Inorg. Chem. **2003**, *42*, 4288–4292

Inorganic Chemistry
Article

Dinuclear Iron Isonitrile Complexes: Models for the Iron Hydrogenase Active Site

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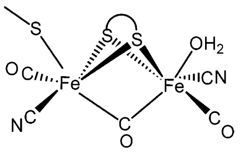
Received March 28, 2003

Reaction of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ (**1**) with 2 equiv of *t*-BuNC affords a disubstitued species $Fe_2(\mu\text{-}S_2C_3H_6)(CN\text{-}t\text{-}Bu)_2(CO)_4$ (**2**). The structure of **2** has been determined by X-ray crystallography, which shows that in the solid state both isonitrile ligands are cis to sulfur. In solution, NMR and IR spectroscopy suggest that multiple isomers are present. Protonation of **2** occurs at the Fe–Fe bond to give a cationic complex **3** as four different isomeric species. Complex **3** does not react with deuterium gas (98 psi) in the absence of light. Irradiation of solutions of **3** with visible light under D_2 gas leads to formation of HD.

Introduction

Crystallographic studies of the Fe hydrogenase enzymes from two organisms[1] show that the active site contains a novel Fe_2 moiety with diatomic ligands shown by infrared spectroscopy[2] to be carbonyl and cyanide ligands.



The bridging sulfur atoms may be part of a propanedithiolate or possibly an azapropanedithiolate ligand. Computational studies[3] favor the latter possibility, since heterolysis of bound dihydrogen is facilitated. More recent crystallographic work is also consistent with this hypothesis.[4] The active site is anchored to the protein through a single cysteine sulfur which bridges to an adjacent Fe_4S_4 cluster.

Several model systems for this active site based on well-studied organometallic precursors have been investigated.[5] Darensbourg and co-workers reported the crystal structure of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ (**1**) and pointed out the close structural resemblance to the active site.[6] Pickett and co-workers have reported a very promising Fe_2S_3 model system which mimics the active site with a pendant thioether moiety attached to the central carbon of a propanedithiolate bridging ligand. Importantly, this system has been shown to form a transient bridging carbonyl species upon reaction with cyanide.[7] Interesting model complexes with azadithiolate bridging ligands have recently been prepared by a novel synthetic approach.[8] Rauchfuss and co-workers have reported the cyanation of **1** to give a reactive dianionic dicyano species $[Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CN)_2]^{2-}$, which is readily oxidized or protonated to afford insoluble materials.[9] Protonation of this dicyano dianion was reported by Darensbourg to lead to a transiently stable bridging hydride species.[10] Treatment of a related phosphine/cyano monoanionic derivative with acid was reported by Rauchfuss and co-workers to lead to a robust hydride complex which catalyzed proton reduction/H_2 evolution.[11] In related work, efficient (comparable to Pt) electrocatalytic hydrogen oxidation has been demonstrated at a graphite electrode impregnated with a NiFe hydrogenase.[12] The importance of such results in catalysis has been recently summarized.[13]

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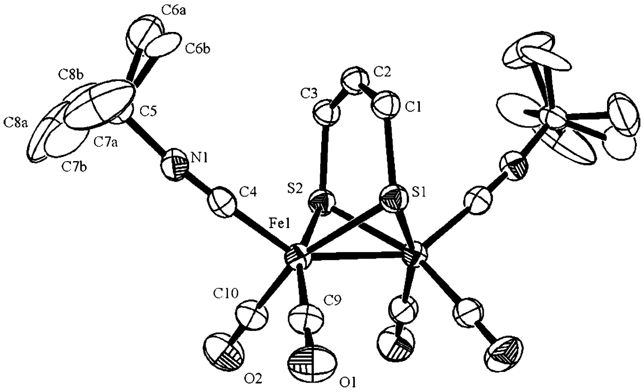

Figure 1. ORTEP representation (50% probability) of the molecular structure of complex **2**. Atoms without numbers are related to the numbered atoms by mirror symmetry.

