4(py)(His)^{2+} \rightarrow ZnP^{+}$ (ET^b)	0.74	4.2×10^5	<0.5	−34	1.5×10^6	−1.8	−37
$ZnP^* \rightarrow Ru_4(py)(His)^{3+}$ (ET*)	0.97	3.3×10^6	2.2	−22	8.9×10^6	0.2	−27
$Ru_5(His)^{2+} \rightarrow ZnP^{+}$ (ET^b)	1.01	2.2×10^6	−0.4	−31	5.7×10^6	−0.2	−29
$ZnP^* \rightarrow Ru_4(isn)(His)^{3+}$ (ET*)	1.05	2.9×10^6	<0.5	−30	1.0×10^7	0.2	−27

[a] From ref 21. [b] a = NH_3, [c] k_{ET} values are reported for 22 °C (μ 0.1 M sodium phosphate; pH 7.0); thermodynamic parameters were calculated from rate data obtained in the range 5–35 °C.

proteins.[6-15] In non-protein systems, the evidence suggests that ET rates depend upon the number of covalent bonds separating the donor and the acceptor, rather than upon their direct separation distance.[2,3] There is a bewildering array of potential ET pathways in proteins;[16-19] interestingly, the through-peptide routes (if there are any!) generally involve so many bonds that they cannot possibly account for the observed rates.[20,21] Pathways that include ionic contacts (e.g., hydrogen bonds) or small through-space jumps often can be found, and it has been postulated that such shortcuts greatly enhance the donor–acceptor electronic coupling.[16,22] In searching for good pathways through cytochrome *c*, we discovered a relatively short route from His-39 to the heme in the *Candida krusei* (*C.k.*) protein.[23] Along this route, the crucial shortcut is a hydrogen bond that bridges Gly-41 and the heme. Since experimental information relevant to protein pathway models is lacking, we have extracted donor–acceptor electronic coupling constants from an analysis of the driving-force dependence of ET rates in Ru(His-39)-modified *C.k.* zinc cytochrome *c*.

Ruthenium [$Ru(NH_3)_4L$(His-39), with L = NH_3, pyridine, isonicotinamide] derivatives of *C.k.* Zn-substituted cyt *c* [Ru-(His-39)-Zn-cyt *c*] were prepared by standard procedures.[9,23,24] Intramolecular ET can be initiated in these protein derivatives by photoexcitation of the Zn porphyrin (ZnP) to its strongly reducing triplet excited state.[21] In addition to its intrinsic radiative and nonradiative decay pathways, this triplet can decay by ET to a histidine-bound Ru(III)–ammine complex (ET*). The metastable product of the ET* reaction, Ru(II)–ZnP^+, relaxes via a thermal ET process (ET^b) to reform the ground-state complex. The kinetics of these ET reactions were measured with the three *C.k.* Ru(His-39)-Zn-cyt *c* derivatives by laser flash photolysis.[9] ET rates and activation parameters for both *C.k.* and horse heart proteins[21] are set out in Table I.

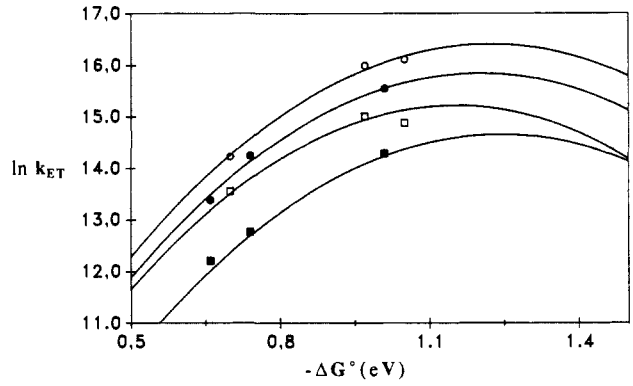

Figure 1. Plots of ln k_{ET} vs $-\Delta G°$ for the ruthenated Zn-cytochrome *c* ET reactions (see Table I): ET* (○) and ET^b (●), *C.k.* protein; ET* (□) and ET^b (■), horse heart protein. Solid lines represent best fits to eq 1. *C.k.* protein: ET*, λ = 1.22 eV, H_{AB} = 0.24 cm^{-1}; ET^b, λ = 1.20 eV, H_{AB} = 0.18 cm^{-1}. Horse heart protein: ET*, λ = 1.15 eV, H_{AB} = 0.13 cm^{-1}; ET^b, λ = 1.24 eV, H_{AB} = 0.10 cm^{-1}.

