mol %) of tetrakis(triphenylphosphine)palladium(0) under argon was added 10 mL of dry THF followed by a solution of 0.51 g (1.8 mmol) of vinyl triflate **1** and 0.62 g (1.8 mmol) of tetrabutyltin in 10 mL of THF. This slurry was heated to reflux for 17 h, cooled to room temperature, and diluted with 60 mL of pentane. After washing with a 10% ammonium hydroxide solution (3 × 25 mL) and drying ($MgSO_4$), the resulting solution was filtered through a short pad of silica gel and concentrated under reduced pressure to give 0.28 g (80%) of 1-butyl-4-*tert*-butylcyclohexene[6] (example 2) as a colorless oil.

This methodology was applied to the synthesis of pleraplysillin-1 (**14**),[14] as shown in Scheme II. (*E*)-Vinyltin **11** was formed by addition of the lithium (*E*)-vinyltin cuprate **10**[15] to 3-furfuryl bromide[16] (73% yield). Triflate **13** was prepared as one regioisomer from 5,5-dimethyl-2-cyclohexenone[17] by conjugate reduction[18] followed by enolate trapping with *N*-phenyltriflimide.[12] Palladium-catalyzed coupling of **11** with **13** afforded pleraplysillin-1 (**14**) in 75% yield.[19,20] No other isomers were observed.

Thus, vinyl triflates couple with organostannanes in the presence of lithium chloride and palladium(0) catalysts to give a variety of olefin-substituted products. This reaction represents the first case of a transition-metal-catalyzed reaction of a vinyl sulfonate. In effect, this allows the conversion of the oxygen of regioselectively formed enolates into a leaving group for palladium-catalyzed reactions.

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(15) Corey, E. J.; Wollenberg, R. H. *Tetrahedron Lett.* **1975**, *16*, 2225–2226.

(16) Parker, K. A.; Johnson, W. S. *Tetrahedron Lett.* **1969**, *10*, 1329–1332.

(17) Hiegel, G. A.; Burk, P. *J. Org. Chem.* **1973**, *38*, 3637–3639.

(18) (a) Ganem, B. *J. Org. Chem.* **1975**, *40*, 146–147. (b) Fortunato, J. M.; Ganem, B. *Ibid.* **1976**, *41*, 2194–2200.

(19) For a prior synthesis of **14**, see: Masaki, Y.; Hashimoto, K.; Serizawa, Y.; Kaji, K. *Chem. Lett.* **1982**, 1879–1880.

(20) NMR and IR spectra of **14** were identical with spectra of authentic material. The authors thank Professors Faulkner, Masaki, and Minale for copies of the spectra of **14**.

Reversible Protonation of the Oxo Bridge in a Hemerythrin Model Compound. Synthesis, Structure, and Properties of (μ-Hydroxo)bis(μ-acetato)bis[hydrotris(1-pyrazolyl)borato]diiron(III), $[(HB(pz)_3)Fe(OH)(O_2CCH_3)_2Fe(HB(pz)_3)]^+$

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Recently the synthesis and properties of binuclear iron complexes that serve as structural, spectroscopic, and chemical models for the (μ-oxo)bis(μ-carboxylato)diiron(III) core of the met forms of marine invertebrate respiratory proteins hemerythrin (Hr) and myohemerythrin (myoHr)[1,2] were described.[3,4] Oxo-bridged binuclear iron centers are also believed to occur in ribonucleotide reductase from *Escherichia coli*[5] and in some purple acid phosphatases.[6] Here we report that, from the reaction mixture used by us to produce binuclear iron model compounds for metHr and metmyoHr, we have now isolated the novel hydroxo-bridged derivative $[(HB(pz)_3)Fe(OH)(O_2CCH_3)_2Fe(HB(pz)_3)]^+$ (**1**). This complex has properties quite distinct from those of the oxo-bridged model compound $[(HB(pz)_3)FeO(O_2CCH_3)_2Fe(HB(pz)_3)]$ (**2**). Compounds **1** and **2** may be reversibly interconverted by direct protonation–deprotonation reactions which, to our knowledge, are unprecedented in iron chemistry. These discoveries strongly support the current belief, based on physical studies of the proteins, that the two iron atoms in methemerythrins are linked by oxo, rather than hydroxo, bridges and raise the possibility that analogous hydroxo-bridged diiron(III) centers may exist in biology.

