1544 *Organometallics* **2006,** *25,* 1544−1547

Communications

Two Novel Bridgehead-C-Substituted Diiron Propanedithiolate Complexes as Active Site Models for Fe-Only Hydrogenases

Li-Cheng Song,* Jia Cheng, Jing Yan, Hu-Ting Wang, Xu-Feng Liu, and Qing-Mei Hu

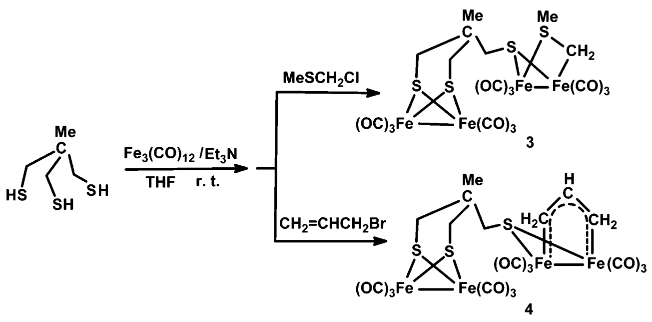
Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Received January 4, 2006

Summary: The two novel diiron propanedithiolate model compounds $[Fe_2(\mu\text{-}CH_2SMe)(\mu\text{-}SCH_2)(CO)_6][Fe_2(\mu\text{-}SCH_2)_2CMe(CO)_6]$ *(**3**) and* $[Fe_2(\mu\text{-}CH_2CH{=}CH_2)(\mu\text{-}SCH_2)(CO)_6][Fe_2(\mu\text{-}SCH_2)_2CMe(CO)_6]$ *(**4**) have been unexpectedly obtained through a "one-pot" route by reaction of the trithiol* $MeC(CH_2SH)_3$ *with* $Fe_3(CO)_{12}$ *in the presence of* Et_3N*, followed by treatment with* $MeSCH_2Cl$ *and* $CH_2{=}CHCH_2Br$*, respectively. The structures of **3** and **4** have been fully characterized, and the possible pathway for formation of **3** and **4** is suggested. In addition, some electrochemical properties of **3** related to the* H_2 *evolution function of Fe-only hydrogenases are also reported.*

Fe-only hydrogenases are a naturally occurring class of metalloenzymes, which catalyze hydrogen evolution or uptake at rapid rates in a wide variety of microorganisms.[1] Recent studies on structures of two Fe-only hydrogenases isolated from *C. pasteurianum* and *D. desulfuricans* have revealed[2] that the active site (so-called H cluster) consists of a butterfly 2Fe2S cluster core that bears three unusual ligands, CO, CN^-, and the cysteine-S-substituted cubic 4Fe4S cluster; in addition, a less defined three-atom linker bridges between two S atoms of the 2Fe2S cluster core. This structural information has greatly stimulated synthetic studies aimed at obtaining model compounds which can perform catalytic activities similar to those found in natural systems.[3] So far, numerous models have been synthesized, which can be classified into three major types according to the three-atom linker: namely, diiron propanedithiolate (PDT) complexes,[4] diiron azadithiolate (ADT) complexes,[5] and diiron oxadithiolate (ODT) complexes.[6] Among the three types of models, the diiron PDT type models are probably the earliest and most extensively studied models. Recently, during our investigation on the new trithiol reaction system $MeC(CH_2SH)_3/Fe_3(CO)_{12}/Et_3N$/electrophiles, we obtained two novel bridgehead-C-substituted diiron PDT type models. This is completely unexpected, since the similar trithiol reaction systems $N(CH_2CH_2SH)_3/Fe_3(CO)_{12}/Et_3N$/electrophiles and 1,3,5-$(HSCH_2)_3C_6H_3/Fe_3(CO)_{12}/Et_3N$/electrophiles were known to give starlike complexes containing three terminal butterfly Fe/S cluster cores.[7] Now, we report two such PDT-type model complexes along with details of their syntheses, structures, and electrochemical properties.

