-21 to -30 cm^{-1}.[34] The reduction in exchange coupling can be explained by the fact that there is a decrease in e^- density at the μ_3-oxo resulting from its bridging to an additional Lewis acid metal ion. The EXAFS data do not eliminate the possibility of a highly distorted cubane structure at S_2.[5c]

In summary, the EXAFS data on oriented PSII preparations suggest the possibility of a dimer-of-dimers structure for the PSII WOC.[3-5] On the basis of the Mn K-edge inflection point energy and the edge shape, a Mn(III,IV,III,IV) oxidation state at S_1 has been suggested, although a Mn(III,III,III,III) oxidation state cannot be ruled out.[5b,c] Additionally, this state has been shown to be EPR active exhibiting an integer spin signal consistent with an $S = 1$ ground state.[7] Thus, an analogous dimer-of-dimers model complex has been synthesized[12] in the Mn(III,IV,III,IV) oxidation state which exhibits a similar EPR resonance. We have shown that an electronic model which reflects this general structure and oxidation state provides insight into the origin of this triplet EPR signal. Each Mn(III,IV) dimer is strongly antiferromagnetically exchanged coupled with $S' = {}^1/_2$, and the two dimers are weakly exchange coupled resulting in a low-lying singlet and triplet state. For the observed case of weak interdimer antiferromagnetic exchange coupling, the triplet state has been shown to be the ground state. Within this electronic structure description of a dimer-of-dimers, oxidation by one electron would produce an $S = {}^1/_2$ ground state analogous to that of MnWOC at S_2. The EPR of the ground-state doublet would possess hyperfine contributions from all four Mn ions due to mixing of specific excited-state doublets into the ground-state wave function. However, in order to explain the increase in the square of the effective magnetic moment upon going from S_1 to S_2, a significant but EXAFS indiscernible structural change would be required.

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(34) Hendrickson, D. N.; Christou, G.; Schmitt, E. A.; Libby, E.; Bashkin, J. S.; Wang, S.; Tsai, H.; Vincent, J. B.; Boyd, F. D. W.; Huffman, J. C.; Folting, K.; Li, Q.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 2455-2471.

Radical Cage Effects in Adocobinamide (Axial-Base-Off Coenzyme B_{12}): A Simple Method for Trapping [Ado·Co^{II}] Radical Pairs, a New β-H Elimination Product from the Radical Pair and Measurement of an Unprecedentedly Large Cage-Recombination Efficiency Factor, $F_c \geq 0.94$

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Abstract: A simple method is reported for trapping organometallic caged radical pairs in adocobinamide (axial-base-off coenzyme B_{12}) Co-C bond thermolysis using high, ca. 1 M, concentrations of the stable nitroxide free radical TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy). The product studies as a function of [TEMPO] resolve a literature controversy by showing that β-H elimination is not concerted, but rather proceeds through an [Ado··Co^{II}] caged pair. The method permits the first measurement of the thermal fractional cage-efficiency factor (F_c) for adocobinamide, $0.94 \leq F_c \leq 1.0$. This result, one of the few precise F_c values for metal-carbon homolysis in an organometallic complex and a rare F_c value for a bioorganometallic cofactor, is unprecedentedly large in comparison to all literature bond homolysis F_c values in solvents of comparable viscosity. It thereby serves to confirm the literature's prediction of sizable (≥ 0.5) F_c values in large, massive organometallic radicals.

Introduction

The concept of solvent-caged radical pairs, known for over half a century since Frank and Rabinowitch's original 1934 paper,[1] has enjoyed a broad applicability in organic chemistry. In organometallic and inorganic chemistry, however, our 1988 overview of the literature[2] revealed that solvent-cage effects are relatively little studied and often overlooked,[3] especially in metal-ligand (M-L) bond homolyses (i.e., as opposed to M-L heterolyses[4]), save a few notable exceptions.[5] The powerful tool of direct observation of caged radical pairs by pico- or femtosecond

(1) (a) Franck, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30*, 120. (b) Rabinowitch, E.; Wood, W. C. *Trans. Faraday Soc.* **1936**, *32*, 1381. (c) Rabinowitch, E. *Trans. Faraday Soc.* **1937**, *33*, 1225.

(2) Koenig, T. W.; Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1499. See refs 1-14 therein for a list of lead references in the radical-cage chemistry area.

(3) This is especially true of studies of M-L bond dissociation energies by solution kinetic measurements; see ref 2 for a more complete discussion and references on this point.

(4) The fast kinetic studies of the San Diego groups of D. Magde and T. Traylor should be consulted for cage studies of M-L heterolyses: (a) Traylor, T. G.; Magde, D.; Taube, D. J.; Jongeward, K. A.; Bandyopadhyay, D.; Luo, J.; Walda, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 417. (b) Bandyopadhyay, D.; Walda, K. N.; Magde, D.; Traylor, T. G.; Sharma, V. S. *Biochem. Biophys. Res. Commun.* **1990**, *171*, 306. (c) Traylor, T. G.; Taube, D. J.; Jongeward, K. A.; Magde, D. *J. Am. Chem. Soc.* **1990**, *112*, 6875. (d) Chatfield, M. D.; Walda, K. N.; Magde, D. *J. Am. Chem. Soc.* **1990**, *112*, 4680. (e) Jongeward, K. A.; Magde, D.; Taube, D. J.; Traylor, T. G. *J. Biol. Chem.* **1988**, *263*, 6027. (f) Jongeward, K. A.; Magde, D.; Taube, D. J.; Marsters, J. C.; Traylor, T. G.; Sharma, V. S. *J. Am. Chem. Soc.* **1988**, *110*, 380. (g) Traylor, T. G.; Magde, D.; Taube, D. J.; Jongeward, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 5864. (h) Jongeward, K. A.; Marsters, J. C.; Mitchell, M. J.; Magde, D.; Sharma, V. S. *Biochem. Biophys. Res. Commun.* **1986**, *140*, 962. (i) Campbell, B. F.; Magde, D.; Sharma, V. S. *J. Biol. Chem.* **1985**, *260*, 2752. (j) Campbell, B. F.; Magde, D.; Sharma, V. S. *J. Mol. Biol.* **1984**, *179*, 143.