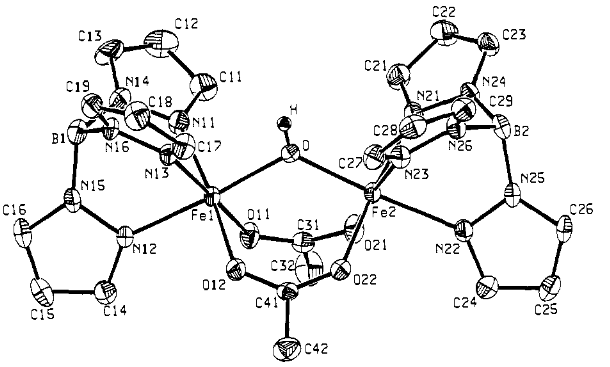

Figure 1. Structure of the (μ-hydroxo)bis(μ-acetato)bis[hydrotris(1-pyrazolyl)borato]diiron(III) cation (**1**) showing the 40% probability thermal ellipsoids and atom labeling scheme. The hydrogen atom bound to atom O is depicted at its refined position with an arbitrary *B* value of 1.0 Å^2. The remaining hydrogen atoms are omitted for clarity.

Table I. Comparison of Structural Features of $[Fe_2(OH)(O_2CCH_3)_2(HB(pz)_3)_2]^+$ (**1**)[a] and $[Fe_2O(O_2CCH_3)_2(HB(pz)_3)_2]$ (**2**)[b]

bond length, Å or angle, deg[c]	**1**[d]	**2**[d]
Fe(1)···Fe(2)	3.439 (1)	3.1457 (6)
Fe–O$_{\text{bridge}}$	1.960 (4), 1.952 (4)[e]	1.780 (2), 1.788 (2)
Fe(1)–O–Fe(2)	123.1 (2)	123.6 (1)
Fe–N	2.087 (4)–2.110 (5) mean 2.102	2.148 (3)–2.200 (3) mean 2.165
Fe–O$_{\text{acetate}}$	1.994 (4)–2.001 (4) mean 1.999	2.040 (2)–2.050 (3) mean 2.043

[a] This work. [b] Reference 3b. [c] Atoms are labeled for both compounds as shown in Figure 1. [d] Numbers in parentheses are estimated standard deviations in the last digit. [e] The H atom was first located on a difference Fourier map at 0.94 Å from the O atom; the refined O–H distance is 0.70 (6) Å.

The perchlorate salt of **1** was first isolated from the same reaction mixture that produced **2**,[3] but with use of shorter reaction times and a different workup procedure. It was found that using less than 1 equiv of $KHB(pz)_3$ per iron atom decreased the amount of $[Fe(HB(pz)_3)_2]^+$[7] in the crude product. Addition of 0.500 g (1.98 mmol) of potassium hydrotris(1-pyrazolyl)borate ($KHB(pz)_3$) in 20 mL of water to a stirred solution of 2.12 g (3.97 mmol)

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(1) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618–622. (b) Sanders-Loehr, J.; Loehr, T. M. *Adv. Inorg. Biochem.* **1979**, *1*, 235–252. (c) Wilkins, R. G.; Harrington, P. C. *Ibid.* **1983**, *5*, 51–85. (d) Klotz, I. M.; Kurtz, D. M., Jr. *Acc. Chem. Res.* **1984**, *17*, 16–22.

(2) (a) Hendrickson, W. A. In "Invertebrate Oxygen-Binding Proteins: Structure, Active Site, and Function"; Lamy, J., Lamy, J., Eds.; Marcel Dekker: New York, 1981; pp 503–515. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *Life Chem. Rep.* **1983**, *Suppl. 1*, 305–308.

(3) (a) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837–4838. (b) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *Ibid.* **1984**, *106*, 3653–3667.

(4) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem.* **1983**, *95*, 739–740.

(5) (a) Reichard, P.; Ehrenberg, A. *Science (Washington, D.C.)* **1983**, *221*, 514–519. (b) Sjöberg, B.-M.; Gräslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87–110. (c) Lammers, M.; Follman, H. *Struct. Bonding (Berlin)* **1983**, *54*, 27–91.

(6) (a) Davis, J. C.; Averill, B. A. *Proc. Nat. Acad. Sci. U.S.A.* **1982**, *79*, 4623–4627. (b) Antanaitis, B. C.; Aisen, P.; Lilienthal, H. R. *J. Biol. Chem.* **1983**, *258*, 3166–3172. (c) Sinn, E.; O'Connor, C. J.; de Jersey, J.; Zerner, B. *Inorg. Chim. Acta* **1983**, *78*, L13–L15. (d) Antanaitis, B. C.; Ainsen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111–136.

(7) Armstrong, W. H.; Lippard, S. J., manuscript in preparation.