Hydrogenase active site model complexes which show reactivity with hydrogen gas are rare. One such report is the work of Darensbourg and co-workers demonstrating that a cationic Fe_2 bis(phosphine) complex with a hydride bridge exhibits isotope exchange with D_2 gas, leading to HD formation upon irradiation with visible light.[14]

We now describe the characterization of a bis(isonitrile) derivative of complex **1** which gives a moderately stable bridging hydride complex upon protonation. The isonitrile ligands are a reasonable surrogate for the cyanide ligands found in the enzyme. Reaction of the protonated species with hydrogen has been detected by isotope exchange with added deuterium gas upon illumination with visible light.

Results

Reaction of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ (**1**) with 2 equiv of *t*-BuNC affords a disubstituted species $Fe_2(\mu\text{-}S_2C_3H_6)(CN\text{-}t\text{-}Bu)_2(CO)_4$ (**2**). Complex **2** was isolated in good yield after chromatography on silica gel, which removed small amounts of the mono- and trisubstituted species. The infrared spectrum of **2** (CH_2Cl_2) exhibits ν_{CN} at 2145 and 2133 cm^{-1} and ν_{CO} at 1997, 1972, and 1933 cm^{-1}. ^1H NMR spectra at ambient temperature show three resonances in the ratio of 2:4:18. The former (multiplet (2H) and triplet (4H), $J = 8$ Hz) are assigned to the propyl moiety. The latter is a slightly broadened singlet resonance at $\delta = 1.44$ ppm attributed to the tertiary butyl groups of the bound isonitrile ligands. Upon lowering of the temperature to 200 K, greater complexity is observed for the propyl resonances due to slowing of the inversion of the propyl moiety. The *t*-Bu resonance also broadens as the temperature is lowered, and decoalescence to three resonances at 1.45, 1.50, and 1.66 ppm (1:1:3) was observed at 230 K.

The structure of **2** in the solid state was determined by X-ray diffraction. Data collection and refinement procedures are summarized in Table 1. A summary of important bond distances and angles is in Table 2. An ORTEP diagram of the structure of **2** is shown in Figure 1. The structure is well behaved with the exception of some rotational disorder of the tertiary butyl groups.

Table 1. Crystallographic Data[a] and Structure Refinement for Complex **2**

empirical formula	$C_{17}H_{24}Fe_2N_2O_4S_2$
fw	496.20
cryst system	orthorhombic
space group	Pnma
unit cell dimens	
a (Å)	16.3690(4)
b (Å)	15.2380(12)
c (Å)	8.7430(12)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	2180.8(3)
Z	4
d(calcd) (g/cm^3)	1.511
T (K)	130(2)
reflcns measd	4074
reflcns unique	2285
R_{int}	0.0780
refined params/restraints	157/0
R1[b] [$I > 2\sigma(I)$]	0.0465
wR2[c]	0.1139
σ_{fin}(max/min) (e $Å^{-3}$)	0.471/−0.494

[a] Obtained using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [(\Sigma(wD^2)/\Sigma(wF_o^2)]^{1/2}$, where $D = F_o^2 - F_c^2$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Fe−Fe	2.5258(12)	Fe−S(1)−Fe	67.92(5)
Fe−S(2)	2.2511(13)	Fe−S(2)−Fe	68.25(5)
Fe−S(1)	2.2608(13)	S(2)−Fe−S(1)	85.12(5)
Fe−S(1)	2.2608(13)	C(3)−S(2)−Fe	111.9(2)
Fe−S(2)	2.2511(13)	C(1)−S(1)−Fe	112.1(2)
S···S	3.052	C(9)−Fe−C(10)	91.66(18)
Fe(1)−C(9)	1.764(4)	C(9)−Fe−C(4)	100.40(19)
Fe(1)−C(10)	1.770(4)	C(10)−Fe−C(4)	98.41(19)
Fe(1)−C(4)	1.868(5)	C(4)−Fe−S(2)	99.19(12)
N(1)−C(4)	1.163(5)	C(4)−Fe−S(1)	102.17(12)

Protonation of **2** with strong acids such as triflic acid affords a cationic species (**3**). The infrared spectrum of **3** (CH_2Cl_2) exhibits ν_{CN} at 2187 cm^{-1} and ν_{CO} at 2076, 2060, and 2028 cm^{-1}. Complex **3** is readily deprotonated by weak bases, including water.