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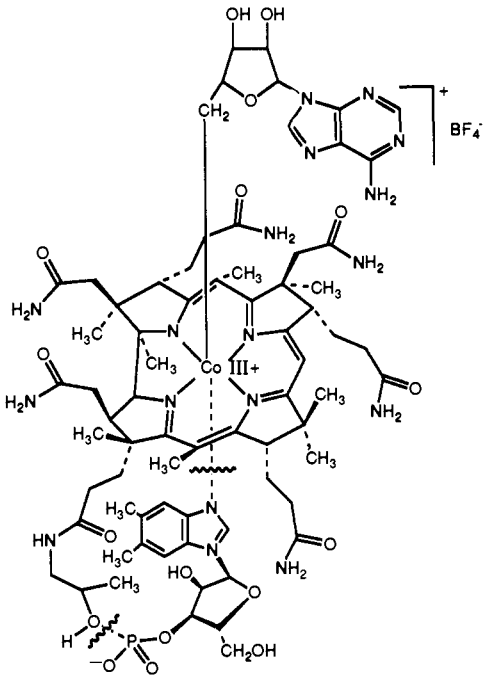

Figure 1. 5′-Deoxy-5′-adenosylcobinamide ($AdoCbi^+BF_4^-$). The wavy lines denote the locations of chemical cleavage during the synthesis[19] of axial-base-free $AdoCbi^+$ from AdoCbl (5′-deoxy-5′-adenosylcobalamin, shown above with its appended 5,6-dimethylbenzimidazole axial base).

spectroscopy holds considerable promise for advancing this area.[6,7] Also desirable, however, is a simple way to detect caged pairs to measure the key indicator of the efficiency ("strength") of the cage, the fractional cage-recombination efficiency factor, F_c (defined as the ratio of cage recombination to the sum of all competing cage processes: $F_c \equiv k_{-1}/\sum k_{\text{cage reactions}}$).

Especially rare are investigations of radical cage effects in bioinorganic and bioorganometallic systems such as coenzyme B_{12}—despite the need for such studies.[8,9] One important exception is Endicott and Netzel's 1979 preliminary laser flash photolysis study[6] of coenzyme B_{12} (adocobalamin, AdoCbl) and a more recent reinvestigation thereof.[7] This lack of cage chemistry studies is despite the prediction[2] of unusually large cage-efficiency factors, $F_c > 0.5$, for such sizable and massive radical pairs (only a few F_c values for organometallics are available)[10-12] and despite tantalizing hints that protein analogs of solution-cage effects may be operative in enzymes which utilize radical mechanisms.[13] (See also the conceptually related topic of photochemical M–L heterolyses from hemes and heme protein CO, NO, O_2, or isonitrile complexes.[4]) Three very recent reports confirm the burgeoning interest in organometallic radical–cage chemistry,[11,12,14] especially that of coenzyme B_{12} and its derivatives.[12,14]

Herein we report a simple radical-trapping method, using the stable nitroxide free radical TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), for detecting caged radical pairs in the thermal Co–C homolysis of adocobinamide ($AdoCbi^+BF_4^-$), the derivative of adocobalamin (AdoCbl) in which the appended 5,6-dimethylbenzimidazole has been chemically cleaved and removed (Figure 1).[15] The key to this new method is straightforward: by extension of our TEMPO trapping method for Co–C homolysis studies[16] to high (ca. 1 M) concentrations, TEMPO becomes a component of the (solvent plus TEMPO) cage walls, thereby becoming able to trap caged radical pairs. Our cage-trapping results resolve a current literature controversy[5b,17] by showing that

(5) (a) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (b) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487. (c) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5. (d) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222. (e) Matsui, Y.; Orchin, M. *J. Organomet. Chem.* **1983**, *244*, 369. (f) Connolly, J. W. *Organometallics* **1984**, *3*, 1333. (g) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023; these authors provide an early demonstration that sizable cage effects can exist for organometallics, even in low-viscosity solvents. (h) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689. (i) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995. (j) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1987**, *109*, 6542.

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

(7) Chen, E.; Chance, M. R. *J. Biol. Chem.* **1990**, *265*, 12987.

(8) Virtually all prior studies of Co–C homolyses would have benefited from the cage-trapping method reported herein, including our own.[9,16] For a few examples where the presence of a cage is an important issue, and thus where the trapping method reported herein would have been especially useful had it been previously available, see: (a) Ohgo, Y.; Wada, H.; Ohtera, C.; Ikarashi, M.; Baba, S.; Takeuchi, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2656. Ohgo, Y.; Orisaku, K.; Hasegawa, E.; Takeuchi, S. *Chem. Lett.* **1986**, 27. Baba, S.; Ohgo, Y.; Takeuchi, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3967. (b) Suggs, J. W.; Jun, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (c) de Bolster, M. W. G.; Kranenburg, R. A. C. *Inorg. Chim. Acta* **1991**, *183*, 119. (d) Zou, X.; Brown, K. L.; Vaughn, C. *Inorg. Chem.*, in press (Facile α,β Diastereoisomerism in Organocorrins...). (e) See elsewhere as well.[2,6,7,9,16,17,28,29]

(9) Studies of the so-called cobalt participation or nonparticipation question in B_{12} chemistry also would have benefited from the trapping method reported herein; for lead references, see: (a) Wang, Y.; Finke, R. G. *Inorg. Chem.* **1989**, *28*, 983 and references therein. (b) Dowd, P.; Hershline, R. *J. Chem. Soc., Perkin Trans. 2* **1988**, 61, and references therein. (c) Dixon, R. M.; Golding, B. T.; Mwesigye-Kibende, S.; Ramakrishna Rao, D. N. *Phil. Trans. R. Soc. London B* **1985**, *311*, 531 and references therein.

(10) Few previous precise measurements of organometallic bond homolysis F_c values exist; three earlier estimates are (see also ref 11) Endicott and Netzel's $F_c \approx 0.7 \pm 0.5$ (range 0.2–1.0) and two we estimated[2] on the basis of literature data [see 2, p 1512, $Ni(CO)_4$ in benzene, F_c(est) $\approx$ 0.5, and p 1501, a trimetallic metal cluster example, F_c(est) $\approx$ 0.5 in benzene. In addition, there are very recent viscosity-derived values[12] which, however, are based on assumed (incorrect[12]) products and associated kinetic equations and thus appear to be quantitatively unreliable;[12a] also, the F_c values for $AdoCbi^+$ are photochemical $F_{c,p}$ values which cannot be directly compared to thermal F_c values[12b]].

(11) A method for the measurement of photochemical cage efficiency factors,[12b] $F_{c,p}$, has been developed. Covert, K. J.; Askew, E. F.; Grunkemeir, J.; Koenig, T.; Tyler, D. R. *J. Am. Chem. Soc.*, following article in this issue.