Scheme 1



Treatment of the trithiol $MeC(CH_2SH)_3$ with $Fe_3(CO)_{12}$ and Et_3N in a 1:3:3 molar ratio in THF at room temperature followed by addition of the organic halide $MeSCH_2Cl$ or $CH_2{=}CHCH_2Br$ resulted in the formation of the two PDT-type model compounds $[Fe_2(\mu\text{-}CH_2SMe)(\mu\text{-}SCH_2)(CO)_6][Fe_2(\mu\text{-}SCH_2)_2CMe(CO)_6]$ (**3**) and $[Fe_2(\mu\text{-}CH_2CH{=}CH_2)(\mu\text{-}SCH_2)(CO)_6][Fe_2(\mu\text{-}SCH_2)_2CMe(CO)_6]$ (**4**) in 45% and 35% yields, respectively (Scheme 1). A possible pathway for the production of **3** and **4** is proposed in Scheme 2. First, the reaction of the trithiol $MeC(CH_2SH)_3$ with $Fe_3(CO)_{12}$ and Et_3N, similar to that of $N(CH_2CH_2SH)_3$ or 1,3,5-$(HSCH_2)_3C_6H_3$ with $Fe_3(CO)_{12}$ and Et_3N,[7] gives the $[Et_3NH]^+$ salt of a trianion containing three μ-CO groups, $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[(\mu\text{-}SCH_2)_3CMe]\}^{3-}$ (**1**). Then, trianion **1** converts to the thermodynamically more favored monoanion containing one μ-CO group, $\{[Fe_2(\mu\text{-}CO)(\mu\text{-}SCH_2)(CO)_6][Fe_2(\mu\text{-}SCH_2)_2CMe(CO)_6]\}^-$ (**2**), via formal intramolecular loss of its two $[(\mu\text{-}CO)Fe(CO)_3]$ units followed by dimerization of the remaining two $[(\mu\text{-}SCH_2)Fe(CO)_3]$ moieties.[8] Finally, monoanion **2** reacts further with the electrophile

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* To whom correspondence should be addressed. Fax: 0086-22-23504853. E-mail: lcsong@nankai.edu.cn.

[1] (a) Adams, M. W. W.; Stiefel, E. I. *Science* **1998**, *282*, 1842. (b) Cammack, R. *Nature* **1999**, *397*, 214. (c) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3683. (d) Song, L.-C. *Acc. Chem. Res.* **2005**, *38*, 21.

[2] (a) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853. (b) Nicolet, Y.; Piras, C.; Legrend, P.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13.

[3] Alper, J. *Science* **2003**, *299*, 1686.

[4] See for example: (a) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268. (b) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518. (c) Razavet, M.; Davies, S. C.; Hughes, D. L.; Barclay, J. E.; Evans, D. J.; Fairhurst, S. A.; Liu, X.; Pickett, C. J. *Dalton Trans.* **2003**, 586.

[5] See for example: (a) Lawrence, J. D.; Li, H.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1768. (b) Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726. (c) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L.; Lomoth, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1006.

[6] Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082.

[7] Song, L.-C.; Cheng, J.; Gong, F.-H.; Hu, Q.-M.; Yan, J. *Organometallics* **2005**, *24*, 3764.

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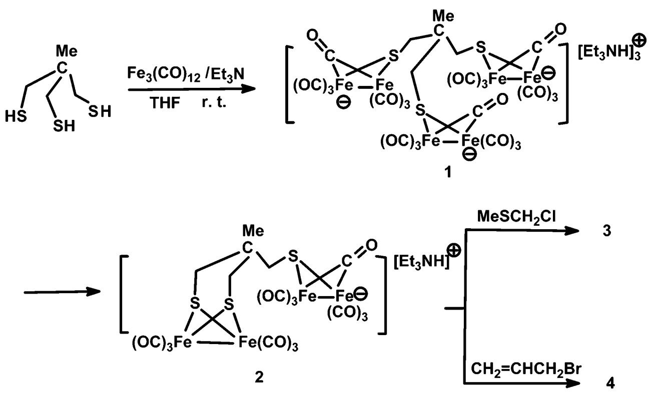
Scheme 2



$MeSCH_2Cl$ or $CH_2{=}CHCH_2Br$ (via nucleophilic attack of the negatively charged Fe atom in **2** at the methylene C atom of $MeSCH_2Cl$ or at the saturated C atom of $CH_2{=}CHCH_2Br$ followed by displacement of the μ-CO ligand in **2**)[9] to afford **3** and **4**, respectively.