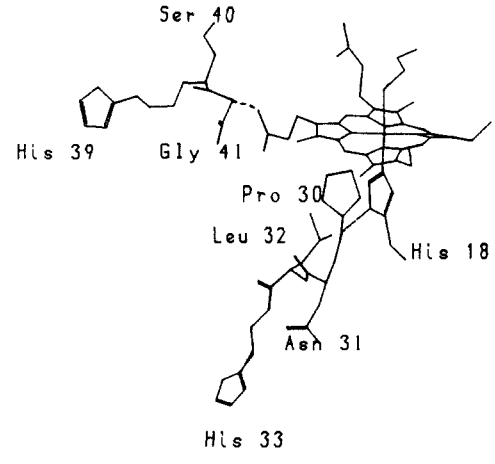

Figure 2. Possible pathways for electron transfer from histidines 33 and 39 to the heme in cytochrome *c*.[31] Edge–edge distances are as follows:[29] His-39 to heme, 13.0; His-33 to His-18, 11.7; His-33 to heme, 13.2 Å.

A nonadiabatic expression (eq 1) can be utilized to analyze long-range ET rates in derivatized proteins.[25] The term H_{AB} in

(4) Isied, S. S.; Vassilian, A.; Wishart, J. W.; Creutz, C.; Schwarz, H.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635–637.
(5) (a) Faraggi, M.; DeFelippis, M. R.; Klapper, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 5141–5145. (b) Schanze, K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180–1186.
(6) (a) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160–167. (b) Bowler, B. E.; Raphael, A. L.; Gray, H. B. *Prog. Inorg. Chem.*, in press.
(7) (a) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science (Washington, D.C.)* **1986**, *233*, 948–952. (b) Gray, H. B. *Chem. Soc. Rev.* **1986**, *15*, 17–30. (c) Axup, A. W.; Albin, M.; Mayo, S. L.; Crutchley, R. J.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 435–439. (d) Mikkelsen, K. V.; Ulstrup, J.; Zakaraya, M. G. *J. Am. Chem. Soc.* **1989**, *111*, 1315–1319. (e) Gray, H. B.; Malmström, B. G. *Biochemistry* **1989**, *28*, 7499–7505.
(8) (a) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249–1252. (b) Liang, N.; Mauk, A. G.; Pielak, G. J.; Johnson, J. A.; Smith, M.; Hoffman, B. M. *Science (Washington, D.C.)* **1988**, *240*, 311–313.
(9) Elias, H.; Chou, M. H.; Winkler, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 429–434.
(10) Conrad, D. W.; Scott, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 3461–3463.
(11) (a) Pan, L. P.; Durham, B.; Wolinska, J.; Millett, F. *Biochemistry* **1988**, *27*, 7180–7184. (b) Durham, B.; Pan, L. P.; Long, J. E.; Millett, F. *Biochemistry* **1989**, *28*, 8659–8665.
(12) Farver, O.; Pecht, I. *FEBS Lett.* **1989**, *244*, 379–382.
(13) (a) Jackman, M. P.; McGinnis, J.; Powls, R.; Salmon, G. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 5880–5887. (b) Osvath, P.; Salmon, G. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 7114–7118.
(14) Faraggi, M.; Klapper, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 5753–5756.
(15) (a) Hazzard, J. T.; McLendon, G.; Cusanovich, M. A.; Das, G.; Sherman, F.; Tollin, G. *Biochemistry* **1988**, *27*, 4445–4451. (b) Cusanovich, M. A.; Meyer, T. E.; Tollin, G. *Adv. Inorg. Biochem.* **1987**, *7*, 37–91.
(16) Beratan, D. N.; Onuchic, J. N. *Photosynth. Res.*, in press.
(17) Bowler, B. E.; Meade, T. J.; Mayo, S. L.; Richards, J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 8757–8759.
(18) Kuki, A.; Wolynes, P. G. *Science (Washington, D.C.)* **1987**, *236*, 1647–1652.
(19) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034–4040; *J. Chem. Soc., Faraday Trans.* **1983**, *79*, 1375–1388.
(20) Cowan, J. A.; Upmacis, R. K.; Beratan, D. N.; Onuchic, J. N.; Gray, H. B. *Ann. N.Y. Acad. Sci.* **1989**, *550*, 68–84.
(21) Meade, T. J.; Gray, H. B.; Winkler, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 4353–4356.
(22) (a) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.*, in press. (b) Beratan, D. N.; Onuchic, J. H.; Hopfield, J. J. *J. Chem. Phys.* **1987**, *86*, 4488–4498. (c) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1985**, *83*, 5325–5329.
(23) Selman, M. Ph.D. Thesis, California Institute of Technology, 1989.
(24) Yocom, K. M.; Shelton, J. B.; Shelton, J. R.; Schroeder, W. A.; Worosila, G.; Isied, S. S.; Bordignon, E.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 7052–7055.