(12) (a) A viscosity-dependence-based study of the photochemical cage effect in AdoCbl and $AdoCbi^+$, and of the thermal cage effect in AdoCbl (but not $AdoCbi^+$), appeared as this paper was being readied for submission.[12c] Unfortunately, the $AdoCbi^+$ photolysis products assumed therein differ from those proven herein[12d] and, more importantly, from those we have since established in a preliminary reinvestigation[12d] of that work.[12c] Specifically, 4′,5′-didehydroadenosine is a previously unrecognized[12c] nucleoside product for $AdoCbi^+$ under even the milder cage conditions of a 1.6 cP viscosity solution employed by Balt et al.[12c] (3% for 25 °C photolysis; 22% for 108 °C thermolysis[12d]); it is likely a much greater percentage of the products at the very high viscosities of[12e] ca. 150 cP in 90% glycerol at 25 °C, also part of their studies[12c] (evidence for this statement is provided in the supplementary material). This means that the associated mechanistic scheme and key kinetic equation (no. 7; p 49)[12c] in that paper is in error as is a key equation used to curve-fit the data; they should, instead, contain a $k_{\beta H}$ term [$k_{obsd} = (k_1k_d)/(k_{-1} + k_d + k_{\beta H})$] and an α_3 term [$k_{obsd} = \alpha_1/(1 + \alpha_2\eta + \alpha_3)$]. Thus, the true products at each viscosity[12c] need to be measured, and the curve-fit-derived kinetic constants and $F_{c,p}$ values[12b] therein need to be recalculated. (The products, kinetic constants, and F_c and $F_{c,p}$ values for AdoCbl may have similar problems, but only at the higher viscosities, since we find[12d] no detectable 4′,5′-didehydroadenosine at their lower (e.g., 1.6 cP) viscosity conditions.[12c]) (b) Photochemical $F_{c,p}$ and thermal F_c values should be compared only with caution (especially in cases where a triplet state or an unknown spin state results from photolysis), something we[2] and others[12c] have previously noted. (Evidence does exist, however, that photolysis of methylcobalamin at least gives a singlet state initially.[14]) (c) Gerards, L. E. H.; Bulthuis, H.; de Bolster, M. W. G.; Balt, S. *Inorg. Chim. Acta* **1991**, *190*, 47. (d) Garr, C. D.; Finke, R. G. Preliminary results (summarized as supplementary material; also available elsewhere[15]). (e) Sequr, J. B.; Oberster, H. E. *Ind. Eng. Chem.* **1951**, *43*, 2117. This is the incorrectly cited reference (see ref 18)[12c] used to obtain the viscosities employed by others.[12c] Viscosities used herein from this paper were obtained by plotting the (nonlinear) viscosity vs temperature data and interpolating to 25 °C.

(13) Three examples are from the B_{12} binding proteins: (a) Toraya, T.; Ishida, I. *Biochemistry* **1988**, *27*, 7677. (b) Chen and Chance's paper[7] discusses the possibility that B_{12} binding enzymes may help separate Ado• and $•Co^{II}B_{12r}$ radical pairs. (c) Brown, K. L.; Brooks, H. B.; Behnke, D.; Jacobsen, D. W. *J. Biol. Chem.* **1991**, *266*, 6737.

(14) By using viscous solvents like glycerol that impart a sizable cage effect, a magnetic field dependence on the separation of [Me• and •Cbl] singlet radical pairs has been detected: Grissom, C. B.; Chagovetz, A. M.; Wang, Z. Poster and *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 5–10, 1992; American Chemical Society: Washington, DC, 1992; BIOL 82.

(15) Garr, C. D. Ph.D. Thesis, University of Oregon, Eugene, OR, 1992.

(16) (a) Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3041. (b) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4820. (c) Hay, B. P.; Finke, R. *Polyhedron* **1988**, *7*, 1469.

β-H elimination is not concerted but, instead, proceeds through an [Ado$^{\bullet}$ $^{\bullet}$Co^{II}] caged pair. The results reported herein also permit the first measurement of the near-unity fractional cage-efficiency factor (F_c) for adocobinamide, $0.94 \leq F_c \leq 1.0$ (in 110 °C ethylene glycol, viscosity 1.73 cP).[18]

Experimental Section

General. Thermolysis samples, prepared under N_2 in a Vacuum Atmospheres inert atmosphere glove box in Schlenk UV–visible cuvettes,[16] were (1.0–1.2) × 10^{-4} M in pure[19] AdoCbi$^+$$BF_4^-$ and contained from 0.0 to 0.89 M sublimed (Aldrich) TEMPO (mp 39 °C; lit.[20a] mp 37–39 °C) dissolved in ethylene glycol (Baker), which had been distilled previously under N_2 from 4-Å molecular sieves. Using the exact same samples (cuvettes) as were used for a given kinetic run, the organic nucleoside thermolysis products were identified and quantitated by HPLC in comparison to previously characterized, authentic samples[16] and their HPLC detector response factors; the latter were obtained from (linear) plots of peak area vs concentration (1×10^{-3} to 5×10^{-5} M nucleoside). HPLC conditions employed were as follows: PRP-1 semipreparative C_{18} column (Hamilton); λ = 260 nm detection; 2 mL/min flow; 10% CH_3CN/90% H_2O for all nucleosides except Ado-TEMPO, which is retained on the column under these conditions (30% CH_3CN/70% H_2O was used instead), and except for α-AdoCbi$^+$ (discussed in a separate section below).

4′,5′-Didehydroadenosine Product Studies. Authentic 4′,5′-didehydroadenosine [9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)adenine], a gift from Syntex Discovery Research that had been synthesized according to the literature procedure,[20b] was 97% pure by HPLC and, therefore, was used as received. This nucleoside was established as an AdoCbi$^+$ thermolysis product in ethylene glycol both by HPLC studies and by comparison (by NMR and MS vs the authentic material) of product isolated (vide infra) from the thermolysis reaction. In the HPLC experiments, both the "unknown" nucleoside thermolysis product as well as authentic 4′,5′-didehydroadenosine were shown to have an HPLC retention time of ca. 11 min using the 10% CH_3CN/90% H_2O conditions cited in the general section above. Also, authentic 4′,5′-didehydroadenosine was coinjected (spiked) with the normal thermolysis product as follows: a thermolysis cuvette sample (i.e., the exact same sample as used for the kinetic runs at [TEMPO] = 0 and 1.7×10^{-2} M) was coinjected onto the HPLC with authentic 4′,5′-didehydroadenosine. A single peak at ca. 11 min of increased peak area (relative to either sample alone) was seen as expected, along with a concomitant decrease of the other nucleoside peaks (due to dilution of the thermolysis sample). In the isolation experiments, 5 mL of 2.5×10^{-3} M AdoCbi$^+$ in ethylene glycol was thermolyzed and ca. 0.5 mg of impure 4′,5′-didehydroadenosine was subsequently isolated laboriously from the product solution by preparative HPLC (ca. 75-μL injections over a period of ca. 3 weeks, followed by removal of the resultant ca. 2 L of CH_3CN/H_2O HPLC solvent). Although the small amount of isolated material meant that the ^{1}H NMR sample was very dilute (poor signal to noise) and showed impurities, the following spectral data confirm that the isolated nucleoside is in fact 4′,5′-didehydroadenosine: ^{1}H NMR (300 MHz) in DMSO-d_6 of the isolated material δ 8.34 and 8.11 (s, 1 H, C2-H and C8-H), 7.32 (s, 2 H, NH_2), 6.10 (d, 1 H, C1′-H), 5.68 and 5.55 (d, 1 H, C2′ and C3′-OH), 4.79 (m, 1 H, C2′-H), 4.67 (m, 1 H, C3′-H), 4.26 (s, 1 H, C5′-H_a), 4.15 (s, 1 H, C5′-H_b); ^{1}H NMR (300 MHz) in DMSO-d_6 of the authentic 4′,5′-didehydroadenosine δ 8.34 and 8.12 (s, 1 H, C2-H and C8-H), 7.33 (s, 2 H, NH_2), 6.11 (d, 1 H, C1′-H), 5.66 and 5.50 (d, 1 H, C2′ and C3′-OH), 4.80 (m, 1 H, C2′-H), 4.67 (m, 1 H, C3′-H), 4.26 (s, 1 H, C5′-H_a), 4.16 (s, 1 H, C5′-H_b). Similarly, the mass spectrum of both isolated and authentic material contained the same key peaks: low-resolution FAB-MS (3-nitrobenzyl alcohol matrix) calcd for $C_{10}H_{11}N_5O_3^+$ 250, found *m/e* 250, plus a strong adenine fragment $C_5H_5N_5^+$ peak at 136.

