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 $\leqslant T \leqslant$ 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.

Acknowledgment. This work was supported by National Institutes of Health Grant GM-32134 from the National Institute of General Medical Sciences. W.H.A. gratefully acknowledges support under NCI Training Grant CA-09112. Magnetic measurements were made at the SQUID magnetometer facility of the Francis Bitter National Magnet Laboratory.

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.

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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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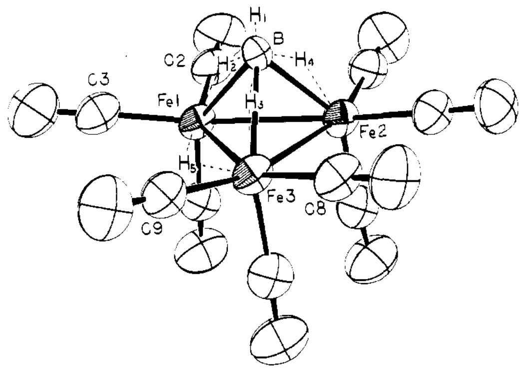

Figure 1. Structure of $HFe_3(CO)_9BH_4$. The hydrogen atom locations indicated are based on the spectroscopic results.

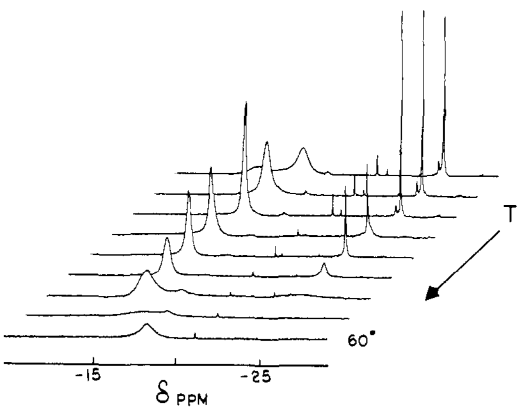

Figure 2. Variable-temperature 300-MHz ^1H NMR spectra of I in $C_6D_5CD_3$ in the hydride region. Nominal temperatures decrease in 20 °C steps beginning with a 60 °C spectrum. The resonance at 3.2 (not shown) sharpens on cooling due to thermal decoupling; however, no exchange of this proton with the other four protons is observed. The signals at δ −24, −20, and −17 (lowest temperature spectrum) are minor known impurities.

and an isolobal analogue of $HFe_3(CO)_9SR$,[8] B_4H_8,[9] $B_2H_6Fe_2(CO)_6$,[10] and $H_4Ru_4(CO)_{12}$.[11] The compound also can be considered to contain a tridentate tetrahydroborate ligand capping a trimetal cluster, and its fluxional properties provide further insight on the mobility of hydrogen atoms on a molecular cluster.

The reaction of $Na[Fe(CO)_4C(O)CH_3]$ in THF with 2 equiv of commercial BH_3·THF at 70 °C for 1 h yields a red mixture of anionic ferraboranes and iron carbonyl hydrocarbyls.[12] Removal of the solvent, followed by treatment with 80% aqueous H_3PO_4 and extraction with hexane, yields an orange-brown extract. Chromatography on silica gel followed by recrystallization at −10 °C from hexane yields red-orange needles of the title compound, I. The compound is modestly air stable, and measurement of the spectroscopic properties[13] permits the formulation of I as $(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-}BH_4)$.

Confirmation of structure and geometrical details of I resulted from a single-crystal X-ray structure determination[14] summarized in Figure 1. The structure consists of a metal triangle of $Fe(CO)_3$ fragments capped with a boron. Each iron atom is six-coordinate with an approximately octahedral arrangement of nearest neighbors and has three CO ligands in an eclipsed arrangement. There are one long (2.674 (2) Å) and two short (2.602 (2), 2.591 (2) Å) iron–iron distances in the triiron triangle, suggesting placement of the metal–metal bridging hydride on the Fe_1Fe_3 edge (Figure 1). This is confirmed by the displacement of the carbonyl groups away from that edge: e.g. the $Fe_1Fe_3C_9$ and $Fe_3Fe_1C_3$ angles are 108.6 (3)° and 108.9 (3)°, respectively, while the $Fe_2Fe_3C_8$ and $Fe_2Fe_1C_2$ angles are 92.7 (3)° and 90.8 (3)°, respectively. Although the H atoms are not observed at the present state of refinement, it is clear from the spectroscopic data[13] that the iron triangle is capped with a BH_4 group and that each iron is joined to the capping boron via an FeHB interaction. The Fe–B distances (2.199 (8), 2.130 (9), 2.176 (9) Å) indicate that these bonds are of the open three-center type.[15]