The proposed pathway described above is actually well-based on the established chemistry of the butterfly μ-CO-containing Fe/E (E = S, Se) clusters.[7−9] Further experimental findings are as follows: (i) the suggested intermediate **1** was intercepted by the P atom based electrophile Ph_2PCl to give the starlike complex $[Fe_2(\mu\text{-}Ph_2P)(CO)_6]_3[(\mu\text{-}SCH_2)_3CMe]$ (**5**) (see the Supporting Information); (ii) the suggested intermediate **2** was trapped by the C atom based electrophile $MeSCH_2Cl$ or $CH_2{=}CHCH_2Br$ to give products **3** and **4**, which have been fully characterized; (iii) the IR spectrum of the brown-red solution before the C atom based electrophiles are added showed a medium absorption band at 1745 cm^{-1}. This band is typical of the μ-CO ligands in **1** and **2**, although they cannot be distinguished (note that the differences between the μ-CO bands of the analogous butterfly anions containing one and three μ-CO groups, usually 1738−1745 cm^{-1},[7,9] are very small). In addition, similar to the case for the reported μ-CO-containing butterfly anions, the suggested anions **1** and **2** are quite air-sensitive and thermally unstable. For example, when the brown-red solution containing these anions was exposed to air or refluxed in N_2 for 45 min, the original μ-CO band at 1745 cm^{-1} almost completely disappeared. It should be noted that at present we do not know the relative amounts of **1** and **2**. However, it is believed that the relative amounts of the corresponding two intermediates are most likely dependent upon the nature of the trithiols and electrophiles utilized. In this case it might be that the reaction rate of the C-based electrophiles used is much faster with intermediate **2** than with **1**, which may induce further conversion of **1** to **2**; thus, compounds **3** and **4** as major products were obtained.

The molecular structures of **3** and **4** have been characterized by spectroscopy[10] and X-ray crystallography.[11] The structural study (Figure 1) indicated that **3** consists of a methyl-substituted diiron PDT moiety that is connected through a methylene group to the bridged S atom of an open butterfly Fe_2S_2C cluster. In the diiron PDT moiety of **3** the six-membered ring C(14)C(13)S(1)Fe(1)S(2)C(15) exists as a chair conformer and another six-membered ring, C(14)C(13)S(1)Fe(2)S(2)C(15), exists as a boat conformer. This case is similar to that of the two fused six-membered rings in $(\mu\text{-PDT})Fe_2(CO)_6$.[12] The methyl C(17) is axially bonded to C(14),[4a] whereas the methylene C(16) is equatorially bound to both C(14)[4a] and S(3).[13] This molecule is actually the most favored conformational isomer of **3**, since the bulky diiron PDT moiety and the bulky open butterfly cluster both lie in equatorial positions.[4a,13]

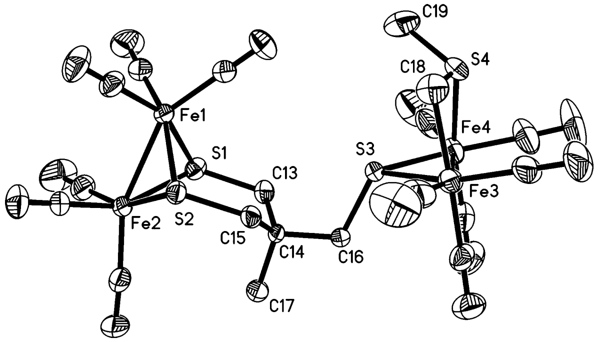


Figure 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.4949(14), Fe(3)−Fe(4) = 2.6045(16), Fe(1)−S(1) = 2.2531(19), Fe(3)−S(3) = 2.246(2), Fe(3)−C(18) = 2.11(3), S(4)−C(18) = 1.785(17); S(1)−Fe(1)−Fe(2) = 56.92(6), S(2)−Fe(1)−S(1) = 83.76(7), S(2)−Fe(2)−S(1) = 83.32(7), S(2)−Fe(2)−Fe(1) = 56.32(5), S(1)−Fe(2)−Fe(1) = 56.17(5), S(3)−Fe(3)−Fe(4) = 54.24(6), S(4)−C(18)−Fe(3) = 96.7(13).