The following control experiment was done to rule out the possibility of 4′,5′-didehydroadenosine reacting directly with TEMPO (under our thermolysis conditions of 110 °C anaerobic heating for ca. 6 h in ethylene glycol) to give Ado-TEMPO, the observed high [TEMPO] product, even though such a reaction has no precedent to our knowledge. (We felt this control was still needed since, if present, such a reaction would presumably be an argument against the cage-effect interpretations provided herein.) A sample containing 1.3×10^{-4} M authentic 4′,5′-didehydroadenosine and 0.9 M TEMPO in ethylene glycol was prepared as described previously. This sample was heated at 110 °C for ca. 6 h and then analyzed for nucleoside products by HPLC. All of the initial 1.3×10^{-4} M 4′,5′-didehydroadenosine remained unreacted, that is, none of it had been diverted to any product including Ado-TEMPO, and there is not, therefore, any type of direct reaction of 4′,5′-didehydroadenosine with TEMPO.

α-AdoCbi$^+$$H_2PO_4^-$ and Associated Control Experiments. A sample of authentic α-AdoCbi$^+$ was generously provided by Professor K. L. Brown[8d] for the control experiment below, demonstrating that the α-AdoCbi$^+$ isomer is *not* an initial, cage-recombination product in the thermolysis of β-AdoCbi$^+$. Note that β-AdoCbi$^+$ is the "normal" isomer of adenosylcobinamide where the Ado alkyl occupies the "top" or β-position as depicted in Figure 1; it is this β-AdoCbi$^+$ isomer whose thermolysis is reported herein. Alternatively, α-AdoCbi$^+$ is the "bottom" or α-alkyl isomer that has only recently been prepared and unequivocally characterized for the first time in Brown's laboratories.[8d] Control studies were required since the α-AdoCbi$^+$ isomer is a conceivable initial cage-recombination product, one that (if formed) would have to be added to the mechanistic Scheme I and associated kinetic equations, resulting in a considerably more complicated mechanistic scheme.

To test for the initial formation of α-AdoCbi$^+$, four standard solutions (1×10^{-4} M α-AdoCbi$^+$ in Schlenk cuvettes in ethylene glycol under N_2) were thermolyzed at 110 °C until 5, 10, 25, and 50% reaction, respectively, followed by quenching (accomplished by cooling) and then HPLC analysis at 254 nm. The HPLC conditions below, kindly provided by Professor K. L. Brown, were used to resolve α-AdoCbi$^+$ and β-AdoCbi$^+$ (albeit not to a base-line resolution) with 9.8 and 10.4 min retention times, respectively. The only difference is that we used a new analytical 3.9 mm i.d. by 300 mm long C_{18} column (Phenomenex), whereas Professor Brown and co-workers used a C_8 Beckman Ultrasphere column. The other HPLC conditions were as follows: 5% CH_3CN/95% 0.05 M (pH 3) ammonium phosphate buffer for 2 min, a gradient to 13% CH_3CN/87% buffer over 3 min, then a gradient to 30% CH_3CN/70% buffer over 8 min followed by a isocratic hold at 30% CH_3CN/70% buffer; 2 mL/min flow rate; 254 nm UV detection. No increase in the α-AdoCbi$^+$ that is over and above the small amount present in the starting β-AdoCbi$^+$ (vide infra) was detected. Hence, α-AdoCbi$^+$ is not formed as an initial cage-recombination product.

HPLC Studies of the Isomer Purity of β-AdoCbi$^+$. The β-AdoCbi$^+$ starting material used in the present studies were previously reported[19a] to contain "<2% corrin impurity by HPLC and ^{1}H NMR" (see p 8013).[19a] The recent preparation and characterization of authentic[8d] α-AdoCbi$^+$ for the first time allows us to probe more rigorously the isomeric purity of β-AdoCbi$^+$.

Using the HPLC column and conditions described in the previous section, still only ca. 2% α-AdoCbi$^+$ impurity was found in the β-AdoCbi$^+$ starting material. We note that this low level of isomeric impurity could be the nearly unavoidable result to trace light photohomolysis of β-AdoCbi$^+$ followed by recombination (in the absence of traps like TEMPO or O_2) of initially out-of-cage radicals.

Kinetic Studies. Kinetic runs were carried out in Schlenk cuvettes as previously reported[16,19a] by immersing the Schlenk cuvettes in a 110.0 ± 0.2 °C oil bath for predetermined time periods, removing them for rapid thermal quenching in a 20 °C bath, equilibrating the sample for >10 min at 25.0 °C in a Beckman DU-7 visible spectrophotometer, and then monitoring the growth of the $Co^{II}B_{12r}$ product at 555 nm (not 468 nm as before[19]) while using a reference cell containing the identical concentration of TEMPO in ethylene glycol; see the text for further discussion of these points. The temperature control required for the kinetic studies was obtained using a Pt thermocouple (Omega) attached to a Variac. The actual temperature in the oil bath was measuring using NBS-calibrated thermometers with 0.2 °C gradations with a published accuracy of ±0.2 °C.

