Figure 2B shows part of the 2D ROESY spectrum, recorded with a 60-ms mixing time. A large number of intense NOE interactions can be seen between the amide/aromatic resonances and the aliphatic resonances. In the spin-locked NOE method, originally proposed by Bothner-By et al.,[12] the NOE is always positive, independent of the molecular correlation time. Spin diffusion effects are therefore generally not observed[17] and the interpretation of NOE intensities may be more straightforward. Relay of NOE intensity via the HOHAHA effect[17,18] could in principle give rise to false NOE cross peaks. In practice, these types of relay peaks in proteins are limited almost exclusively to NOE interactions with a methylene proton, where Hartmann-Hahn relay to the second methylene proton can occur. Because methylene protons are commonly treated with the pseudoatom approach,[19] this does not affect the structure refinement process. Another interesting feature of the spin-locked NOE spectrum is that NOE and exchange cross peaks are of opposite sign. Exchange cross peaks between NH and H_2O resonances in Figure 2B are not visible (apart from small truncation artifacts from these intense resonances) because only resonances with opposite sign to the diagonal (NOE cross peaks) are displayed in this spectrum. A cross section taken at the H_2O F_1 frequency is shown along the left-hand side of the 2D spectrum and displays the amide protons that show a significant amount of hydrogen exchange during the 60-ms mixing period.

The approach described above makes it possible to record HOHAHA and ROESY spectra in H_2O solution in a routine fashion. Neither of the two experiments is particularly critical to fine tuning of parameters and the final spectra do not require any base-line correction procedure. To the best of our knowledge, Figure 2B also represents the first application of spin-locked NOE to a protein. The spectrum indicates that the quality is comparable to that of a NOESY spectrum; major advantages are that spin diffusion is eliminated and that chemical exchange peaks are identified by their opposite sign.

(17) Bax, A.; Sklenar, V.; Summers, M. F. *J. Magn. Reson.* **1986**, *70*, 327.
(18) Neuhaus, D.; Keeler, J. *J. Magn. Reson.* **1986**, *68*, 568.
(19) Wuthrich, K.; Billeter, M.; Braun, W. *J. Mol. Biol.* **1983**, *180*, 949.
(20) Wagner, G.; Wuthrich, K. *J. Mol. Biol.* **1982**, *155*, 347.

Formation and Dehydration of an (α,β-Dihydroxyethyl)rhodium Porphyrin Complex: Potential Relevance to Coenzyme B_{12}-Substrate Complexes

Bradford B. Wayland,* Seth L. Van Voorhees, and Kenneth J. Del Rossi

Department of Chemistry and the Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received May 22, 1987

Diol dehydratase functions in concert with coenzyme B_{12}, (5′-deoxyadenosyl)cobalamin (Co-CH_2R), to catalyze the dehydration of vicinal diols to aldehydes through the intermediacy of geminal diol species (eq 1),[1,2] One of the proposed pathways

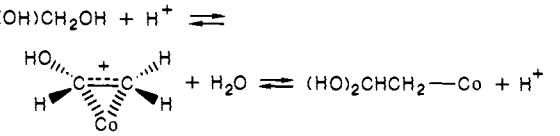
$$RCH(OH)CH_2(OH) \rightarrow RCH_2CH(OH)_2 \rightarrow RCH_2CHO + H_2O \quad (1)$$

for diol dehydratase catalyzed dehydration of ethylene glycol involves the formation and interconversion of organometallic intermediates derived from B_{12r}, (Co^{II}•), and the substrate radical (•$CH(OH)CH_2OH$) (eq 2 and 3).[1-4] Dehydroxylation of the

$$Co^{II}\bullet + \bullet CH(OH)CH_2(OH) \rightleftharpoons Co\text{-}CH(OH)CH_2(OH) \quad (2)$$

$$Co\text{-}CH(OH)CH_2(OH) \rightleftharpoons Co\text{-}CH_2CH(OH)_2 \quad (3)$$

β-OH group of Co-$CH(OH)CH_2(OH)$ by an acid site, assisted by formation of a vinyl alcohol π-complex and subsequent readdition of hydroxide to the π-complex, has been suggested as a convenient route to the required geminal diol species.[2] Model



