Inorg. Chem. **2003**, *42*, 2489–2494

Requirements for Functional Models of the Iron Hydrogenase Active Site: D_2/H_2O Exchange Activity in $\{(\mu\text{-SMe})(\mu\text{-pdt})[Fe(CO)_2(PMe_3)]_2^+\}[BF_4^-]$

Irene P. Georgakaki, Matthew L. Miller, and Marcetta Y. Darensbourg*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received September 5, 2002

Hydrogen uptake in hydrogenase enzymes can be assayed by H/D exchange reactivity in H_2/D_2O or $H_2/D_2/H_2O$ mixtures. Diiron(I) complexes that serve as structural models for the active site of iron hydrogenase are not active in such isotope scrambling but serve as precursors to $Fe^{II}Fe^{II}$ complexes that are functional models of $[Fe]H_2$ase. Using the same experimental protocol as used previously for $\{(\mu\text{-H})(\mu\text{-pdt})[Fe(CO)_2(PMe_3)]_2^+\}$, **1-H**$^+$ (Zhao et al. *J. Am. Chem. Soc.* **2001**, *123*, 9710), we now report the results of studies of $\{(\mu\text{-SMe})(\mu\text{-pdt})[Fe(CO)_2(PMe_3)]_2^+\}$, **1-SMe**$^+$, toward H/D exchange. The **1-SMe**$^+$ complex can take up H_2 and catalyze the H/D exchange reaction in D_2/H_2O mixtures under photolytic, CO-loss conditions. Unlike **1-H**$^+$, it does not catalyze H_2/D_2 scrambling under anhydrous conditions. The molecular structure of **1-SMe**$^+$ involves an elongated Fe···Fe separation, 3.11 Å, relative to 2.58 Å in **1-H**$^+$. It is proposed that the strong SMe^- bridging ligand results in catalytic activity localized on a single Fe^{II} center, a scenario that is also a prominent possibility for the enzyme active site. The single requirement is an open site on Fe^{II} available for binding of D_2 (or H_2), followed by deprotonation by the external base H_2O (or D_2O).

Introduction

The connection between enzymes that take up and activate molecular hydrogen and noble metals that show similar functions has intrigued scientists since the discovery of hydrogenases in 1931.[1] The recent wave of attention has been fueled by protein crystal structures which provide striking snapshots of binuclear active sites in both nickel−iron[2] and iron hydrogenases.[3] The similarity of the active site structure of Fe-only hydrogenase, $[Fe]H_2$ase, to easily synthesized and well-known dinuclear Fe^IFe^I organometallic complexes[4] (Figure 1a and b, respectively) has inspired the preparation of derivatives modified in such a way to better mimic the features of the enzyme active site.[5] Whereas the enzyme is characterized by at least three different oxidation levels, mixed-valent Fe^IFe^{II} is a prominent candidate for the form that is responsible for H_2 uptake; heterolytic (H^+/H^-) cleavage; and, by microscopic reversibility, H_2 production and evolution.[6]

* Author to whom correspondence should be addressed. E-mail: marcetta@mail.chem.tamu.edu.

(1) Stephenson, M.; Stickland, L. H. *Biochem. J.* **1931**, *25*, 205.
(2) (a) Volbeda, A.; Charon, M.-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**, *373*, 580. (b) Volbeda, A.; Garcin, E.; Piras, C.; De Lacey, A. L.; Fernandez, V. M.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 12989. (c) Garcin, E.; Vernede, X.; Hatchikian, E. C.; Volbeda, A.; Frey, M.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 557. (d) Higuchi, Y.; Yagi, T.; Yasuoka, N. *Structure* **1997**, *5*, 1671. (e) Higuchi, Y.; Ogata, H.; Miki, K.; Yasuoka, N.; Yagi, T. *Structure* **1999**, *7*, 549.
(3) (a) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853. (b) Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13. (c) Nicolet, Y.; De Lacey, A. L.; Vernéde, X.; Fernandez, V. M.; Hatchikian, E. C.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 1596. (d) Lemon, B. J.; Peters, J. W. *Biochemistry* **1999**, *38*, 12969.
(4) Seyferth, D.; Womack, G. B.; Gallagher, M. K.; Cowie, M.; Hames, B. W.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1987**, *6*, 283.
(5) (a) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3178. (b) Schmidt, M.; Contakes, S. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 9736. (c) Le Cloirec, A.; Best, S. P.; Borg, S.; Davies, S. C.; Evans, D. J.; Hughes, D. L.; Pickett, C. J. *Chem. Commun.* **1999**, 2285. (d) Lawrence, J. D.; Li, H.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1768. (e) Razavet, M.; Davies, S. C.; Hughes D. L.; Pickett, C. J. *Chem. Commun.* **2001**, 847.
(6) (a) Popescu, C. V.; Münck, E. *J. Am. Chem. Soc.* **1999**, *121*, 7877. (b) Pereira, A. S.; Tavares, P.; Moura, I.; Moura, J. J. G.; Huynh, B. H. *J. Am. Chem. Soc.* **2001**, *123*, 2771. (c) De Lacey, A. L.; Stadler, C.; Cavazza, C.; Hatchikian, E. C.; Fernandez, V. M. *J. Am. Chem. Soc.* **2000**, *122*, 11232. (d) Bennett, B.; Lemon, B. J.; Peters, J. W. *Biochemistry* **2000**, *39*, 7455.