The molecular structure of **4** (Figure 2) is quite different from that of **3**, although they all contain a diiron PDT moiety and an open butterfly cluster. First, the bidentate σ-coordinated $MeSCH_2$ ligand in **3** has been replaced by a tridentate π-coordinated allyl ligand, in which the two terminal carbon atoms are bound symmetrically across the two Fe atoms (Fe(3)−C(18) = 2.096(5) Å; Fe(4)−C(20) = 2.134(4) Å). This is consistent with its ^1H NMR spectrum, which displayed the CH_2 proton signals of the allyl group as two doublets at ca. 0.5 ppm ($J \approx$ 13 Hz) and ca. 2 ppm ($J \approx 7$ Hz), attributed respectively to the anti and syn hydrogens.[14] Furthermore, in contrast to **3**, the methyl C(17) is equatorially attached to C(14),[4a] whereas the methylene C(16) is axially bound to C(14)[4a] and equatorially to S(3).[13] This means that such a conformational isomer of **4**,

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[8] Similar intermolecular processes are known, by which the $[Et_3NH]^+$ salts of the monoanions $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (E = S, Se) can be converted to the dimers $(\mu\text{-RE})_2Fe_2(CO)_6$; see for example: (a) Seyferth, D.; Hoke, J. B.; Womack, G. B. *Organometallics* **1990**, *9*, 2662. (b) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, J.; Sun, J.; Huang, X.-Y. *J. Organomet. Chem.* **2001**, *627*, 255.

[9] Such chemical reactivities are virtually the same as those of the monoanions containing one μ-CO group $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (E = S, Se); see: Song, L.-C. In *Trends in Organometallic Chemistry*; Atwood, J. L., Corriu, R., Cowley, A. H., Lappert, M. F., Nakamura, A., Pereyre, M., Eds.; Research Trends: Trivandrum, India, 1999; Vol. 3, p 1.

[10] **3**: a mixture of $Fe_3(CO)_{12}$ (1.512 g, 3.0 mmol), THF (20 mL), $MeC(CH_2SH)_3$ (0.168 g, 1.0 mmol), and Et_3N (0.42 mL, 3.0 mmol) was stirred at room temperature for 0.5 h, and then $MeSCH_2Cl$ (0.579 g, 6.0 mmol) was added. The new mixture was stirred at 40 °C for 4 h, at room temperature for 36 h. After the solvent was removed under reduced pressure, the residue was subjected to TLC using CH_2Cl_2/petroleum ether (1/4 v/v) as eluent. From the main band **3** was obtained as a red solid. Yield: 0.356 g (45%). IR (KBr disk): $\nu_{C\equiv O}$ 2065 (s), 2025 (vs), 1991 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): 1.06 (d, $J = 9.0$ Hz, 1H, endo-FeC*H*H), 1.20 (s, 3H, CCH_3), 1.59 (d, $J = 8.7$ Hz, 1H, exo-FeCH*H*), 1.95 (s, 3H, SCH_3), 2.20−2.76 (m, 6H, $3SCH_2$) ppm. Similarly, **4** was prepared as a red solid. Yield: 0.265 g (35%). IR (KBr disk): $\nu_{C\equiv O}$ 2070 (s), 2036 (vs), 2009 (vs), 1981 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): 0.48 (d, $J = 12.6$ Hz, 2H, 2 anti-FeC*H*H), 1.00 (s 3H, CH_3), 1.96 (d, $J = 6.9$ Hz, 2H, 2 syn-FeCH*H*), 2.02−2.28 (m, 6H, $3SCH_2$), 4.74−4.89 (m, 1H, CH) ppm.

[11] Crystal data are as follows. **3**: triclinic, $P\bar{1}$, $a = 9.760(3)$ Å, $b = 10.927(4)$ Å, $c = 13.709(5)$ Å, $\alpha = 87.922(6)°$, $\beta = 82.140(7)°$, $\gamma = 85.031(7)°$, $F(000) = 784$, $V = 1442.5(9)$ Å^3, $D_c = 1.809$ g cm^{-3}, μ(Mo Kα) = 2.316 mm^{-1}, $R = 0.0621$, $R_w = 0.1004$, GOF = 0.986. **4**: monoclinic, $P2_1/c$, $a = 9.007(3)$ Å, $b = 11.562(4)$ Å, $c = 26.729(9)$ Å, $\alpha = 90°$, $\beta = 97.350(6)°$, $\gamma = 90°$, $F(000) = 1528$, $V = 2760.4(16)$ Å^3, $D_c = 1.843$ g cm^{-3}, μ(Mo Kα) = 2.345 mm^{-1}, $R = 0.0461$, $R_w = 0.0785$, GOF = 1.047.