studies focused on emulating the pathway utilizing organometallic intermediates have had considerable success,[5-10] but investigations using cobalt macrocycles are limited by the thermodynamic and kinetic instability of α-hydroxyalkyl complexes relative to dissociation into aldehyde and metal hydride.[11,12] Mulac and Meyerstein have succeeded in forming the proposed cobalamin-substrate complex Co-$CH(OH)CH_2(OH)$ by the reaction of $Co^{II}\bullet$ (B_{12r}) with the substrate radical •$CH(OH)CH_2(OH)$,[6a] which mimics the manner by which the cobalamin-substrate complex would form in the enzymatic reaction. Co-$CH(OH)CH_2(OH)$ is a transient species in neutral aqueous media and dissociates into $Co(I)^-$, H^+, and $CH_2(OH)CHO$ without observation of the dehydration reaction,[6] and this result has been used as evidence against invoking Co-$CH(OH)CH_2(OH)$ as an intermediate in the enzymatic dehydration of vicinal diols.[13] However, Co-C-$H(OH)CH_2(OH)$ would be kinetically stabilized toward formation of glycoaldehyde in the enzyme environment by use of the α-OH group in substrate-protein binding. A thermodynamically stable complex that models Co-$CH(OH)CH_2(OH)$ outside of the enzyme environment is needed in order to evaluate whether or not this type of complex could be useful in the enzymatic substrate reactions.

Rhodium macrocycles are potentially useful model complexes for the cobalt macrocycle in B_{12} due to their related electronic structures (Co(III), $3d^6$; Rh(III), $4d^6$) and because the substantially stronger Rh-C bond[14,15] provides thermodynamic stabilization for organometallic species that may have only transient existence in the analogous cobalt species. One of the consequences of the strong Rh-C bond is the observation of α-hydroxyalkyl complexes of rhodium porphyrins[12,16] in equilibrium with rhodium porphyrin hydrides and aldehydes, where the corresponding cobalt porphyrin derivatives have not been detected. This paper reports on the formation and dehydration of the α,β-dihydroxyethyl derivative of rhodium octaethylporphyrin, (OEP)Rh-$CH(OH)CH_2OH$ (**1**), which may be relevant to the structure and reactivity

(1) Golding, B. T. B_{12}; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, pp 543-582.
(2) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114.
(3) Babior, B. M. *J. Biol. Chem.* **1970**, *245*, 6125.
(4) Silverman, R. B.; Dolphin, D.; Babior, B. M. *J. Am. Chem. Soc.* **1972**, *94*, 4028.
(5) (a) Silverman, R. B.; Dolphin, D.; Carty, T. J.; Krodel, E. K.; Abeles, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 7096. (b) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 4626.
(6) (a) Mulac, W. A.; Meyerstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 4124. (b) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540.
(7) (a) Brown, K. L.; Chu, M. M. L.; Ingraham, L. L. *Biochemistry* **1976**, *15*, 1402. (b) Brown, K. L.; Ramamurthy, S. *Organometallics* **1982**, *1*, 413.
(8) Finke, R. G.; McKenna, W. *J. Chem. Soc., Chem. Commun.* **1980**, 460.
(9) (a) Golding, B. T.; Sakrikar, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1183. (b) Golding, B. T.; Holland, H. L.; Horn, U.; Sakrikar, S. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 959.
(10) Schrauzer, G. N.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1022.
(11) (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927. (b) Vaughn, G. D.; Gladysz, J. A. *J. Chem. Soc.* **1981**, *103*, 5608.
(12) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634.
(13) Finke, R. G.; Schiraldi, D. A.; Mayer, B. J. *Coord. Chem. Rev.* **1984**, *54*, 1.
(14) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.
(15) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.
(16) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

0002-7863/87/1509-6513$01.50/0

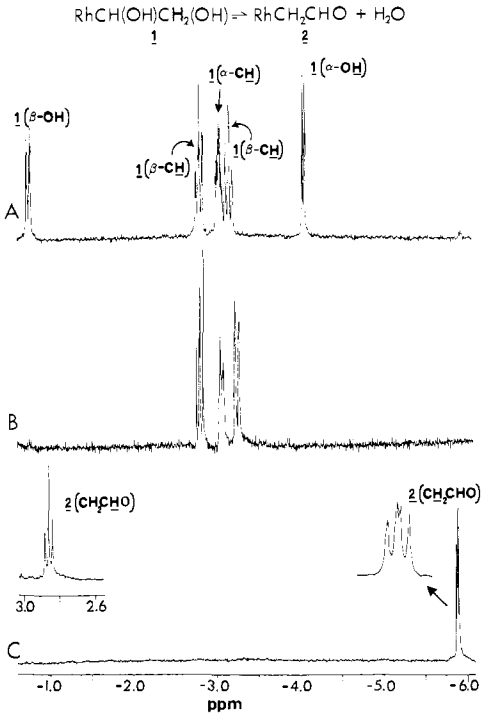


Figure 1. High-field region of ^1H NMR spectra for (OEP)Rh–X in THF-d_8: (A) X = $CH(OH)CH_2(OH)$; (B) X = $CH(OD)CH_2(OD)$; (C) X = CH_2CHO.

of potential cobalamin–substrate complexes in diol dehydratase catalyzed reactions.