10.1021/ic026005+ CCC: $25.00
Published on Web 02/11/2003

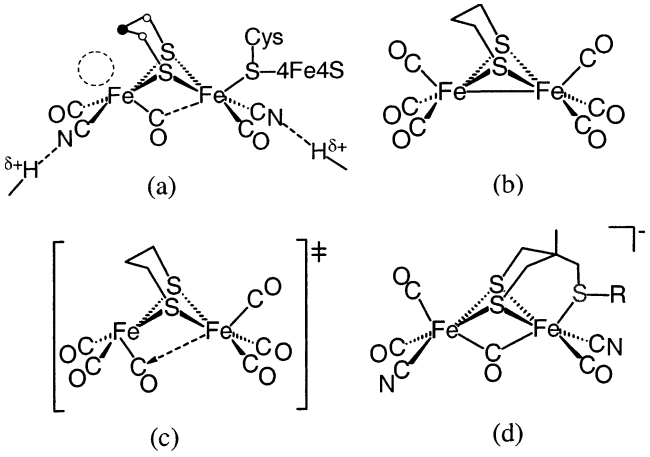


Figure 1. Stick drawing structures of (a) active site of [Fe]H_2ase,[3] (b) ground state of (μ-pdt)$Fe_2(CO)_6$, (c) calculated transition state of $Fe(CO)_3$ unit rotation in (μ-pdt)$Fe_2(CO)_6$,[8] and (d) a spectroscopically observed Fe^{II}-Fe^{I} complex.[7]

The synthesis of mixed-valent complexes is not easily achieved in the chemist's laboratory. A recent spectroelectrochemical study provided evidence for such an $Fe^{II}Fe^{I}$ species generated by one-electron oxidation of a diiron(I) model.[7] The mixed-valent product is a good spectroscopic match for the CO-inhibited oxidized form of the enzyme,[3d] resulting in the proposed structure shown in Figure 1d. The bridging carbonyl of the $Fe^{II}Fe^{I}$ complex has not heretofore been observed in (μ-SRS)$[Fe^{I}(CO)_2L]_2$ model complexes. Nevertheless, DFT computations suggest an analogous structure as a transition state for a rotation process that equilibrates CO ligands in individual $Fe(CO)_3$ units as seen in ^{13}C NMR spectra. This rotation accounts for the observed fluxionality or intramolecular site exchange that interchanges CO_{apical} with CO_{basal} (Figure 1c).[8]

Although the electrochemically generated $Fe^{II}Fe^{I}$ species has not, as yet, been isolated, homovalent $Fe^{II}Fe^{II}$ complexes are readily obtained from $Fe^{I}Fe^{I}$ precursors via the binuclear oxidative addition of electrophiles such as H^+ or SMe^+.[9] Reaction of (μ-pdt)$[Fe(CO)_2(PMe_3)]_2$, complex **1** (pdt = $SCH_2CH_2CH_2S$), with H^+ or SMe^+ produces {(μ-H)(μ-pdt)-$[Fe(CO)_2(PMe_3)]_2^+$}, **1-H**$^+$,[10] or {(μ-SMe)(μ-pdt)$[Fe(CO)_2$-$(PMe_3)]_2^+$}, **1-SMe**$^+$, respectively, with concomitant blue shifts in the ν(CO) IR spectrum (Figure 2). The role of the PMe_3 ligands, analogues to cyanide in the enzyme active site, is to both increase the electron density in the $Fe^{I}Fe^{I}$ bond and to stabilize the $Fe^{II}Fe^{II}$ oxidation level following oxidative addition.