[12] Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3178.

[13] Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

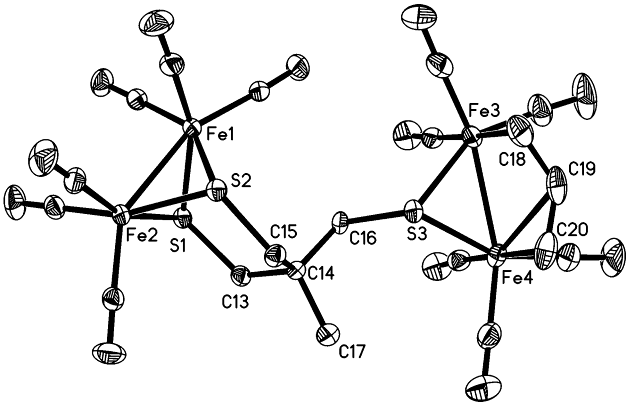

Figure 2. Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.4923(10), Fe(3)−Fe(4) = 2.6625(11), Fe(1)−S(1) = 2.2671(12), Fe(3)−S(3) = 2.2466(13), Fe(3)−C(18) = 2.096(5), Fe(4)−C(20) = 2.134(4), C18−C19 = 1.406(6); S(1)−Fe(1)−Fe(2) = 56.49(3), S(2)−Fe(1)−S(1) = 83.54(5), S(3)−Fe(3)−Fe(4) = 54.13(4), Fe(2)−S(1)−Fe(1) = 66.78(4), Fe(2)−S(2)−Fe(1) = 66.88(4), C(18)−C(19)−C(20) = 127.6(5).

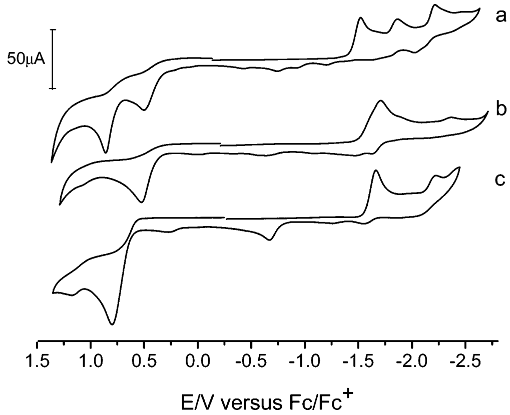

Figure 3. Comparison of the cyclic voltammetric responses recorded at a glassy-carbon electrode in MeCN−Bu_4NPF_6 (scan rate 100 mV s^{-1}): (a) **3**; (b) **6**; (c) (μ-PDT)$Fe_2(CO)_6$.

though less stable than that with methylene C(16) equatorially bonded to both C(14) and S(3), is still stable enough to exist, presumably due to the reduced steric hindrance caused by the open butterfly unit being equatorially but not axially bonded to C(16).[13] The Fe−Fe distance in the diiron PDT moiety of **3** (2.4949(14) Å) is almost the same as that of **4** (2.4923(10) Å); these distances are only ca. 0.12 Å shorter than the corresponding distances reported for the enzymes *C. pasteurianum* (2.62 Å)[2a] and *D. desulfuricans* (2.60 Å).[2b]

The cyclic voltammetric behavior of model **3** was compared with that of the parent compound (μ-PDT)$Fe_2(CO)_6$ and the new complex (μ-*t*-BuS)(μ-$MeSCH_2S$)$Fe_2(CO)_6$ (**6**)[15] (Figure 3). Such a comparison can facilitate the electrochemical assignment of model **3**, since the last two complexes are structurally similar to the corresponding two diiron portions in **3**. While **3** displays four irreversible one-electron reductions (−1.52, −1.86, −2.21, and −2.47 V), (μ-PDT)$Fe_2(CO)_6$ (−1.66 and −2.23 V) and **6** (−1.71 and −2.37 V) exhibit two irreversible reductions, respectively. Through comparison with the two reductions of (μ-PDT)$Fe_2(CO)_6$, the first and third reductions of **3** can be attributed to the two Fe atoms in its diiron PDT moiety. In addition, since the two reductions of **3** are positively shifted with respect to those of (μ-PDT)$Fe_2(CO)_6$, the open butterfly unit in **3** should be an electron-withdrawing group, which causes the diiron PDT moiety in **3** to be reduced much more easily than the parent PDT compound. On further comparison with the two reductions of **6**, we can similarly ascribe the second and fourth reductions of **3** to the two Fe atoms in the electron-withdrawing open butterfly unit.