(17) For example, see: (a) Schrauzer, G. N.; Lee, L. P.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 2997. (b) Schrauzer, G. N.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1022. (c) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4060. (d) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 233. (e) Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601. (f) Gjerde, H. B.; Epsenson, J. H. *Organometallics* **1982**, *1*, 435. (g) Until later,[17j] Pratt too apparently believed in a concerted β-H elimination; see: Pratt, J. M. In *B_{12}*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. I, Chapter 10 (see p 362 and the "synchronous elimination", eq 7). (h) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2259. Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2267. (i) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2274. (j) Baldwin, D. A.; Betterson, E. A.; Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1613. (k) Kim, S.-H.; Chen, H. L.; Feilchenfeld, N.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3120 and see 3124. (l) Ng, F. T. T.; Rempel, G. L.; Mancuso, C.; Halpern, J. *Organometallics* **1990**, *9*, 2762.

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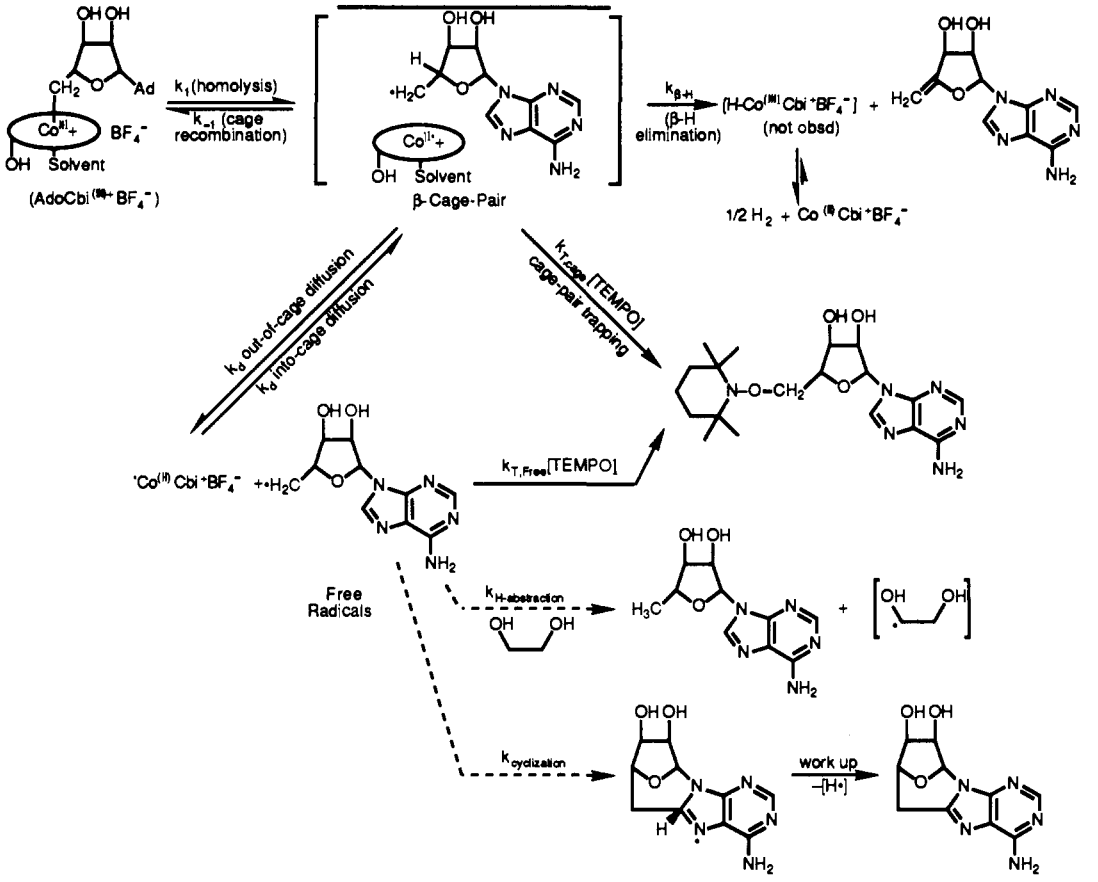
(19) (a) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 8012. (b) Pagano, T. G.; Yohannes, G.; Hay, B. P.; Scott, J. R.; Finke, R. G.; Marzilli, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 1482.

(20) (a) Rozantzev, E. G.; Neiman, M. B. *Tetrahedron* **1964**, *20*, 131. (b) Prisbe, E. J.; Smejkal, J.; Verheydwn, J. P. H.; Moffatt, J. G. *J. Org. Chem.* **1976**, *41*, 1836.

Scheme I. Reversible Formation of the (β-Oriented Only) Caged Pair During β-AdoCbi$^+BF_4^-$ Thermolysis in Ethylene Glycol and Subsequent Pathways to the Observed Products[a]



[a] Under low [TEMPO], where the only radical trapping is free radical trapping (i.e., no caged-pair trapping), $k_{obsd} = k_1(1-F_c)$ [where $F_c \equiv$ fractional cage efficiency $\equiv k_{-1}/(k_{-1} + k_d + k_{\beta\text{-H}})$]. Alternatively, at high [TEMPO], where all Ado• is scavenged from the cage (caged-pair trapping only), $k_{obsd} = k_1$ (see the supplementary material for kinetic derivations).

Other experimental details in general follow our prior publications on alkylcobamide thermolyses,[16,19] and a thesis can be consulted if needed,[15] one of which will include our results[15] with $AdoB_{12}$.

Results and Discussion

Product Studies. The nucleoside products were carefully quantitated throughout the range of [TEMPO] examined and are summarized in Table I. The observed products are dependent on the concentration of TEMPO, as expected for cage scavenging by the TEMPO radical trap, and they account for 100% of the starting Ado nucleoside in $AdoB_{12}$. The observed products characteristic of Co–C homolysis[16,19] include 8,5′-anhydroadenosine (cyclic-Ado) and 5′-deoxyadenosine. (There is also 3 ± 1% of adenine, a product characteristic of Co–C heterolysis.[16b])

In addition, a new product never before detected in AdoCbi$^+$ thermolysis in H_2O (weaker cage conditions)[19a] or in any (base-on) AdoCbl thermolysis was isolated by preparative HPLC and characterized by ^1H NMR and mass spectroscopy in comparison to independently synthesized, authentic material (see the Experimental Section), the β-H elimination olefin product, 4′,5′-didehydroadenosine (Table I and Scheme I). This product and how it varies with [TEMPO] is, by itself, strong evidence for the cage mechanism shown below in Scheme I. Specifically, this new product is not detected in AdoCbi$^+$ thermolysis in H_2O,[19a] yet is "induced" by running the reaction in ethylene glycol (i.e., under stronger cage conditions) and can also be diverted with high (0.85 M) [TEMPO] to yield the Ado•-trapped product, Ado-TEMPO. Moreover, this new olefin product cannot in any precedented way be the result of a direct reaction with ethylene glycol—that is, there is no known (or even readily imaginable!) reaction of AdoCbi$^+$ or Ado• with ethylene glycol that will give 4′,5′-didehydroadenosine. Instead, these results and our other mechanistic data are consistent only with Ado• as a common intermediate in a solvent-cage reaction, with the 4′,5′-didehydroadenosine olefin product being formed under strong cage conditions (and with lower [TEMPO]), but then being diverted to the normal and characteristic Ado• free radical products under weak cage conditions (i.e., 90–110 °C H_2O).[19a]