Four high-field resonances were detected in the ^1H NMR spectrum at $\delta = -14$ to $\delta = -19$ ppm (see Figure 2) along with 4 distinct singlet resonances for *t*-Bu protons. The propyl region of the spectrum was very complex. Attempts to isolate pure samples of **3** under various conditions led to oily precipitates. A satisfactory combustion analysis could not be obtained. These difficulties are attributed to the presence of four distinct isomers (see Discussion).

Methylene chloride solutions of complex **3** were reacted with D_2 gas in the expectation that formation of HD would indicate a reaction with hydrogen followed by isotope exchange. No reaction was observed at ambient temperature in the dark under 90 psi of deuterium. Under the same conditions, upon irradiation with visible light, production of HD (1:1:1 signal centered at 4.58 ppm, $J_{H-D} = 43$ Hz) was observed over several days, along with extensive decomposition of **3**. A significant amount of H_2 was also observed, as shown by ^1H NMR spectroscopy. Control experiments

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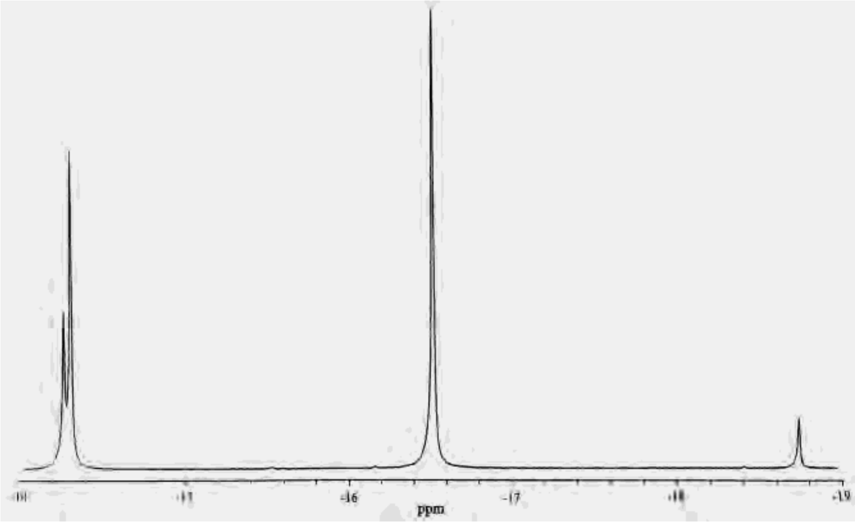


Figure 2. Partial (hydride region) ^{1}H NMR spectrum (750 MHz) of complex **3**.

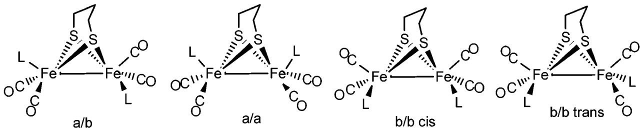
demonstrated that **3** undergoes slow decomposition in solution with formation of H_2.

Discussion

The structure of complex **2** in the solid state consists entirely of one of the four possible isomers, designated as apical/apical, abbreviated as a/a. The Fe−Fe distance is 2.526 Å, very similar to the corresponding distance reported by Darensbourg and co-workers for complex **1**[6] and for a related bis PMe_3 derivative.[14] The Fe−S and S−S distances are essentially identical to those seen in related dimeric species with three atom bridges between the thiolate ligands. The angle between the two carbonyl ligands on each Fe atom is very close to 90°, but the angles between the two carbonyls and the isonitrile ligand are 98 and 100°. A similar geometry was reported for the all-carbonyl analogue **1**, suggesting that steric factors are not appreciable in determining the structure.

In contrast to the solid-state structure, complex **2** in solution exists as at least two major isomers, leading to two different CN stretching modes in the infrared spectrum. While the NMR spectrum at ambient temperature exhibits a single *t*-Bu resonance, low-temperature spectra show decoalescence to give three *t*-Bu resonances in a 3:2:1 ratio. Low-temperature observations also lead to additional complexity of the signals due to the propyl bridge, consistent with slowing of propyl group inversion. The observation of multiple *t*-Bu resonances is consistent with the slowing of a basal/axial ligand permutation process and the freezing out on the NMR time scale of isomer interconversion. These results are similar to those reported by Darensbourg and co-workers on complex **1**, where both propyl group inversion and basal/equatorial CO ligand interchange was slow on the NMR time scale at −80 °C.[15] It has been suggested that this conformational flexibility may play a role in ligand substitution reactions of dimers of this type and may be relevant to the mechanism of action of the hydrogenase enzymes. In the case of complex **2**, at least two isomers are present in solution, likely those shown below as a/a and b/b. It is not possible to make a rigorous assignment of the *t*-Bu resonances. Apparently absent is the a/b isomer, which would be expected to show two *t*-Bu resonances of equal intensity.