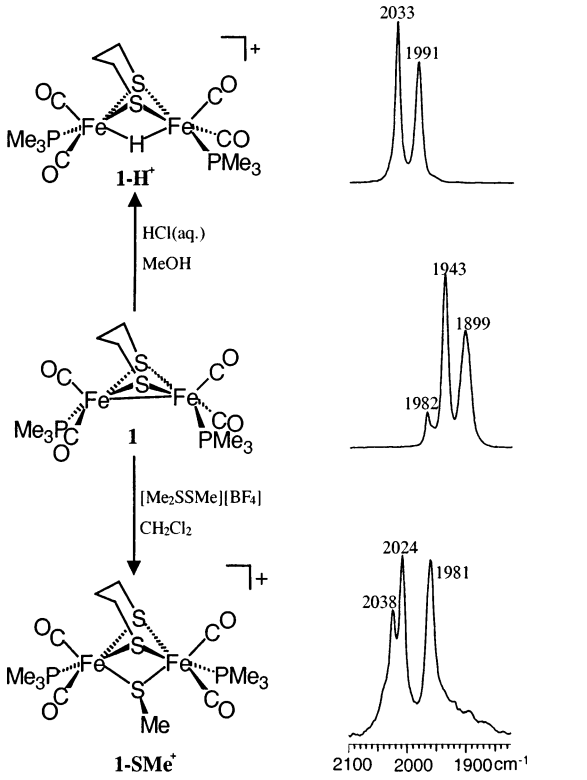
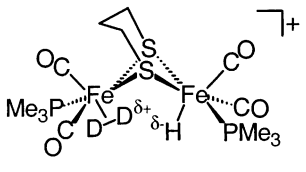


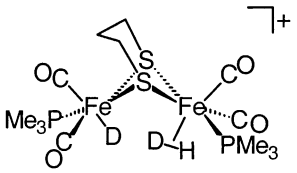
Figure 2. Stick drawing structures and infrared spectra of **1**, **1-H**$^+$, and **1-SMe**$^+$.

As early as 1934, Farkas, Farkas, and Yudkin demonstrated that hydrogenase from *B. coli* (*Balantidium coli*) catalyzed the isotope exchange reaction between D_2O and H_2.[11] This reactivity, together with ortho/para H_2 interconversion, the mechanism of which was studied in detail by Krasna and Rittenberg,[12] has provided the basis for hydrogenase activity assays that typically demonstrate H_2 uptake as indicated by H/D exchange in H_2/D_2O mixtures.[13] Mixtures of H_2/D_2 have also been reported to show scrambling,[14] presumably via H_2O mediation. On the basis of such test reactions, our previous studies indicated that the diiron(II) complex, **1-H**$^+$, serves as a functional model of [Fe]H_2ase in the catalytic isotopic scrambling of D_2/H_2O and H_2/D_2 mixtures.[10,15] During these processes, all of which require photolysis, **1-H**$^+$ becomes **1-D**$^+$, indicating involvement of the bridging hydride in the isotope exchange mechanism. Intermediates such as structures **A** and **B**, call upon the μ-H to shift to a terminal position and serve as an internal base under anhydrous conditions to deprotonate the proximate (η^2-H_2)Fe^{II} moiety. A weak external base such as H_2O can also deprotonate the acidic (η^2-H_2)Fe^{II} intermediate.[16]

(7) Razavet, M.; Borg, S. J.; George, S. J.; Best, S. P.; Fairhurst, S. A.; Pickett, C. J. *Chem. Commun.* **2002**, 700.
(8) (a) Georgakaki, I. P.; Thomson, L. M.; Lyon, E. J.; Hall, M. B.; Darensbourg, M. Y. *Coord. Chem. Rev.*, manuscript submitted. (b) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268.
(9) (a) Fauvel, K.; Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1976**, *15*, 976. (b) Savariault, J.-M.; Bonnet, J.-J.; Mathieu, R.; Galy, J. *C. R. Acad. Sci.* **1977**, *284*, C663. (c) Lyons, L. J.; Anderson, L. L.; Crane, R. A.; Treichel, P. M. *Organometallics* **1991**, *10*, 587. (d) Treichel, P. M.; Crane, R. A.; Matthews, R.; Bonnin, K. R.; Powell, D. *J. Organomet. Chem.* **1991**, *402*, 233.
(10) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Yarbrough, J. C.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 9710.
(11) Farkas, A.; Farkas, L.; Yudkin, J. *Proc. R. Soc. (London)* **1934**, *B115*, 373.
(12) Krasna, A. I.; Rittenberg, D. *J. Am. Chem. Soc.* **1954**, *76*, 3015.
(13) (a) Adams, M. W. W.; Mortenson, L. E.; Chen, J.-S. *Biochim. Biophys. Acta* **1981**, *594*, 105. (b) Albracht, S. P. J. *Biochim. Biophys. Acta* **1994**, *1188*, 167.
(14) Yagi, T. *J. Biochem.* **1970**, *68*, 649.
(15) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Mejia-Rodriguez, R.; Chiang, C.-Y.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 3917.
(16) Landau, S. E.; Morris, R. H.; Lough, A. J. *Inorg. Chem.* **1999**, *38*, 6060.