Glycolaldehyde ($HOCH_2CHO$) is found to react with rhodium octaethylporphyrin hydride ((OEP)Rh–H) in THF or benzene solution to produce an equilibrium distribution with (OEP)Rh–$CH(OH)CH_2OH$ (**1**) (eq 4). Proton NMR spectra of **1** (Figure

$$(OEP)Rh–H + HOCH_2CHO \rightleftarrows (OEP)Rh–CH(OH)CH_2OH \quad (4)$$

1A) have been assigned with the aid of both decoupling experiments and deuteriation of the hydroxyl functional groups (Figure 1B).[17] The ^1H NMR peaks on the high-field side of TMS are unambiguously associated with the $-CH(OH)CH_2(OH)$ unit bonded to Rh(OEP) (Figure 1). Inequivalent coupling of the β-OH with the diastereotopic methylene hydrogens (2.9 and 10.3 Hz) clearly indicates a preferred gauche conformation of the OH groups similar to that observed for ethylene glycol.[18]

Dehydration of **1**, which occurs slowly (~24 h) at 80 °C in benzene, is observed to be catalyzed by acids (CF_3CO_2H, CF_3SO_3H) such that formation of (OEP)Rh–CH_2CHO (**2**) is completed within the time required to record the NMR spectrum (Figure 1C) (eq 5). Compound **2** is the exclusive product from

$$(OEP)Rh–CH(OH)CH_2OH \rightleftarrows (OEP)Rh–CH_2CHO + H_2O \quad (5)$$

the acid-catalyzed dehydration of **1**. Acid catalysis of reaction 5 probably occurs by selective dehydroxylation of the β-OH in **1** assisted by formation of an intermediate vinyl alcohol π-complex, $[(OEP)Rh(CH(OH)=CH_2)]^+$. Rapid formation of **2** has thus far prohibited the direct observation of the proposed vinyl alcohol π-complex intermediate, but an organometallic species of this type is clearly observed upon dehydroxylation of the β-hydroxyethyl derivative (OEP)Rh–CH_2CH_2OH (**3**), prepared by reaction of (octaethylporphyrin)rhodium(I) anion with ethylene oxide.[19]

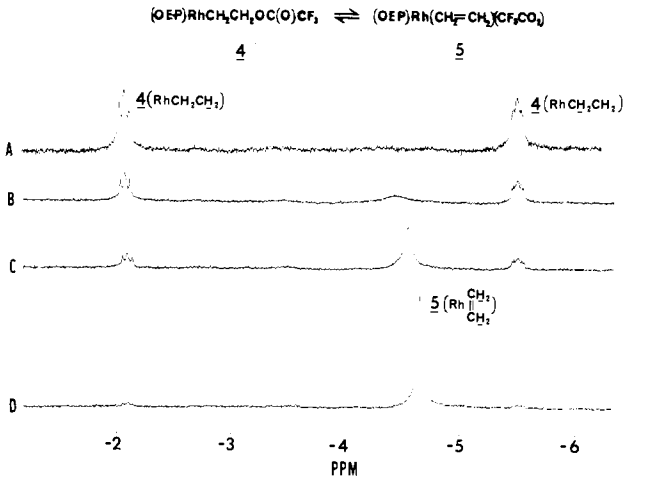


Figure 2. Variable-temperature ^1H NMR spectra for a toluene-d_8 solution of (OEP)Rh–CH_2CH_2OH with a 30-fold excess of CF_3COOH: (A) 315 K; (B) 295 K; (C) 268 K; (D) 243 K.