The solution structure of **2** differs from that reported by Darensbourg and co-workers for the related complex $Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4$, which adopts the b/b (trans) structure in the solid state and in solution. (The presence of an unidentified minor isomer in solution was indicated by low-temperature ^{31}P NMR spectroscopy.[14]) While interconversion of the various isomers of **2** is rapid on the NMR time scale, crystallization affords only one isomer, designated as a/a (see Figure 1). This situation is analogous to that reported for the dicyano dianion $(\mu\text{-}S_2C_3H_6)[Fe_2(CO)_2(CN)]_2^{2-}$, where more than one isomer exists in solution, as indicated by IR spectroscopy, but only one isomer (a/b) is present in the solid state.[9] In general, complexes of this type can adopt several isomeric structures of comparable stability in solution. Facile interconversion among these structures may allow the solid-state structure observed to be dictated by subtle crystal packing forces.



As expected due to the presence of two isonitrile ligands, complex **2** is more difficult to reduce than the hexacarbonyl complex **1**, as shown by CV measurements. Acetonitrile solutions of complex **2** are reduced in an apparently two-electron process occurring at $E_p^{red} = -1.56$ V vs NHE. As expected, this value falls between the values for **1** (−0.94 V) and $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(PMe_3)_2$ (−1.64 V) and is in rough agreement with the value reported[16] for $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CNMe)_2$ of −1.42 V. The E_p^{ox1} for compound **2** is at 0.76 V. Compound **2** is more easily oxidized than hexacar-

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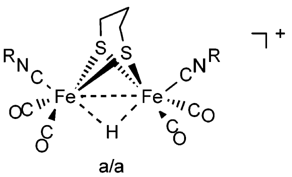
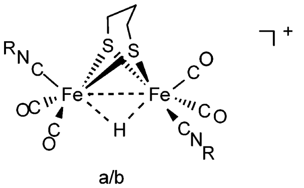
bonyl compound **1** (1.42 V) and has an oxidation potential similar to that reported for $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CNMe)_2$ of 0.87 V. The bis(phosphine) derivative $Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4$ is more difficult to reduce (−1.64 V),[17] consistent with the presence of the strong donor PMe_3 ligands.

Consistent with the greater basicity of the metal centers in **2** versus **1**, protonation of complex **2** affords a cationic species **3**, while **1** shows no reaction with acids. Infrared spectroscopy is consistent with significant reduction in electron density at the Fe centers upon this formal dinuclear oxidative addition reaction. The stretching frequencies of the CO reporter ligands shift to higher energy by ca. 90 cm^{-1}. Similar results have been reported by Darensbourg and coworkers for the protonation of $Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4$ and related complexes.[14] While the infrared spectrum of **3** exhibits a single, somewhat broadened CN stretching mode, the ^1H NMR spectrum shows *four* distinct hydride resonances, suggesting that all possible isomers are present. The hydride resonances at −14.25 and −14.29 ppm together account for nearly 50% of the total hydride signal (see Figure 2). On the basis of the very similar chemical shifts, it is reasonable to attribute these two signals to the two basal/basal isomers, designated below as b/b (cis) and b/b (trans). This suggests that, in this quasi-octahedral Fe environment, hydrides trans to carbonyl ligands resonate to lower field. By extension, the resonance at −16.49 ppm can be tentatively assigned to the low-symmetry a/b isomer. The highest field resonance at −18 ppm is attributed to the a/a isomer. This assignment would predict that a total of five *t*-Bu resonances should be observed, with two signals of equal intensity for the low-symmetry a/b isomer and one signal for each of the higher symmetry species. Careful examination of the *t*-Bu region of the ^1H NMR spectrum recorded at 750 MHz reveals only four resonances, suggesting the possibility that overlap of *t*-Bu resonances occurs.