0002-7863/84/1506-4632$01.50/0

of $Fe(ClO_4)_3{\cdot}10H_2O$ and 1.08 g (7.94 mmol) of $NaO_2CCH_3{\cdot}3H_2O$ in 20 mL of water caused immediate precipitation of a golden-brown solid. After the suspension was stirred for several minutes the precipitate was filtered off, dried briefly in air, dissolved in ~50 mL of CH_2Cl_2, and separated from the residual H_2O. The CH_2Cl_2 layer was evaporated to dryness, the residue was then dissolved in 10 mL of CH_2Cl_2, and 50 mL of Et_2O were layered on top. Orange-brown crystals formed after several days. These were collected by filtration and washed with 4 × 1 mL of CH_2Cl_2 (which removes traces of $[Fe(HB(pz)_3)_2]^+$ salts) and then by 5 mL of CH_2Cl_2/Et_2O (1:2) to yield 0.194 g (22.8% based on $KHB(pz)_3$) of $\mathbf{1}(ClO_4){\cdot}CH_2Cl_2$. The air-dried crystals proved to be suitable for X-ray diffraction studies. A portion of this material was powdered, dried in vacuo, and analyzed.[8]

The structure[9] of **1**, shown in Figure 1, consists of two iron atoms bridged by hydroxide and two acetate groups with two capping tridentate hydrotris(1-pyrazolyl)borate ligands. The H atom position of the hydroxo group was located on a difference Fourier map and refined. The geometry is similar to that of **2** with the principal difference being the longer Fe–O–Fe distances (Table I), which agree with results for other hydroxo-bridged diiron(III) complexes.[10] The Fe–O–Fe angles in compounds **1** and **2** are virtually identical. The Fe–N and $Fe{-}O_{acetate}$ bond lengths in **1** are characteristic of high-spin iron(III) and are slightly shorter than in **2**. Lengthening of bonds trans to the bridging oxygen atom is not evident in **1** in contrast to the findings for **2** and for azidometmyohemerythrin.[3]

The magnetic and spectral properties of **1**[8] differ markedly from those of **2** and the methemerythrins.[3b] Preliminary magnetic susceptibility data were obtained on powdered samples of the perchlorate salt of **1** by SQUID susceptometry in the range 6 K $\leq T \leq$ 300 K and were fit to the expression[11] for χ_M vs. T derived from the spin-exchange Hamiltonian, $H' = -2J\vec{S}_1{\cdot}\vec{S}_2$, with $S_1 = S_2 = {}^5/_2$ using $g = 2.0$, TIP = 0, and $J = -17$ cm^{-1}. This J value reveals substantially less magnetic coupling than in the oxo-bridged complex **2**, which has $J = -121$ cm^{-1},[3] or in methemerythrin, $J = -134$ cm^{-1}.[12] The room-temperature (300 K) moment of **1**, 4.36 μ_B per iron atom, compares favorably with the value of 4.42 μ_B obtained in CD_2Cl_2 solution at 295 K by using an NMR method.[13] The O–H stretching frequency occurs at 3560 cm^{-1} in the infrared spectrum and shifts to 2640 cm^{-1} in the O–D derivative prepared in the same fashion using D_2O. The ultraviolet spectrum of **1** consists of a single broad absorption with a maximum at 375 nm; there is no absorption in the 320–340-nm region. The spectra of **2** and the methemerythrins all have a strong, characteristic band at ~320–340 nm. Paramagnetically shifted resonances in the ^1H NMR spectrum of **1** in CD_2Cl_2 were detected in the range +14 to –69 ppm at 295 K (positive shifts are upfield from Me_4Si). In the more strongly coupled compound **2**, all proton NMR resonances occur between –3.0 and –12.2 ppm. In contrast to another hydroxo-bridged diiron(III) compound[10a] that has only a broad resonance centered at $g = 2$, the X-band ESR spectrum of powdered $\mathbf{1}(ClO_4)$ has several resonances in the range 0–5.3 kOe. Titration experiments followed by optical spectroscopy reveal that **1** may be directly generated from **2** by protonation using $HBF_4{\cdot}Et_2O$ in CH_2Cl_2/Et_2O solution. Spectrophotometric studies also showed that deprotonation of **1** to yield **2** can be effected by Et_3N in CH_2Cl_2.[14]

In summary, the protonated (hydroxo-bridged) derivative **1** of our previously reported synthetic hemerythrin model **2** has been isolated from aqueous solution and structurally characterized. The facile interconversion of **1** and **2** by direct protonation–deprotonation reactions is noteworthy. The stability of **1** is most likely due to the presence of the additional carboxylate bridges. Marked differences in the spectral and magnetic properties of this new hydroxo-bridged diiron(III) complex compared to oxo-bridged analogues substantiate the assignment of oxo vs. hydroxo bridges in the methemerythrins and should facilitate the identification of species such as **1** in biological systems.