When a toluene solution of **3** is mixed with CF_3CO_2H at 295 K, an equilibrium distribution of two new species is observed in the ^1H NMR spectrum (Figure 2)[20] (eq 6 and 7). The pair of

$$(OEP)Rh–CH_2CH_2OH + CF_3CO_2H \rightleftarrows (OEP)Rh–CH_2CH_2OC(O)CF_3 + H_2O \quad (6)$$

$$(OEP)Rh–CH_2CH_2OC(O)CF_3 \rightleftarrows (OEP)Rh(CH_2=CH_2)(CF_3CO_2) \quad (7)$$

multiplets (δ = −1.99 and −5.38) are assigned to (OEP)Rh–$CH_2CH_2OC(O)CF_3$ (**4**), and the singlet (δ = −4.46) is assigned to a symmetrically bonded π-ethene complex, $(OEP)Rh(CH_2=CH_2)(CF_3CO_2)$ (**5**), in analogy with the recently reported isoelectronic complex $(OEP)Ru(CH_2=CH_2)$ (δ = −4.0).[21] Both reactions 6 and 7 are well-behaved equilibria. Addition of hydroxide results in re-formation of **3**, and the reversible temperature dependence (Figure 2) has been analyzed to give the enthalpy change for reaction 7 ($\Delta H°_7$ = −5.9 ± 0.5 kcal). When the stronger acid CF_3SO_3H is used, only the NMR corresponding to **5** is observed (δ = −4.43). Observation of a π-ethene complex of Rh^{III}(OEP) reinforces previous studies on related cobalt species that provided evidence for π-alkene complexes of cobalt(III).[2,5,9]

Scheme I outlines a possible pathway for the enzymatic dehydration of ethylene glycol that invokes cobalamin–substrate complexes as intermediates.

Scheme I

$$Co–CH_2R \rightleftarrows Co^{II\bullet} + {}^\bullet CH_2R \quad (i)$$

$${}^\bullet CH_2R + CH_2(OH)CH_2(OH) \rightleftarrows CH_3R + {}^\bullet CH(OH)CH_2(OH) \quad (ii)$$

$$Co^{II} + {}^\bullet CH(OH)CH_2(OH) \rightleftarrows Co–CH(OH)CH_2(OH) \quad (iii)$$

$$Co–CH(OH)CH_2(OH) \rightleftarrows Co–CH_2CH(OH)_2 \quad (iv)$$

$$Co–CH_2CH(OH)_2 \rightleftarrows Co^{II\bullet} + {}^\bullet CH_2CH(OH)_2 \quad (v)$$

$$(OH)_2CHCH_2{}^\bullet + CH_3R \rightleftarrows (OH)_2CHCH_3 + {}^\bullet CH_2R \quad (vi)$$

$$Co^{II\bullet} + {}^\bullet CH_2R \rightleftarrows Co–CH_2R \quad (vii)$$

$$CH_3CH(OH)_2 \rightleftarrows CH_3CHO + H_2O \quad (viii)$$

(17) ^1H NMR data (ppm) for **1** (THF-d_8, 295 K): 10.12 (s, 4 H, CH=), 4.10 (m, 16 H, CH_2CH_3), 1.91 (t, 24 H, CH_2CH_3), −0.69 (dd, 1 H, β-OH), −2.80 (m, 1 H, β-CH, J_{gem} = 11.5 Hz, J_{trans} = 9.35 Hz, J_{HOH} = 2.9 Hz), −3.04 (m, 1 H, α-CH, J_{cis} = 2.52 Hz, $^2J_{RhH}$ = 2.60 Hz, J_{HOH} = 6.6 Hz), −3.15 (m, 1 H, β-CH, J_{HOH} = 10.3 Hz), −4.07 (d, 1 H, α-OH).

(18) Buckley, P.; Giguere, P. A. *Can. J. Chem.* **1967**, *45*, 397.

(19) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Organomet. Chem.* **1980**, *185*, 95.

(20) ^1H NMR data (ppm) for **4** (toluene-d_8, 295 K): 10.25 (s, 4 H, CH=), 3.99 (m, 16 H, CH_2CH_3), 1.90 (t, 24 H, CH_2CH_3), −1.99 (t, 2 H, $C_\beta H_2$, $^3J_{HH}$ = 6.6 Hz), −5.38 (m, 2 H, $C_\alpha H_2$, J_{RhH} = 3.4 Hz). ^1H NMR data (ppm) for **5** (toluene-d_8, 295 K): 10.44 (s, 4 H, CH=), 3.97 (q, 16 H, CH_2CH_3), 1.88 (t, 24 H, CH_2CH_3), −4.46 (s, 4 H, CH_2=CH_2).

(21) (a) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570. (b) Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209.