Table I. Nucleoside Products[a] from the 110 °C Anaerobic Thermolysis of AdoCbi$^+BF_4^-$ in Ethylene Glycol

PRODUCTS (TEMPO)	TEMPO (5′-deoxyadenosine-TEMPO, Ado-TEMPO)	(4′, 5′-didehydroadenosine)	8,5′-anhydroadenosine, cyclic-Ado)	(5′-deoxyadenosine, Ado-H)	(adenine, Ad)	Total
0	0%	33%	45%	15%	4%	97%
0.12 M	73%	24%	1%	0%	2%	100%
0.75 M	89%	9%	0%	0%	2%	100%
0.85 M	91%	7%	0%	0%	3%	101%

[a] Determined by reversed-phase HPLC as described in the Experimental Section.

This new product also convincingly illustrates that the overall course of a reaction, and not just the reaction's rate, can be significantly influenced by the presence of a strong solvent cage. In the present case, multiple encounters between the caged pair [Ado• •$Co^{II}B_{12r}$] effectively "turn on" kinetically the otherwise relatively slow β-H elimination reaction (i.e., "slow" relative only to the very fast cage escape by diffusion).

Under all conditions, the $Co^{II}Cbi^+BF_4^-$ yield is 100 ± 10%, again consistent with the initial reaction being Co–C homolysis.[21]

However, this corrin product plus the nucleoside products and mass and charge balance require the formation of 0.5 equiv of H_2 (i.e., a trace 0.5 × 10^{-4} M) for each equivalent of 4′,5′-didehydroadenosine formed. The pathway here is undoubtedly the precedented two-step sequence of β-H elimination[22] to form the olefin-containing 4′,5′-didehydroadenosine plus (the often reported, but still ill-characterized) "$HCo^{III}Cbi^+$",[23] followed by the known disproportionation[17] of $2HCo^{III}Cbi^+$ to give H_2 plus $2Co^{II}Cbi^+$, all as shown in Scheme I. It is noteworthy that the above, demonstrated products differ from those assumed in a recent paper examining the viscosity dependence of $AdoCbi^+$ photolysis.[12]

Overall, the products and how they vary with the increasing [TEMPO] are strongly supportive of the caged-pair mechanism shown in Scheme I. Note that we also considered, and were able to rule out, the formation of the α-isomer, α-$AdoCbi^+$, as an initial thermolysis product from cage recombination of an α-oriented radical pair (see the Experimental Section). This means that the initial, β-oriented [Ado· ·$Co^{II}B_{12r}$] radical pair produced by Co–C homolysis of β-$AdoCbi^+$ *does not undergo internal rotation to any measurable extent* in competition with the other cage reactions[24] of β-H elimination and cage trapping by TEMPO ($k_{\beta\text{-H}}$ and $k_{T,cage}$, respectively, Scheme I). Restated, the product studies allow the relative rate estimates of $25k_{\beta\text{-H}} \approx k_{T,cage}$ and also the $k_{\beta\text{-H}} \gg k_{\beta,\alpha}$ in the moderately viscous, H-bonding solvent ethylene glycol ($k_{\beta,\alpha}$ is the rate constant for β-cage pair to α-cage pair conversion or internal rotation; see the supplementary material for a mechanistic scheme with these relative rate derivations). Such estimates of cage rate constants are rather rare,[25] especially for a large radical pair of the size and type derived from $AdoCbi^+$.

Worth noting here is the important mental image the above findings provide, one of a relatively "tight" solvent cage reminiscent of Doering's 1986 results[25a] for a small organic radical pair in *o*-dichlorobenzene at 300 °C (see, however, the results of Koenig[25b]). Given that the barrier to cage escape is "totally enthalpic",[2] the H-bonding of ethylene glycol would seem to be the obvious source of the tightness of the "strong" cage.

Kinetic Studies. A crucial difference from our previous kinetic work[19] is the choice of 555 nm to monitor the appearance of the $Co^{II}Cbi^+BF_4^-$ product (λ_{max} = 468 nm). The choice of 555 nm (ϵ_{555} = 1.9 × 10^3 M^{-1} cm^{-1}) is a simple but important change because the interfering absorbance of TEMPO is 10-fold less at 555 than at 468 nm (TEMPO λ_{max} = 443 nm, ϵ_{443} = 10.3 M^{-1} cm^{-1}, ϵ_{555} = 1.05 M^{-1} cm^{-1}). This change, plus the use of a standard reference cell (i.e., with the same concentration of TEMPO in ethylene glycol as employed in each particular experiment), allowed a maximum of ca. 0.9 M TEMPO to be accessed (since, at 0.9 M, TEMPO is already absorbing ca. 80% of the spectrophotometer's light; another relevant fact is that neat molten TEMPO is ca. 6 M, i.e., only ca. 6-fold higher in concentration). The low [TEMPO] (≤0.08 M) kinetics was followed for 1.0–1.5 half-lives at two or more wavelengths, during which isosbestic points were maintained at 405 and 355 nm (monitoring of these $t_{1/2}$ > 60 h reactions for a longer time is precluded by corrin decomposition[19a]). End points were obtained by photolyzing the Schlenk cuvettes for ca. 30 min with a 350-W tungsten lamp placed 20 cm away; the photolysis isosbestics were unchanged from the thermal isosbestic points, confirming the identical nature of the corrin products in the two reactions. High [TEMPO] (≥0.08 M) kinetics was followed for ≥3 half-lives from 540 to 600 nm. Finally, first-order rate constants (±6–15% typically) were obtained from linear regression of the ln [$Abs_\infty/(Abs_\infty - Abs_t)$] kinetic data; the results are tabulated in Table II and are plotted in Figure 2.