$$k_{ET} = \frac{2\pi(H_{AB})^2}{\hbar(4\pi\lambda kT)^{1/2}} \exp\left[\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT}\right] \quad (1)$$

eq 1 is the electronic coupling matrix element for the ET reaction, and λ is the nuclear reorganization parameter. Analyses of the Ru(His-33)-Zn-cyt *c* and Ru(His-39)-Zn-cyt *c* data are shown in Figure 1. Only an increase in H_{AB}, as opposed to small variations in λ or ΔG°, can account for the fact that the Ru(His-39)-Zn-cyt *c* ET rates are 3 times the Ru(His-33)-Zn-cyt *c* rates over the 0.66–1.05 eV driving-force range.[26] The invariance of λ found in the ET* and ET^b reactions of the two proteins is consistent with theoretical considerations.[25,27,28]

The H_{AB} values for Ru(His-39)-Zn-cyt *c* (ET*, 0.24 cm^{-1}; ET^b, 0.18 cm^{-1}) are almost twice as large as those for Ru(His-33)-Zn-cyt *c* (ET*, 0.13 cm^{-1}; ET^b, 0.10 cm^{-1}).[21] It is likely that the electronic couplings in both proteins involve a superexchange mechanism in which electronic states of the intervening medium mix with localized donor states to produce a nonzero H_{AB}.[16,29,30] Calculations indicate that there are two relatively good pathways for ET from His-33 to the metalloporphyrin:[31] a 16-bond route to the Zn atom through His-18 that includes a 1.85-Å H bond between the Pro-30 carboxyl oxygen and the proton on the His-18 nitrogen and a 13-bond route ending with a 3.6-Å through-space contact between the δ-carbon of Pro-30 and a pyrrole carbon of the porphyrin. The shortest pathway from His-39 is a 13-bond route that includes a 2.4-Å H bond between the α-amino hydrogen atom of Gly-41 and the carboxyl oxygen of a propionate side chain on the porphyrin (Figure 2). Because a hydrogen bond is predicted[16] to be a better shortcut than a through-space jump, the 13-bond route from His-39 to the porphyrin should lead to stronger electronic coupling than the 13-bond pathway from His-33. The 16-bond bridge from His-33 to the Zn that includes an H bond may also provide better coupling than the 13-bond (Pro-30 through space to porphyrin) pathway. It should be only slightly less effective in coupling the ruthenium and porphyrin centers than the 13-bond pathway in Ru(His-39)-Zn-cyt *c*.[32]

Our work highlights the need for in-depth theoretical and experimental investigations of the possible role of hydrogen bonds in the pathways for long-range electron transfer through proteins. Systematic studies of electronic couplings in donor–(spacer)–acceptor molecules with variable H-bond connectors could be particularly valuable.

Acknowledgment. We thank David Beratan and Bruce Bowler for helpful discussions. M.J.T. acknowledges a postdoctoral fellowship from the National Institutes of Health. Research at the California Institute of Technology was supported by National Science Foundation Grant CHE88-22988. Research performed at Brookhaven National Laboratory was carried out under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