This scheme is essentially that elaborated by Abeles and Dolphin[2] but differs by terminating the role of cobalamin–substrate complexes (step v) prior to the dehydration of the geminal diol. Both enzyme[22] and model[23] studies have provided convincing evidence that a β-formyl complex, Co–CH_2CHO, cannot be a productive intermediate. In this modified scheme, formation of the geminal diol (step iv) results in a change in the substrate derivative–protein binding that promotes homolysis of the Co–$CH_2CH(OH)_2$ bond (step v) in a manner that parallels the generally accepted role of substrate binding in triggering the Co–CH_2R bond homolysis (step i).[1,2] Deconvolution of the overall process into this set of individual steps is rather artificial in that several steps could occur simultaneously in concerted transformations. As an example, formation of the substrate radical and subsequent binding with cob(II)alamin (steps ii and iii) could occur in a concerted process. The term cobalamin–substrate complex is also an exaggeration and probably should be replaced with the term cobalamin–substrate interaction, because restrictions of the protein binding sites for cobalamin and the substrate would undoubtedly produce highly strained Co–C bonds.[24,25]

The first two steps, which produce the substrate radical ($^{\bullet}CH(OH)CH_2(OH)$), and steps vi–viii, which convert the geminal diol radical ($^{\bullet}CH_2CH(OH)_2$) into acetaldehyde with regeneration of coenzyme B_{12} (Co-CH_2R), are widely accepted aspects of the enzyme mechanism.[1,2,13] The pathway that the enzyme uses in directing the isomerization of 1,2-diols to 1,1-diols has not yet been convincingly elucidated, even though the enzymatic reactions have been elegantly and exhaustively studied by isotopic labeling.[26-28] The mechanisms operative in the 1,2-rearrangements in other coenzyme B_{12} dependent enzymatic reactions also remain unresolved.[29] The primary issue is whether or not cob(II)alamin formed in the initiation step interacts with the substrate radical (step iii) and directs the isomerization (step iv). An alternate pathway is for the enzyme-bound substrate radical to rearrange through a series of intermediates to products without the influence of cob(II)alamin.[13,30] EPR studies of functioning enzymes,[31,32] radical rearrangement reactions,[33-35] and model studies[6,23] have been used to illustrate the plausibility for aspects of the radical rearrangement mechanism. The mechanistic issues and relevant enzyme and models studies have been brought into focus in a recent review.[13] In our opinion, all of the results of the enzyme studies can be accommodated by a substrate rearrangement reaction that is promoted and guided by relatively weak cobalamin–substrate organometallic interactions. The principal arguments used against invoking organometallic cobalamin–substrate derivative intermediates are the lack of direct observation of these intermediates in the enzymatic reaction and absence of a model system that illustrates the proposed reactivity for the cobalamin–substrate complex, Co–$CH(OH)CH_2(OH)$.[13] Direct observation of productive intermediates is often precluded by their efficiency in producing the desired result, and when detailed kinetic mechanistic studies are made, the observed "intermediates" often prove to be involved in only nonproductive pathways.[36] Formation of (OEP)Rh–$CH(OH)CH_2(OH)$ at equilibrium has provided the first opportunity to observe the reactivity of an α,β-dihydroxyethyl complex under controlled conditions, and this model complex does manifest the type of reactivity proposed[2] for Co–$CH(OH)CH_2(OH)$. Acid-catalyzed dehydration of **1** to produce (OEP)Rh–CH_2CHO (**2**) selectively and the dehydroxylation of (OEP)Rh–$CH_2CH_2(OH)$ to form a π-ethene complex (**5**) illustrate the potential utility of cobalamin–substrate derivative interactions in promoting and directing an enzyme-catalyzed dehydration of 1,2-diols. We presently prefer the organometallic intermediate mechanism because selective β-OH dehydroxylation of Co–$CH(OH)CH_2(OH)$ and subsequent 1,2-rearrangement that converts 1,2-diols into 1,1-diols would be a natural consequence of a vinyl alcohol π-complex intermediate, $Co(CH_2{=}CH(OH))^+$. The intermediacy of cobalamin–substrate derivative complexes in diol dehydratase catalyzed reactions remains an open question, and we hope that model studies will stimulate and focus the requisite enzyme investigations.

Acknowledgment. We acknowledge the National Science Foundation for support of this research.