A



B

Because an open site on Fe can, under photolysis, be created by a hydride shift or by CO loss, we questioned whether the hydride was a requirement for the heterolytic H_2/H_2O or D_2/H_2O cleavage reaction. Hence, the following study was designed to assess the requirement of a H^- ligand in candidates for H_2ase functional models.

Experimental Section

Materials and Techniques. All manipulations were performed using standard Schlenk-line and syringe/rubber-septa techniques under N_2 or in an argon atmosphere glovebox. Solvents were of reagent grade and purified as follows: Dichloromethane was distilled over P_2O_5 under N_2. Acetonitrile was distilled once from CaH_2, distilled once from P_2O_5, and freshly distilled from CaH_2 immediately before use. Diethyl ether was distilled from sodium/benzophenone under N_2. The following materials were of reagent grade and used as received: $Fe_3(CO)_{12}$, 1,3-propanedithiol, MeSSMe, Me_3OBF_4 and NH_4PF_6 (Aldrich Chemical Co.); deuterated solvents and D_2 (Cambridge Isotope Laboratories).

Infrared spectra were recorded on a Mattson 6021 FTIR spectrometer with DTGS and MCT detectors. ^{1}H, ^{13}C, and ^{31}P NMR (85% H_3PO_4 was used as an external reference) spectra were recorded on a Unity+ 300-MHz superconducting NMR instrument operating at 299.9, 75.43, and 121.43 MHz, respectively. ^{2}H NMR spectra were recorded on a Unity Inova-400 NMR instrument with a 5-mm autoswitchable probe operating at 61.35 MHz and on a VXR-300 NMR instrument operating at 46.05 MHz.

Preparations. The neutral dinuclear iron compounds were prepared according to literature procedures.[15]

[Me_2SSMe^+][BF_4^-]. Following the published procedure,[17] a solution containing 0.74 mL of methyl disulfide (8.06 mmol) in ~7 mL of CH_3CN was added dropwise to an equimolar amount of $Me_3O^+BF_4^-$ (1.04 g, 8.06 mmol) dissolved in ~8 mL of CH_3CN at 0 °C. After the mixture had been stirred for ~2 h at 0 °C, dry ether was added to precipitate dimethylthiomethylsulfonium fluoroborate ([Me_2SSMe^+][BF_4^-]) as a white solid that was stored in the glovebox at −36 °C (1.1 g; yield, 69%).

Synthesis of {(μ-SMe)(μ-pdt)[$Fe(CO)_2(PMe_3)]_2^+$}[BF_4^-]. A red solution of 0.97 g of (μ-pdt)[$Fe(CO)_2(PMe_3)]_2$ (2 mmol) in ~50 mL of dry CH_2Cl_2 was transferred via cannula into a Schlenk flask containing 0.41 g (2 mmol) of [Me_2SSMe^+][BF_4^-]. Following overnight stirring at 22 °C, the IR spectrum [ν(CO) region] showed the presence of a mixture of the neutral precursor and the cationic product in the brown solution. After the mixture had been fitered through Celite under Ar and concentrated in a vacuum, dry Et_2O was added to precipitate the product and remove the unreacted neutral complex, **1**. Crystals suitable for an X-ray crystal structure determination were grown from CH_2Cl_2 solutions layered with Et_2O at −5 °C. Infrared spectrum, ν(CO), CH_2Cl_2: 2038(m), 2024(s), 1981(s) cm^{-1}. Because of the difficulty in isolating the product in the solid form as its BF_4^- salt, the PF_6^- salt was prepared by ion exchange reaction of {(μ-SMe)(μ-pdt)[$Fe(CO)_2(PMe_3)]_2^+$}[BF_4^-] with saturated aqueous solution of NH_4PF_6 in MeOH. The solid was collected, washed with H_2O and Et_2O, and dried in air (0.6 g; yield, 44%). ^{31}P NMR, acetone-d^6: 20.95 (PMe_3) and −142.7 ppm (PF_6^-). Elemental analysis, calculated for $Fe_2C_{14}H_{27}S_3O_4P_3F_6$ (found)%: C, 24.92 (24.66); H, 4.00 (4.03).

Test for Catalytic Formation of HD in H_2/D_2 Mixture. A medium-pressure NMR tube (Wilmad, 528-PV-7) was charged with a solution containing 20 mg of {(μ-SMe)(μ-pdt)[$Fe(CO)_2(PMe_3)]_2^+$}-[PF_6^-] in 1 g of CD_2Cl_2. The tube was then pressurized with 5 bar H_2 and with D_2 to a total pressure of 10 bar and exposed to sunlight. ^{1}H NMR spectra were taken daily over the course of 8 days to check the formation of HD. None was observed.