(25) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.
(26) The $Ru^{2+} \rightarrow Fe^{3+}$ ET rate in Ru_5(His-39)-Fe-cyt *c* (~170 s^{-1}; $-\Delta G^\circ$ = 0.17 eV; 22 °C)[23] also is substantially higher than that (~30 s^{-1}; $-\Delta G^\circ$ = 0.18 eV; 22 °C)[21] in Ru_5(His-33)-Fe-cyt *c*.
(27) (a) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 6858–6859. (b) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657–3668.
(28) Dielectric continuum models of solvent reorganization predict that the outer-sphere contribution to λ (λ_o) will increase with donor–acceptor separation.[25,27] Modeling the Ru-Zn-cyt *c* systems as single spheres suggests that λ_o for the Ru(His-33)-Zn-cyt *c* reactions should be nearly the same as that for the Ru(His-39)-Zn-cyt *c* reactions (0.58 and 0.59 eV, respectively). The cyt *c* molecule was taken as a 17-Å sphere and the Ru–ammine group as a 6-Å sphere. These two interpenetrating spheres were enclosed by a third sphere of radius 17.6 Å for Ru(His-33)-Zn-cyt *c* and 18.2 Å for Ru(His-39)-Zn-cyt *c*. The Zn and Ru redox centers were taken as 6.0 and 14.6 Å from the center of the sphere, respectively, and separated from one another by 18.6 Å in Ru(His-33)-Zn-cyt *c*. The corresponding distances for the Ru(His-39)-Zn-cyt *c* model were 6.3, 15.2, and 19.3 Å. The dielectric constant of the sphere was taken as 1.8; the solvent was assigned a static dielectric constant of 78.54 and an optical dielectric constant of 1.78.
(29) The shortest direct distances between porphyrin carbon atoms and imidazole carbon atoms of His-33 (13.2 Å) and His-39 (13.0 Å) are much too long for any direct donor–acceptor interaction.[16] Calculations were made using BIOGRAF/III version 1.34 (BIOGRAF was designed and written by S. L. Mayo, B. D. Olafson, and W. A. Goddard III). The structures of horse heart cytochrome *c* and its Ru(His-33) derivatives were built from the structure of the tuna protein by side-chain substitution and molecular mechanics energy minimization.[7a,7c,21] The structure of *C.k.* cytochrome *c* was generated from the structure of the tuna protein by side-chain substitution.[23] In both *C.k.* and horse heart proteins, an imidazole carbon on His-33 is 11.7 Å from an imidazole carbon of His-18, an axial ligand of the metalloporphyrin. This value has been used as the edge-to-edge distance in previous studies.[9,21] His-18 is not likely to be as strongly coupled to the porphyrin-localized donor and acceptor states as are carbon atoms of the porphyrin ring.[30] Hence, in comparing donor–acceptor coupling in Ru(His-33)-Zn-cyt *c* and Ru(His-39)-Zn-cyt *c*, distances to porphyrin carbon atoms have been used.
(30) (a) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1–105. (b) Hanson, L. K. *Photochem. Photobiol.* **1988**, *47*, 903–921.
(31) Beratan, D. N.; Onuchic, J. N.; Betts, J. N.; Bowler, B. E.; Gray, H. B. *J. Am. Chem. Soc.*, submitted for publication.
(32) The H bonds in the His-33 (horse) and His-39 (*C.k.*) pathways are assumed to be the same as in the tuna protein. This assumption is reasonable, because the amino acids involved in these interactions (His-18, Pro-30, Gly-41) are conserved in the three proteins.[23]

Novel Pentacoordinate Anionic Silicate, [*o*-$C_6H_4(SiPhF_2)_2F]^-$,K^+·18-Crown-6, Containing a Bent Fluoride Bridge between Two Silicon Atoms

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Received October 30, 1989

Pentacoordinate anionic silicates have recently received much attention from structural and mechanistic points of view,[1] including the nature of bonding,[2] intramolecular ligand exchange,[3] intermolecular ligand exchange with tetracoordinate silanes,[4] enhanced reactivity toward nucleophiles,[5] and activation of the silicon–carbon bonds.[6] New aspects should further be accumulated.

(1) Review: (a) Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99–189. (b) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Ed.; John Wiley: Chichester, 1989; p 1241.
(2) For example: (a) Sini, G.; Hiberty, P. C.; Shaik, S. S. *J. Chem. Soc., Chem. Commun.* **1989**, 772. (b) Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553. (c) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601. (d) Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760. (e) Kira, M.; Sato, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 3747.
(3) Recent papers: (a) Johnson, S. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3182. (b) Johnson, S. E.; Payne, J. S.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3190. (c) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 3250. (d) Damrauer, R.; O'Connell, D.; Danahey, S. E.; Simon, R. *Organometallics* **1989**, *8*, 1167. (e) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (f) Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340.
(4) (a) Brownstein, S. *Can. J. Chem.* **1980**, *58*, 1407. (b) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 1167, 3845. (c) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155.
(5) (a) Carre, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 489 and references cited therein. (b) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 6429. (c) Hayashi, T.; Matsumoto, Y.; Kiyoi, T.; Ito, Y.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5667. (d) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. See also ref 3c.

0002-7863/90/1512-2422$02.50/0