(22) Krouwer, J. S.; Babior, B. M. *J. Biol. Chem.* **1977**, *252*, 5004.
(23) Finke, R. G.; Schiraldi, D. A. **1983**, *105*, 7605.
(24) (a) Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869. (b) Halpern, J. In B_{12}; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 1, pp 501-541.
(25) (a) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (b) Summers, M. F.; Toscano, P. J.; Bresciani-Pahor, N.; Nordin, G. Randaccio, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1983**, *105*, 6259.
(26) Retey, J.; Umani-Ronchi, A.; Seible, J.; Arigoni, D. *Experientia* **1966**, *22*, 502.
(27) (a) Abeles, R. H. S.; Lee, N. A., Jr. *Brookhaven, Symp. Biol.* **1962**, *15*, 310. (b) Frey, P. A.; Karabatsos, G. L.; Abeles, R. H. *Biochem. Biophys. Res. Commun.* **1965**, *18*, 551. (c) Zagalak, B.; Frey, P. A.; Karabatsos, G. L.; Abeles, R. H. *J. Biol. Chem.* **1966**, *241*, 3028.
(28) Arigoni, D. *Vitamin B_{12}, Proceedings of the 3rd European Symposium on Vitamin B_{12} and Intrinsic Factor*; Zagalah, B., Friedlich, W., Eds.; W. de Gruyter: Berlin, 1979; p 389.
(29) Dowd, P.; Shapiro, M.; Kang, J. *Tetrahedron* **1984**, *40*, 3069.
(30) Dixon, R. M.; Golding, B. T.; Mwesigye-Kibende, S.; Ramakrishna Rao, D. N. *Philos. Trans. R. Soc. London, Ser. B* **1985**, *B311*, 531.
(31) (a) Babior, B. M.; Moss, T. H.; Orme-Johnson, W. H.; Beinert, H. *J. Biol. Chem.* **1974**, *249*, 4537. (b) Boas, J. F.; Hicks, P. R.; Pillbrow, J. R.; Smith, T. D. *J. Chem. Soc., Faraday Trans. 2* **1978**, 417.
(32) Pratt, J. M. B_{12}; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, pp 325-392.
(33) (a) Barchill, C. E.; Perron, K. M. *Can. J. Chem.* **1971**, *49*, 2382. (b) Bansal, K. M.; Gratzel, M.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1973**, *77*, 6.
(34) Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 794.
(35) (a) Wollowitz, S.; Halpern, J. *J. Am. Chem. Soc.* **1984**, *106*, 8319. (b) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575.
(36) (a) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746. (b) Halpern, J. *Trans. Am. Crystallogr. Assoc.* **1978**, *14*, 59. (c) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65.

Novel Organocobalt(III) Porphyrins with an Etheno Bridge between the Cobalt and a Pyrrolic Nitrogen or a Meso Carbon

Jun-ichiro Setsune,* Mitsuhiro Ikeda, and Teijiro Kitao

Department of Applied Chemistry
College of Engineering
University of Osaka Prefecture
Sakai, Osaka 591, Japan
Received May 28, 1987

Metalloporphyrins with a bridged structure between the central metal and one of the four pyrrole nitrogens have drawn much attention as it was proposed that the highly oxidized form of some hemoproteins may contain a ferric porphyrin with an oxygen atom inserted into an N–Fe bond.[1] Bridged metalloporphyrins with an M–O–N linkage (M = Cu,[2] Ni,[3] Fe[4]), an M–N–N linkage (M = Zn,[5] Fe[6]), an M–C–N linkage (M = Ni,[7] Fe,[1] Co[8]), and

(1) (a) Chevrier, B.; Lange, M.; Chottard, J.-C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899. (b) Latos-Grazynski, L.; Cheng, R. J.; La Mar, G. N.; Balch, A. L. *Ibid.* **1981**, *103*, 4270. (c) Lange, M.; Mansuy, D. *Tetrahedron Lett.* **1981**, *22*, 2561.
(2) Andrews, L. E.; Bonnet, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 103.
(3) (a) Balch, A. L.; Chan, Y. W.; Olmstead, M.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2393. (b) Balch, A. L.; Chan, Y. W.; Olmstead, M. *Ibid.* **1985**, *107*, 6510.
(4) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7836.
(5) (a) Callot, H. J. *Tetrahedron* **1979**, *35*, 1455. (b) Ichimura, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1444.
(6) Mahy, J.-P.; Battioni, P.; Mansuy, D. *Ibid.* **1986**, *108*, 1079.
(7) (a) Callot, H. J.; Tschamber, Th.; Chevrier, B.; Weiss, R. *Angew. Chem.* **1975**, *87*, 545. (b) Chan, Y. W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888.
(8) (a) Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. L.; Schelton, G.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076. (b) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 307. (c) Setsune, J.-i.; Dolphin, D. *Organometallics* **1984**, *3*, 440.

0002-7863/87/1509-6515$01.50/0