Table II. Kinetic Results from the 110 °C Anaerobic Thermolysis of $AdoCbi^+BF_4^-$ in Ethylene Glycol as a Function of [TEMPO]

[TEMPO](M)	log [TEMPO]	k_{obsd} × 10^5 s^{-1} (1σ error)	wavelength employed (nm)
0.89	−0.0506	5.9 (0.8)	555
0.85	−0.0706	6.8 (0.6)	555
0.85	−0.0706	6.5 (0.6)	555
0.70	−0.1549	5.2 (0.8)	555
0.34	−0.4685	3.1 (0.25)	555
0.20	−0.6990	2.1 (0.4)	555
0.11	−0.9586	1.7 (0.4)	555
0.077	−1.1135	0.91 (0.12)	380/555
0.04	−1.3979	0.26 (0.04)	380/555
0.031	−1.5086	0.52 (0.05)	380/555
0.012	−1.9208	0.32 (0.02)	380/555
0.009	−2.0555	0.40 (0.01)	380/555
0		0.22 (0.02)	380/555

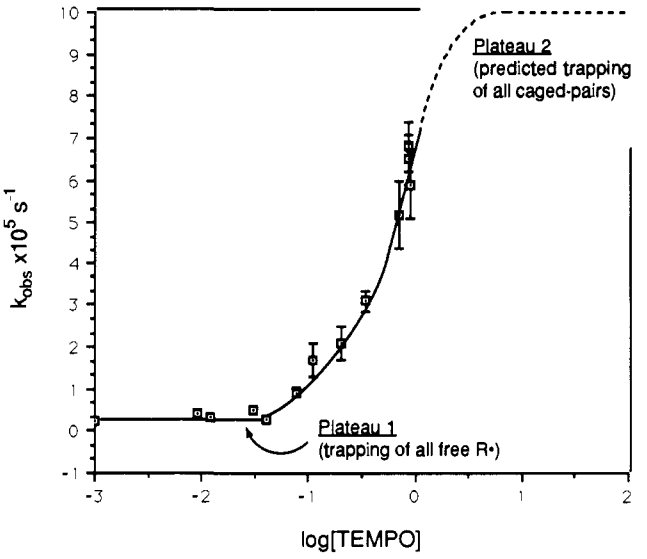


Figure 2. Plot of k_{obsd} vs log [TEMPO]. The data allow the calculation of $F_c \geq 0.94$ as discussed in the text. The broken line (---) shows a calculated plot of the predicted second plateau, assuming F_c = 0.96. (Experimental verification of this putative second plateau was not possible due to the experimental limitations of the maximum [TEMPO] ≤ 0.9 M as discussed in the text.) Error bars are shown at 1σ.

The product studies (especially the formation of 100% $Co^{II}Cbi^+$ and ≥91% trapped Ado· as Ado-TEMPO), the kinetic studies, and our earlier literature reports[16,19a] (demonstrating that these products are the (expected) products of Co–C homolysis) are all strongly supportive of the mechanism shown in Scheme I. (The small, ca. 3 ± 2%, Co–C heterolysis indicated by the formation of that amount of adenine is negligible in comparison to the ca. 3× larger error bars of the kinetic measurements.) Fortifying the caged-pair mechanism depicted in Scheme I is Endicott and Netzel's direct spectroscopic detection of the cage pair[6] for the closely related system of base-on AdoCbl in H_2O at 25 °C. Moreover, other nitroxide-trap-induced (bimolecular) mechanisms, which might at first glance seem to account for the rise in k_{obsd} at very high [TEMPO], were also considered but can be ruled out; see the supplementary material for details. We also considered and were able to rule out a conceivable explanation for the k_{obsd}

(21) The $Co^{II}Cbi^+BF_4^-$ extinction coefficient for yield calculations (ϵ_{555} = 1.9 (± 0.1) × 10^3 cm^{-1} M^{-1}) was obtained both from the 110 °C thermolysis of $AdoCbi^+BF_4^-$ (over 1.5 half-lives) and its photolysis in ethylene glycol; both reactions maintained identical isosbestic points at 405 and 355 nm.

(22) There is also excellent precedent in other organometallic studies for extremely facile β-H elimination from a caged metal plus organic radical pair.[5a,g]

(23) (a) As we have noted before,[23b] the putative "hydridocobalamin, HCo^{III}" (as it is known in the literature), is in fact a very poorly defined species, one that may involve ligand protonation and/or both β and α CoH isomers. (b) Aleyunas, Y. W.; Fleming, P. E.; Finke, R. G.; Pagano, T. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1991**, *113*, 3781; also see p 3790, footnote 49 and references therein to Schrauzer's, Pratt's, and Lexa and Savéant's prior work on "hydridocobalamin".

(24) This finding is fortified by an identical conclusion, but for a different alkylcobalamin and in water, on the basis of the data in ref 23b (see p 3788, Scheme III, and the discussion on that page concerning the α-**1** to β-**2** conversion).

(25) (a) Doering, W. v. E.; Birladeanau, L. *J. Am. Chem. Soc.* **1986**, *109*, 7442 and ref 7–9 therein. (b) Koenig, T. W. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series 69; American Chemical Society: Washington, DC, 1978; pp 134–160. In this example, $k_{int.\ rot.}$ is faster than $k_{diffusion}$ (cage escape); see Table II, p 146.

vs TEMPO data in which a hypothetical decrease in the solution's viscosity, due to the added TEMPO, gives rise to the data and curve in Figure 2. This possibility was excluded unequivocally by showing that added TEMPO in fact does not change the viscosity of ethylene glycol (within experimental error, and up to the 0.9 M TEMPO used herein). These experiments, plus other reasons why the viscosity explanation does not fit the data, are summarized for interested readers in the supplementary material. Finally, recall that the participation by the α-isomer[26,27] of AdoCbi$^+$ was ruled out by the product studies presented earlier.

Key Conclusions and Insights. The results summarized in Scheme I allow several important conclusions and insights. First, the simple but effective caged-pair trapping method reported herein should be applicable to other systems. Second, β-H elimination is the result of a cage reaction between the radical pair [R$^\bullet$ $^\bullet$Co^{II}] as some thought[17j-l] and *not* a concerted reaction as others believed,[17a-i] at least for the present [Ado$^\bullet$ $^\bullet$Co^{II}] and other[17,22] radical pairs. Hence, this controversy would seem to be laid to rest.

Third, the data herein bear strongly on another unsettled point in the literature, that of whether or not the apparent Co–C heterolysis product adenine comes from a Co–C homolysis path and an Ado$^\bullet$ radical precursor[28] or whether adenine is actually the product of a parallel, bimolecular Co–C plus H^+ heterolysis reaction as we have thought.[16b,29] Two facts rule out any mechanism where adenine comes from a pathway involving caged Ado$^\bullet$, specifically: (i) the fact that the adenine (3 ± 1%; Table I) is unaffected by even 0.9 M TEMPO and (ii) our demonstration that such high [TEMPO] does trap caged Ado$^\bullet$ (e.g., in competition with the cage process of 4′,5′-didehydroadenosine formation).

Hence, the simple tool of caged-pair trapping by the nitroxide[30] TEMPO has laid to rest two literature controversies. This both (i) substantiates the claim made in the Introduction concerning the need for such a mechanistic tool and (ii) demonstrates the efficacy of this particular tool or trap.