The BH_4 moiety in I suggests a description of I as an anionic, tridentate tetrahydroborate ligand capping a $HFe_3(CO)_9^+$ fragment. As such the BH_4^- ligand is a six-electron donor to the metal framework, and I would be classed as a saturated 48-electron cluster.[16] A comparison of the geometrical parameters of I with those of $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$,[8] in which the iron triangle is only slightly perturbed by the presence of the Fe–H–Fe bridge, shows that the μ_3-BH_4 ligand has a substantially larger "bite" than the μ_3-SR ligand. This permits a greater rearrangement of the $Fe_3(CO)_9$ fragment to accommodate the ligand requirements of the Fe–H–Fe hydride.

The validity of this simple view is challenged by the ^1H NMR behavior of I. Although the spectrum of I at low temperatures is in full agreement with the solid-state structure illustrated in Figure 1, at elevated temperatures fluxional behavior is observed. At about −50 °C (Figure 2) H_2, H_3, and H_4 become equivalent while at about 60 °C H_2, H_3, H_4, and H_5 exchange rapidly on the NMR time scale. At temperatures up to 60 °C there was no evidence for the participation of H_1 in the exchange processes. In contrast, typical tetrahydroborate complexes[17] exhibit fluxionality in which *all* four hydrogens are involved; i.e., M–H bond rupture is involved. In I H–B bond rupture takes place in preference to Fe–H rupture. Note that the same preference was observed in $B_5H_9Fe(CO)_3$,[18] a compound that contains an Fe–H–B interaction as part of the cluster framework.

$H_3Fe_3(CO)_9CH$[7] (II), which is isoelectronic with I, has three bridging hydrogens spanning the metal–metal edges rather than the carbon–metal edges. Noting a report that on treatment with Lewis bases $H_3Os_3(CO)_9CH$ generates CH_4,[19] a reaction that must involve the transit of the Os–H–Os hydrogens from bridging positions to the capping carbon, we suggest I as a transition-state model for such a reaction. The mobility of hydrogens on the skeleton of I suggests a similar mobility may be a characteristic of II.

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(13) ^1H NMR ($C_6D_5CD_3$, −90 °C), 3.2 (br s, 1 H), −12.8 (br s, 1 H), −15.8 (br s, 2 H), −24.4 (s, 1 H); ^{11}B NMR (C_6D_6, 20 °C) 1.8 (br m, 230 Hz fwhm) {^1H}(br s); IR (hexane, cm^{-1}) 2095 m, 2058 vs, 2038 vs, 2026 vs 2017 m sh, 2008 m sh, 1984 m; MS, the mass spectrum was confused by the presence of small (by NMR) amounts of $HFe_3(CO)_9H_3BR$, R = CH_3 and C_2H_5, in the sample. The presence of I in the vapor was confirmed by the observation of the $BH_5Fe_3^+$ ion resulting from the loss of nine CO's from the parent ion (183.855 measured 183.853 calcd).

(14) The compound crystallizes in the space group $P\bar{1}$ with $a = 8.823$ (5) Å, $b = 11.523$ (5) Å, $c = 7.850$ (4) Å, $\alpha = 98.89$ (4)°, $\beta = 109.82$ (4)°, $\gamma = 87.92$ (4)°, $V = 741.7$ (6) Å^3. The current final conventional residual is $R = 0.061$ and the weighted residual $R_w = [\sum\omega(F_o - F_c)^2/\sum\omega F_o^2]^{1/2} = 0.079$. The largest difference Fourier peak is 1.2 $e^-/Å^3$. Data (3982) were collected on a Syntex $P\bar{1}$ equipped with a graphite monochromated Mo Kα radiation source using θ–2θ scans. Of the independent data, 2157 were regarded as observed and used in the refinements. The temperature factors of all the atoms were treated anisotropically. Check reflections monitored during data collection did not vary significantly. The measured density, complicated by some decomposition, is 1.88 g/cm^3. The density calculated for $Z = 2$ is 1.950 g/cm^3. An empirical absorption correction varying between 0.65 and 1.27 (0.98 av) has been made [μ(Mo Kα) = 29.3 cm^{-1}].

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Registry No. I, 64867-63-6; Na[$Fe(CO)_4C(O)CH_3$], 91128-40-4.

Supplementary Material Available: List of atomic coordinates, thermal parameters, and selected bond angles and distances for $HFe_3(CO)_9BH_4$ (3 pages). Ordering information is given on any current masthead page.