H/D Exchange in D_2/H_2O Mixture. A 0.8-mL portion of a solution made from 0.15 g of [**1-SMe**$^+$][PF_6^-] in 3 mL of CH_2Cl_2 was put in a medium-pressure NMR tube together with 2 μL of H_2O. The tube was pressurized with 10 bar D_2 and exposed to sunlight. ^{2}H NMR spectra were taken at time intervals to follow the formation of HOD.

^{13}CO Exchange Experiment in [(μ-SMe)(μ-pdt)($Fe(CO)_2$-$PMe_3)_2^+$][PF_6^-]. A 0.7-mL portion of a solution made from 23 mg of **[1-SMe**$^+$**]**[PF_6^-] in 1.6 mL of d^6-acetone was transferred into a medium-pressure NMR tube. The tube was lightly degassed, filled with 20 psi ^{13}CO, and exposed to sunlight. The ^{13}C NMR spectrum after 1 day showed two doublets (208.95 and 208.07 ppm, J_{C-P} = 19.5 and 14.6 Hz, respectively) in the CO region, indicating the incorporation of ^{13}CO into the complex. The ν(CO) infrared spectrum in CH_2Cl_2 showed a shift of the stretching frequencies to lower wavenumbers consistent with ^{13}CO/^{12}CO exchange in **1-SMe**$^+$. Infrared spectrum, ν(CO) region: ν(CO), **1-SMe**$^+$ 2038, 2024, 1981; ν(CO), ^{13}CO-enriched **1-SMe**$^+$ 2020, 1981, 1947 cm^{-1}.

X-ray Structure Determination. A single crystal was mounted on a glass fiber at 110 K. The X-ray data were collected on a Bruker Smart 1000 CCD diffractometer and covered a hemisphere of reciprocal space by a combination of three sets of exposures. The space group was determined on the basis of systematic absences and intensity statistics. Crystal data for **[1-SMe**$^+$**]**[BF_4^-]: $C_{14}H_{27}O_4P_2S_3BF_4Fe_2$, M = 616.01, orthorhombic, space group *Pnma*, a = 14.79(3) Å, b = 12.54(2) Å, c = 12.98(2) Å, α = 90°, β = 90°, γ = 90°, V = 2408(7) Å^3, Z = 4, D_c= 1.699 g cm^{-3}. The structure was solved by direct methods. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters. The pdt bridge was refined with "envelope-flap" disorder. Anisotropic refinement for all non-hydrogen atoms was done by a full-matrix least-squares method with R1 = 0.0592 and wR2 = 0.0956. Programs used include SMART[18] for data collection and cell refinement, SAINTPLUS[19] for data reduction, SHELXS-86 (Sheldrick)[20] for structure solution, SHELXL-97 (Sheldrick)[21] for structure refinement, and SHELXTL-Plus, version 5.1 or later (Bruker),[22] for molecular graphics and preparation of material for publication.

Results and Discussion

Reaction of (μ-pdt)[$Fe(CO)_2(PMe_3)]_2$, **1**, with the SMe^+ synthon, [Me_2SSMe^+][BF_4^-], in CH_2Cl_2 results in the

(17) Smallcombe, S. H.; Caserio, M. C.*J. Am. Chem. Soc.* **1971**, *93*, 5826.

(18) *SMART 1000 CCD*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(19) *SAINT-Plus*, version 6.02; Bruker: Madison, WI, 1999.

(20) Sheldrick, G. *SHELXS-86: Program for Crystal Structure Solution*; Institüt für Anorganische Chemie, Universität Gottingen: Gottingen, Germany, 1986.

(21) Sheldrick, G. *SHELXL-97: Program for Crystal Structure Refinement*; Institüt für Anorganische Chemie, Universität Gottingen: Gottingen, Germany, 1997.

(22) *SHELXTL*, version 5.1 or later; Bruker: Madison, WI, 1998.

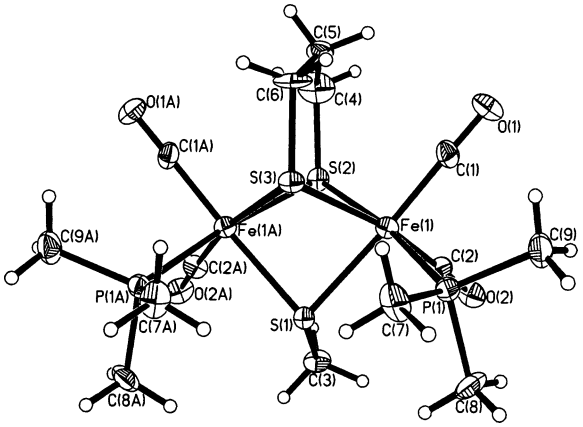


Figure 3. Thermal ellipsoid representation (30% probability) of the molecular structure of **1-SMe**$^+$.