Fourth, the lack of internal rotation (interconversion) of the β- and α-radical pairs mentioned earlier, and the apparent "tightness" of at least the ethylene glycol/B_{12} cage, bears on the fundamental issue of the best phenomenological description of the cage.[31] In particular, our "tight" cage findings support a phenomenological model consisting of only (tighter) primary radical pairs but not looser secondary or "solvent-separated" radical pairs, the model preferred by Hammond[32] and Koenig[31] and the model used herein.

Fifth and lastly, the cage-trapping method allows a lower limit to be placed on the fractional cage-recombination efficiency, F_c (the detailed calculations are provided as supplementary material). In the present case of AdoCbi$^+BF_4^-$ in the moderate-viscosity (1.73 cP)[18] solvent to 110 °C ethylene glycol, the finding is $F_c \geq 0.94$ which, in this case, provides the precise definition of $0.94 \leq F_c \leq 1.0$ since 1.0 is an upper limit to F_c. This result, the first F_c measurement for AdoCbi$^+$ thermal Co–C homolysis and one of the few precise F_c values for an organometallic complex, also constitutes a rare F_c measurement for a bioorganometallic cofactor.[10,12] In addition, the $F_c \geq 0.94$ for AdoCbi$^+$ is unprecedentedly large in comparison to all literature F_c values *in comparable viscosity solvents*;[33] it means that ≥94 out of every 100 cage events are Ado$^\bullet$ plus $^\bullet$Co(II)Cbi$^+$ recombination. This result thereby serves to confirm the earlier prediction[2] of large (≥0.5) F_c values in large, massive organometallic radicals.

Additional results for base-on AdoCbl, and the insights that result from comparing AdoCbl to AdoCbi$^+$, will be reported elsewhere.[15]

Acknowledgment. We thank Professor David Tyler for a preprint of ref 11 and for valuable discussions, Syntex Discovery Research for their gift of 9-(5-deoxy-β-D-*erythro*-pent-4-enofuranosyl)adenine, and Professor Ken L. Brown for a sample of authentic α-AdoCbi$^+$. Support was provided by NIH Grant DK 26214. C.D.G. also gratefully acknowledges support from a grant from the U.S. Department of Education, Graduate Assistance in Areas of National Needs Program.

Supplementary Material Available: Discussions of evidence ruling out the three conceivable mechanisms, (i) a nitroxide-trap-induced biomolecular mechanism, (ii) a nitroxide prior-coordination, nitroxide-induced homolysis mechanism, and (iii) a mechanism where hypothetical TEMPO-induced solution viscosity changes cause the observed rise in k_{obsd} at high [TEMPO], a preliminary reinvestigation of the AdoCbi$^+$ and AdoCbl thermolysis products assumed by others,[12c] demonstrating that their assumed products (and associated kinetic equations) are partially incorrect,[12] kinetic derivations for the fractional cage-recombination efficiency, F_c, and kinetic derivations of the relative ratios of cage rate constants from the relative product ratios (14 pages). Ordering information is given on any current masthead page.

(26) (a) Professor Brown has evidence that, once out of the cage, cage reentry can occur as expected to both the α and β faces of $Co^{II}B_{12r}$, after which recombination occurs (of the α and β [Ado$^\bullet$ $^\bullet$Co^{II}Cbi$^+$] caged pairs) to yield only α and β AdoCbi$^+$, respectively.[8d] (b) α and β isomers of alkylcobamides: Brown, K. L.; Zou, X.; Salmon, L. *Inorg. Chem.* **1991**, *30*, 1949 and references therein. (c) For additional lead references to α and β isomers of alkylcobamides, see ref 23b and ref 1–12 therein.

(27) We wondered whether the α-AdoCbi$^+$ isomer can also give the 4′,5′-didehydroadenosine product; the following experiment shows that it can. A standard solution of 1×10^{-4} M α-AdoCbi$^+$ in ethylene glycol was thermolyzed and then analyzed by HPLC using the 10% CH_3CN/90% H_2O conditions. The results show that 2% of 4′,5′-didehydroadenosine is formed, an amount smaller than the 33% produced by β-AdoCbi$^+$ under identical conditions, results fully consistent with the generally accepted lower steric crowding (and thus more efficient cage reaction) of the β face of B_{12}. (The other products were 2% adenine, 19% 5′-deoxyadenosine, and 77% 8,5′-anhydroadenosine.)

(28) (a) Halpern, J.; Kim, S.-H.; Leung, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 8317. The specific suggestion of Co–C homolysis as a route to adenine was made during the following presentation: Halpern, J. *J. Inorg. Biochem.* **1989**, *36*, 192 (an abstract). (b) See also the discussion in ref 29, pp 256–259 (and the footnotes on those pages).

(29) Finke, R. G. In *Molecular Mechanisms in Bioorganic Processes*; Bleasdale, C., Golding, B. T., Eds.; The Royal Society of Chemistry: Cambridge, England, 1990.

(30) Two valuable papers recently appeared describing the solvent and structural effects on nitroxide radical trapping rate constants, including data for TEMPO: Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983. Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *114*, 4992.

(31) See the discussion in Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J., Ed.; John-Wiley: New York, 1973; Vol. 1, p 166.

(32) Watts, H. P.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 911.

(33) (a) The only reliable comparison presently possible is to the (intrinsically different)[12b] photochemical $F_{c,p}$ values[11] obtained in a 1.50 cP viscosity solution at 22 °C [consisting of 40 mL of paraffin oil/19.6 mL of CCl_4/and enough hexane (1.0 cP viscosity at 20 °C) to total 100 mL]. Those results are $F_{c,p} = 0.331 \pm 0.03$ for $[(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3]_2$ and $F_{c,p} = 0.62 \pm 0.08$ for $[(\eta^5\text{-}C_5H_4CH_3)W(CO)_3]_2$. (b) We emphasize that F_c and $F_{c,p}$ values are of course viscosity (and thus temperature) dependent,[11,12c] increasing with increasingly viscous solvents (and with decreasing temperature). Hence, it is important that F_c (or $F_{c,p}$) comparisons be at constant (macroscopic) viscosity [a comparison that itself ignores the possible differences between the solution structure (the "microscopic solution fluidity or viscosity") and the (macroscopic) solution viscosity as measured by the resistance to viscous flow using a standard viscometer]. (c) Our AdoCbi$^+$ $F_c \geq 0.94$ value in 110 °C, 1.7 cP viscosity ethylene glycol is *apparently* larger than the $F_c \geq 0.4$ that we obtain for AdoCbl measured under identical conditions (apparently because of the ≥ inequality);[15] it is also larger than the reported F_c values of unknown reliability[12] of $F_c = 0.6$ for AdoCbl in 108 °C, ca. 1.6 cP viscosity 70% glycerol/H_2O or the photochemical $F_{c,p} \approx 0.27$ for AdoCbi$^+$ in ca. 1.6 cP viscosity 20% glycerol/H_2O (extrapolated from Table I[12c]).