Relaxation Kinetics in the Homogeneous Gas-Phase Photocatalytic Hydrogenation of Ethylene by $Fe(CO)_4(C_2H_4)$

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Photogenerated coordinatively unsaturated organometallic species are well noted for their catalytic activity in solution.[1-6] As a result, interest in the elementary chemistry of such species has been intense,[7-14] with a number of recent studies isolating relevant elementary reaction pathways and rate processes for reactions in the gas phase.[15-22] Significant among these is work in our own laboratory,[22] which has demonstrated for the first time that free photogenerated organometallic fragments can function as potent homogeneous catalysts for gas-phase organic transformations.

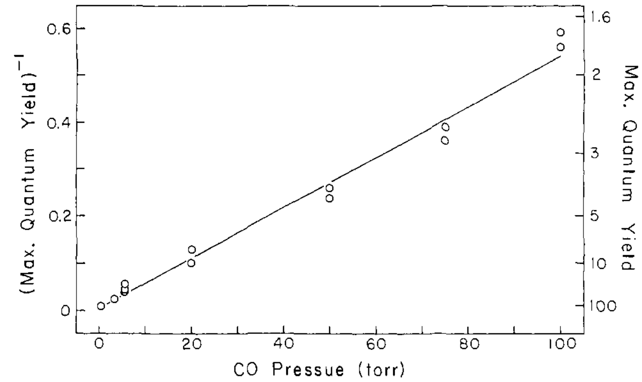

Figure 1. Reciprocal of the quantum yield vs. the total CO pressure at 43 °C and a laser repetition rate of 4 Hz. Initial substrate pressures: $Fe(CO)_5$, 0.3 torr; ethylene, 400 torr; hydrogen, 1400 torr. The plot is linear as predicted by eq 3, but there is a small positive *y* intercept due to catalyst/precatalyst interactions which also shut off catalytic activity.

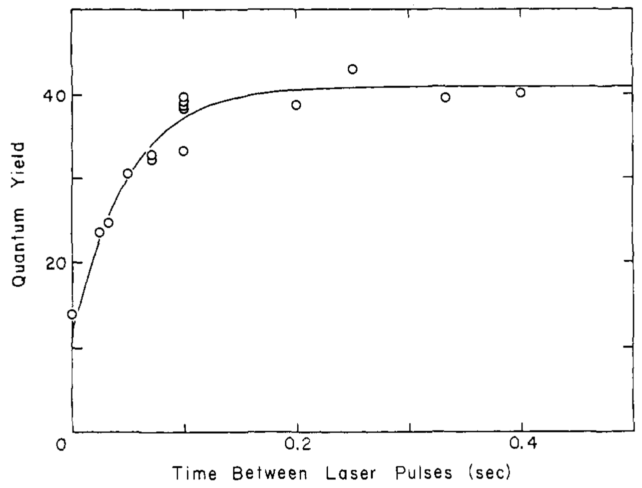

Figure 2. Quantum yield vs. time between laser pulses (reciprocal of repetition rate) at 43 °C. Initial pressures: Fe(CO), 0.3 torr; CO, 3 torr; ethylene, 400 torr; hydrogen, 1400 torr. The solid curve is our theoretical fit (see text). The continuous wave ($\Delta t = 0$) experiment was carried out with a filtered Xe arc lamp (λ 300-410 nm).

A recent study by Ouderkirk et al.[21] has established the rate of a key reaction for gas-phase photocatalysis, the recombination of an unsaturated organometallic fragment with CO to reform a stable photocatalyst precursor. They found that $Fe(CO)_4$ recombines with CO at an extraordinarily fast rate ($k \sim 10^7$ M^{-1} s^{-1}), while $Fe(CO)_3$ and $Fe(CO)_2$ react two orders of magnitude faster.

Our system adds hydrogen and ethylene to $Fe(CO)_5$, and despite the above-cited fast rate for recombinative deactivation, we find very efficient photocatalytic production of ethane. This suggests that our gas-phase organometallic photocatalytic system possesses a characteristic that sets it apart from one composed of unsubstituted $Fe(CO)_x$ fragments. The aim of the present study is to uncover that difference by examining the CO recombination kinetics of a functioning photocatalytic system.

Catalysis is initiated in our homogeneous gas-phase system by temporally distinct pulses of unfocussed light from a Lambda Physik EMG-101 excimer laser (operated on N_2, 337-nm, 1-mJ pulse energy). This light is absorbed only by the iron carbonyl component of our samples. For many experiments excess CO is

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