Table 1. Selected Metric Data for **1**, **1-H**$^+$, and **1-SMe**$^+$

	1	**1-H**$^+$	**1-SMe**$^+$
Fe···Fe	2.555(2)	2.5784(8)	3.109
S···S	3.026	3.064	2.976
Fe−P	2.234(3)	2.2523(12)	2.257(4)
Fe−CO_{ap}	1.772(9)	1.779(4)	1.774(11)
Fe−CO_{ba}	1.742(10)	1.778(4)	1.764(10)
Fe−S(pdt-br)[a]	2.254(2)	2.2717(11)	2.324(4)
Fe−SMe	N/A	N/A	2.304(4)
Fe−S−Fe[a]	69.06(8)	69.15(4)	84.0(2)
S−Fe−S[a]	84.34(11)	84.77(4)	79.50(14)
Fe dsp[b]	0.376	0.231	0.153

[a] Average of all equivalent bonds and angles. [b] Fe dsp = average displacement of the Fe atoms out of the best planes defined by the two S's of the pdt bridge, C of basal CO, and P atoms.

formation of {(μ-SMe)(μ-pdt)[Fe(CO)$_2$(PMe$_3$)]$_2^+$}[BF$_4^-$], **1-SMe**$^+$. Crystals of **[1-SMe**$^+$**][BF$_4^-$]** suitable for X-ray structure determination were grown in CH_2Cl_2 solution layered with Et_2O at −5 °C. The descriptions of **1-SMe**$^+$, as a stick drawing Figure 2 and a thermal ellipsoid plot in Figure 3, display the molecular structure as a bioctahedron, face-bridged by three thiolates.

For the neutral precursor **1** and other (μ-SRS)[Fe^I(CO)$_2$L]$_2$ complexes, which are described as edge-bridged bisquare pyramids, the positions of the L ligands are defined as apical, basal, cisoid, and transoid. Although the oxidative addition products **1-H**$^+$ and **1-SMe**$^+$ are face-bridged bioctahedra, we have retained the designations for the L positions from the neutral precursor. As defined by crystallography, the repositioning of the PMe_3 ligands from the basal/basal transoid conformation in **1** and **1-H**$^+$[10] to basal/basal cisoid in **1-SMe**$^+$ minimizes steric interactions of the PMe_3 ligands with the SMe bridge. The shift in the ν(CO) IR spectral values as **1** is converted to **1-SMe**$^+$ is similar to that for **1-H**$^+$, i.e., approximately +70 cm^{-1} (Figure 2). The change in pattern, i.e., the splitting of the high-frequency band into two, is evidence of the change in symmetry described above.

Key structural metric data for **1**, **1-H**$^+$, and **1-SMe**$^+$ are listed in Table 1. The dramatic increase in the Fe···Fe distance of ca. 0.5 Å with the four-electron donor SMe$^-$ as the bridge has several consequences. The average of the Fe−S−Fe angle increases to 84.0(2)° in **1-SMe**$^+$, from the average of 69° in the parent **1** and **1-H**$^+$, resulting in a flattening of the Fe_2(pdt-S)$_2$ core without significant change in the S···S cross-ring distance. The FeS_2C_3 metallodithiocyclohexane rings are maintained in the typical chair/boat configuration with normal distances. An additional consequence of the four-electron-donor μ-SMe$^-$ vs the two-electron-donor μ-H$^-$ bridge is the increased octahedral character of the $FeS_3(CO)_2PMe_3$ coordination spheres. As measured by the displacement of the Fe from the (pdt-S$_2$)(CO)(P) plane, the value is ∼0.38 Å in complex **1**, which has the two electrons of the Fe−Fe bond in the sixth coordination position; it decreases to 0.23 Å in **1-H**$^+$ and decreases further in **1-SMe**$^+$ to 0.15 Å.

Activity of 1-SMe$^+$ as an H/D Exchange Catalyst. Reactivity studies of **1-SMe**$^+$ were based on the experimental protocol used to explore the H_2 activation and H/D exchange capabilities of **1-H**$^+$ and analogues.[10,15] To establish whether the μ-SMe moiety might exchange with D$^-$ derived from D_2, a medium-pressure NMR tube containing [**1-SMe**$^+$][PF$_6^-$] in CH_2Cl_2 was pressurized with 10 bar D_2 and exposed to sunlight as described in the Experimental Section. The ^{2}H NMR monitor found no (μ-D)Fe$_2^+$ or MeSD formed (eq 1). In the same time period, significant amounts of H/D exchange was observed for **1-H**$^+$/D_2 mixtures.[10,15] Similarly to the experiment with **1-H**$^+$, H_2/D_2 gaseous mixtures were introduced into an anhydrous CD_2Cl_2 solution of **1-SMe**$^+$. In the absence of light, as well as with extended periods of photolysis (sunlight for 8 days or more), no HD was observed in the ^{1}H NMR spectrum (eq 2). Under the same conditions, **1-H**$^+$ showed extensive scrambling of isotopes (formation of HD from H_2 and D_2 as well as formation of **1-D**$^+$).[10,15]