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Registry No. $\mathbf{1}(ClO_4){\cdot}CH_2Cl_2$, 90886-32-1.

Supplementary Material Available: Atomic positional and thermal parameters for compound $\mathbf{1}(ClO_4){\cdot}CH_2Cl_2$ (4 pages). Ordering information is given on any current masthead page.

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(8) Analytical, magnetic, and spectroscopic data. Anal. Calcd for $Fe_2C_{22.5}H_{28}B_2Cl_2N_{12}O_9$ [$\mathbf{1}(ClO_4){\cdot}0.5CH_2Cl_2$]: C, 33.17; H, 3.46; N, 20.63; Cl, 8.70. Found: C, 32.81; H, 3.63; N, 20.38; Cl, 8.68; IR (KBr cm^{-1}) 3560 (OH), 2520 (BH), 1560 (ν_a, COO), 1440 (ν_s, COO), 1100 (ClO_4); magnetic susceptibility, solid state [(T, K) μ_{eff}/Fe atom] (300) 4.36, (201) 3.81, (100) 2.76, (26) 1.26, (6) 0.26, (solution 300 K (CD_2Cl_2)) 4.42 μ_B per iron; UV spectrum (CH_2Cl_2) λ 375 nm (ϵ_{Fe} 4750 cm^{-1} M^{-1}); proton NMR spectrum (250 MHz, 295 K, CD_2Cl_2) δ –68.7, –61.0, –37.1, –28.0, +13.6; X-band ESR spectrum maxima and minima (9.165 GHz) ~0.3, 0.6, 1.23, 2.00, 2.85, 4.45, 5.33 kOe.

(9) X-ray analysis: The compound $[Fe_2(OH)(O_2CCH_3)_2(HB(pz)_3)_2](ClO_4){\cdot}CH_2Cl_2$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 11.756$ (2) Å, $b = 19.925$ (4) Å, $c = 15.580$ (2) Å, $\beta = 92.03$ (1)°, $V = 3647.1$ Å^3, $\rho_{obsd} = 1.55$ (1) g cm^{-1}, $\rho_{calcd} = 1.561$ g cm^{-1}, $Z = 4$. With the use of 3658 unique observed reflections collected at 258 K with Mo K$\bar{\alpha}$ ($\lambda = 0.7107$ Å) radiation out to $2\theta = 48°$ on a single-crystal X-ray diffractometer, the structure was solved by standard direct and difference Fourier methods and refined anisotropically to a current value for the discrepancy index R_1 of 0.048. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

(10) (a) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 2781–2784. (b) Ou, C. C.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2053–2057. (c) Thich, J. A.; Ou, C. C.; Powers, D.; Vasiliou, B.; Mastropaolo, D.; Potenza, J. A.; Schugar, H. J. *Ibid.* **1976**, *98*, 1425–1433.

(11) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 204–283 and references cited therein.

(12) Dawson, J. W.; Gray, H. B.; Hoenig, H. E.; Rossman, G. R.; Schredder, J. M.; Wang, R.-H. *Biochemistry* **1972**, *11*, 461–465.

(13) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(14) The identity of the products in both the protonation and deprotonation reactions was confirmed by proton NMR and infrared spectroscopy.

Cluster Mimetics. 1. The Preparation and Characterization of $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}BH_4)$

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Metallaboranes mimic structural aspects of metal clusters, metal hydroborate complexes, and metal–hydrocarbon π complexes.[1] Particularly striking comparisons between isoelectronic compounds, e.g., $HFe_4(CO)_{12}CH$[2] vs. $HFe_4(CO)_{12}BH_2$[3] and $H_2Os_3(CO)_9CCO$[4] vs. $H_3Os_3(CO)_9BCO$,[5] which differ only in the spatial location of a proton, have been pointed out. In these cases the relative response of cluster geometry and electron density distribution to proton location can be an elegant source of information on cluster bonding.[6] Herein we report the preparation and characterization of a new ferraborane which is isoelectronic with $H_3Fe_3(CO)_9CH$[7]

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(1) Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57.

(2) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem Soc.* **1980**, *102*, 4540. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1980**, *102*, 4542; **1981**, *103*, 1485.

(3) Wong K. S., Scheidt, W. R.; Fehlner, T. P. *J. Am. Chem. Soc.* **1982**, *104*, 1111. Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

(4) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185.

(5) Shore, S. G.; Jan, D.-Y.; Hsu, L.-H.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(6) Wong, K. S.; Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203.

(7) Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966.