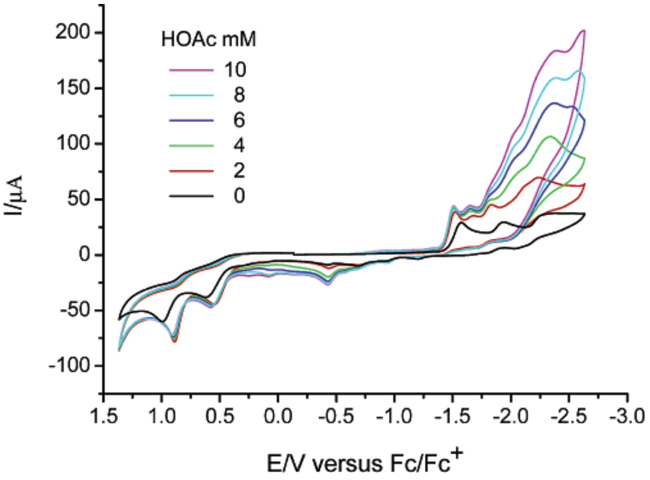

Figure 4. Cyclic voltammogram of **3** (1 mM) with HOAc (0−10 mM) in CH_3CN.

Further electrochemical study demonstrated that model **3** has the catalytic ability to reduce the protons of acetic acid to give hydrogen. As shown in Figure 4, when the first 2 mM portion of HOAc is added, the heights of the first two reduction peaks at −1.52 and −1.86 V slightly increase (with their potentials slightly shifted toward less negative values), but they do not grow further with sequential increments of the acid. However, in contrast to this, when the first 2 mM portion of HOAc is added, the height of the third reduction peak at −2.21 V apparently increases and grows linearly (with its potentials slightly shifted to more negative values) as the acetic acid concentration increases sequentially. In fact, such observations are in good agreement with catalytic proton reduction.[16]

Further evidence for the catalytic activity of **3** was obtained by bulk electrolysis of a CH_3CN solution of HOAc (6.66 mM) in the presence of **3** (0.33 mM) at −2.20 V. A total of 7.4 F/mol of **3** passed over the course of 0.5 h. This corresponds to 3.7 turnovers. In such a large-scale experiment, H_2 evolution is clearly seen. Gas chromatographic analysis showed that the hydrogen yield was about 85%.

In summary, we have prepared and structurally characterized the two novel H cluster models **3** and **4**, in which an open butterfly cluster is connected to the bridgehead C atom of the diiron PDT moiety. In addition, we have demonstrated that one such model indeed possesses the catalytic function for proton reduction to hydrogen under electrochemical conditions. The suggested pathway for production of **3** and **4** is believed to involve the novel intermediate **2**. This intermediate should be potentially very useful for synthesizing such H cluster models, since it contains a very reactive μ-CO functionality.[9]

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(14) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

(15) We prepared the new complex (μ-*t*-BuS)(μ-$MeSCH_2S$)$Fe_2(CO)_6$ (**6**) (see the Supporting Information) and determined its electrochemical data along with those of (μ-PDT)$Fe_2(CO)_6$ under the same conditions as for **3**. For some reported electrochemical data of (μ-PDT)$Fe_2(CO)_6$, see for example: Mejia-Rodriguez, R.; Chong, D.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004.

(16) (a) Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 3982. (b) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476.

Acknowledgment. We are grateful to the National Natural Science Foundation of China and the Research Fund for the Doctoral Program of Higher Education of China for financial support.

Supporting Information Available: Text describing the detailed synthesis and characterization of complexes **3**−**6** and CIF files giving the structural determinations of **3**−**5**, including atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, and data collection and processing parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060004Y