$$\textbf{1-SMe}^+ + D_2 \not\longrightarrow DSMe + \textbf{1-D}^+ \quad (1)$$

$$H_2 + D_2 \xrightarrow{\textbf{1-SMe}^+} 2\,HD \quad (2)$$

$$D_2 + H_2O \xrightarrow{\textbf{1-SMe}^+} HD + HOD \quad (3)$$

In contrast, mixtures of D_2 and H_2O show substantial H/D exchange with both **1-SMe**$^+$ and **1-H**$^+$ as catalysts (eq 3). A sample containing **1-SMe**$^+$ and 2 μL of H_2O in CH_2Cl_2 was pressurized with 10 bar D_2 and exposed to sunlight. To follow the formation of HOD, ^{2}H NMR spectra were recorded after 1, 2, and 4 h of exposure (Figure 4). After 1 h of photolysis, the spectrum showed a resonance at 1.75 ppm corresponding to the dissolved D-enriched water. Its intensity was 0.75 relative to the natural-abundance deuterium in the solvent, CH_2Cl_2, which appears at 5.32 ppm. Within 4 h of exposure to sunlight, this resonance shifted slightly to 1.80 ppm, and its intensity increased to 8.53 times that of the solvent peak, indicating significant exchange between D_2 and H_2O in the presence of **1-SMe**$^+$.

Conclusions

The conclusions and mechanistic implications of the above study are summarized as follows. The bioctahedral Fe^{II}Fe^{II} complex, **1-SMe**$^+$, face-bridged by three thiolates, (μ-SMe)-

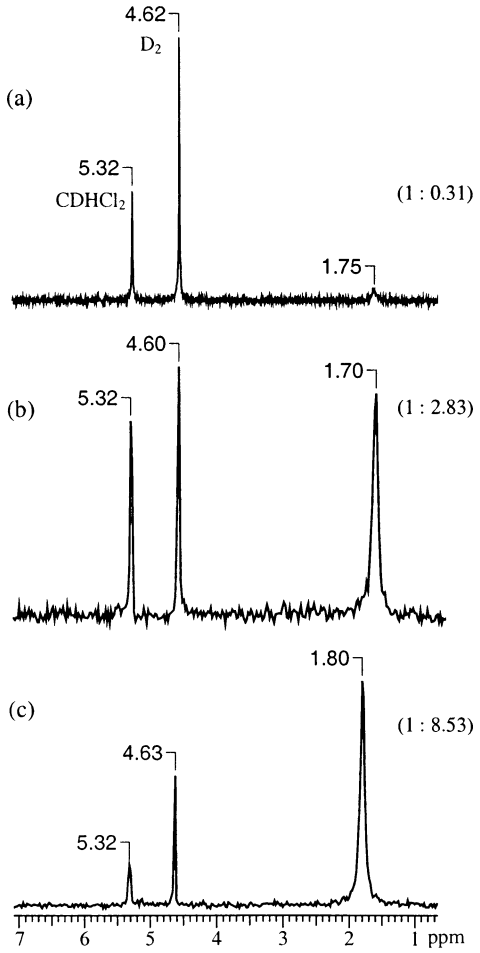
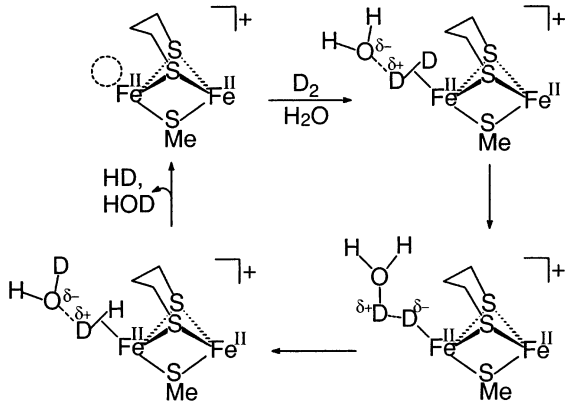


Figure 4. ^{2}H NMR spectra showing the formation of HOD ($\delta = 1.70-1.80$ ppm) in a CH_2Cl_2 solution containing **1-SMe**$^+$ as the PF_6^- salt, 10 bar D_2, and 2 μL of H_2O: (a) before exposure to sunlight, (b) after 2 h of photolysis, and (c) after 4 h of photolysis. Relative ratio of (natural abundance, $\delta = 5.32$ ppm) $CHDCl_2$ and HOD in parentheses.

(μ-pdt), maintains the H/D exchange capability in D_2/H_2O mixtures that was detected for the analogous complex **1-H**$^+$, face-bridged by a hydride and two thiolates. However, **1-SMe**$^+$ loses the capability for catalysis of H/D exchange in H_2/D_2 mixtures in anhydrous solution as was demonstrated for **1-H**$^+$.[10,15] Our mechanistic proposal for the latter called upon an open site created by H^- shift or CO loss, as discussed earlier, and deprotonation of (η^2-H_2)-Fe^{II} by the internal H^- base. Whether the η^2-H_2 and the terminal Fe−H exist on the same Fe^{II} or on adjacent atoms (binuclear activation) depends on whether a CO loss event is concomitant with μ-H → t-H conversion. However, such bridge breakage is either excluded or nonproductive in the case of **1-SMe**$^+$, as conversion of μ-SMe to μ-H was not observed when **1-SMe**$^+$ was pressurized with H_2. This is consistent with the fact that μ-SMe^- is a stronger bridging ligand than μ-H^-, suggesting that the open site needed for H_2 binding in **1-SMe**$^+$ comes from CO loss. Furthermore the elongated Fe···Fe distance of ∼3.1 Å in **1-SMe**$^+$ relative to 2.6 Å in **1-H**$^+$ would prevent involvement of both metals in the H_2 activation process. The rigidity of the bidentate chelating propanedithiolate bridge is expected to prevent further elongation of the Fe···Fe distance and flattening of the butterfly Fe_2S_2 core to a diamond shape, as seen in $L_4Fe^{II}(\mu$-$SR)_2Fe^{II}L_4$ complexes, where the $Fe^{II}\cdots Fe^{II}$ distance expands to ∼3.5 Å.[23]

Scheme 1



For both **1-H**$^+$ and **1-SMe**$^+$, an open site is required, as indicated by the need of photolysis for H_2 activation by the external base, H_2O. The creation of an open site in these complexes is consistent with the lability of the CO's indicated by ^{13}CO/CO exchange under photolysis by sunlight for both **1-H**$^+$ and **1-SMe**$^+$. A compatible mechanism is presented in Scheme 1, where the open site is depicted trans to the μ-SMe, in analogy with the open site in the H_2ase binuclear active site. Formation of the (η^2-H_2)−Fe^{II} interaction is well-precedented, as is the enhanced acidity of the metal-bound H_2.[16]

Thus, the two binuclear model complexes **1-H**$^+$ and **1-SMe**$^+$ mimic the H/D exchange activity of the [Fe]H_2ase enzyme in that both demonstrate H_2 (or D_2) uptake and heterolytic cleavage by D_2O (or H_2O) under photolytic conditions. The singular requirement for these processes is an open site on an Fe^{II} center. A built-in hydride is not needed for H/D exchange reactivity in D_2/H_2O or in H_2/D_2 mixtures in the presence of water; it is needed for anhydrous conditions where the mechanism of H_2 activation calls upon cooperation between the two metal sites in true binuclearity. We propose that the **1-SMe**$^+$ model localizes reactivity on one Fe center and engages the second iron only for thiolate ligand modification, maintaining the low-spin Fe^{II}, d^6 configuration conducive to η^2-H_2 binding. Thus, the reactivity scenario and structural design that is reasonable for the enzyme active site is an attractive archetype for the mechanism for the model complexes.

Both [Fe]H_2ase and [NiFe]H_2ase appear to have been designed, protein engineered, to have an open site on iron in their catalytic active sites. Whether both classes of metalloenzymes follow the same mechanism of H_2 uptake on Fe^{II} and cleavage or H_2 formation and evolution from an (η^2-H_2)Fe^{II} species is not at all clear. Convincing experiments by Sellmann, Geipel, and Moll[24] demonstrated the possibility of D_2 activation at a nickel(II) thiolate under anhydrous conditions, resulting in D^+/D^- cleavage and formation of Ni−D and nickel-bound RSD in a mononuclear nickel

(23) Liaw, W.-F.; Lee, N.-H.; Chen, C.-H.; Lee, C.-M.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2000**, *122*, 488.
(24) Sellmann, D.; Geipel, F.; Moll, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 561.

complex. Would an adjacent Fe^{II} center positioned to trap and hold H_2 in close proximity to Ni−SR enhance this activity? Such a reaction scenario, first expressed by Fontecilla-Camps and co-workers,[3c] is an attractive possibility in the enzyme active site.

Acknowledgment. We acknowledge financial support from the National Science Foundation (Grants CHE-9812355, CHE-0111629, and CHE 85-13273 for the X-ray diffractometer and crystallographic computing system) and contributions from the R. A. Welch Foundation. We also thank Dr. Joseph Reibenspies for his assistance in the X-ray crystal structure analysis.

Supporting Information Available: Molecular structure and X-ray crystallographic tables for **1-SMe**$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026005+