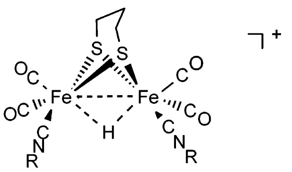
Regardless of the veracity of the detailed assignment suggested above, we must conclude that the isomer distribution in **3** differs from that observed in the neutral precursor **2**, where at most three isomers were present. We postulate that differential basicity in the various isomers could lead to differing rates of protonation of the rapidly equilibrating mixture of isomers of **2**, leading to a significantly different isomer distribution in the cationic manifold.



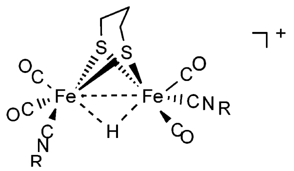
a/a



a/b

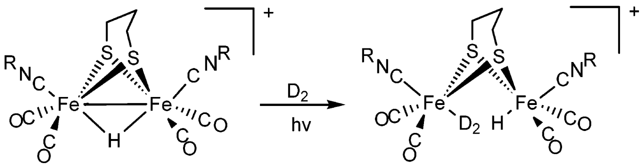


b/b (cis)



b/b (trans)

We anticipated that the formally Fe(II) centers in **3** would be appropriate for binding and activation of hydrogen. This was probed by reaction of **3** with D_2 gas, with the expectation that formation of HD via intramolecular atom scrambling would signal the transient formation of a dihydrogen complex. Prolonged exposure of methylene chloride solutions of complex **2** to D_2 gas at room temperature showed no formation of HD. Gradual decomposition of **2** was observed in methylene chloride, with much more rapid decomposition occurring in acetonitrile or acetone. Some experiments showed traces of HD formation, which was ultimately traced to the effect of room light. Irradiation of solutions with various wavelengths of light was explored. Irradiation with UV light from a mercury arc lamp led to very rapid decomposition with no HD formation. The best results were achieved with visible light using a 450 nm cutoff filter. Even under these conditions, the yield of HD gas is limited by competing decomposition reactions to ca. 5%, based on integration versus complex **2**. Similar but cleaner HD production has been reported by Darensbourg and co-workers for the reaction of D_2 with protonated bis(phosphine) complexes such as $[(\mu\text{-}H)Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4]^+$.[14] A mechanism involving photochemically induced hydride bridge opening was suggested by Darensbourg to explain these observations, and it is reasonable to postulate a similar mechanism for complex **3**, shown as follows: In this scheme, only one of the four possible isomers of complex **3** is depicted. Although we have no direct evidence for the postulated hydrogen (deuterium) complex, the observed HD formation is consistent with binding and activation of hydrogen within the coordination sphere of **3**, where intramolecular atom exchange is expected to be facile.



Conclusions

Using isonitrile ligands as a surrogate for the cyanide ligands found in the active site of Fe hydrogenase enzymes, a model complex which exhibits sufficient basicity to allow protonation at the metal centers has been prepared. The instability upon protonation or oxidation and formation of insoluble materials that follows from the presence of two cyanide ligands in prior model complexes is avoided. The cationic, formally Fe(II)−Fe(II) species **3** exhibits modest reactivity with deuterium gas upon irradiation with visible light.

Further investigations of the oxidation chemistry of complex **2** are underway, with the objective of generating coordinatively unsaturated species which exhibit thermal reactivity with hydrogen.

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Experimental Section

General Procedures. All manipulations were performed using standard Schlenk-line techniques under argon or in an argon atmosphere glovebox. Dichloromethane was distilled over calcium hydride under N_2. The following materials were of reagent grade and used as received: $Fe_3(CO)_{12}$, 1,3-propanedithiol, *t*-Bu isocyanide, and $HOSO_2CF_3$; D_2 (Cambridge Isotope Laboratories). $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ was prepared according to the procedure of Seyferth and co-workers.[18] Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR instrument using 0.1 mm NaCl cells. ^1H NMR spectra were recorded on Bruker DRX-500 and DMX-750 spectrometers. Proton NMR spectra were referenced to the solvent resonance with chemical shifts reported relative to TMS. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cyclic voltammetry employed a Princteon Applied Research 273 potentiostat with a glassy carbon working electrode, a platinum wire counter electrode, a SCE reference elctrode, and 0.1 M $(n\text{-}Bu_4N)(PF_6)$ (in MeCN) as the supporting electrolyte.

Synthesis of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CN\text{-}t\text{-}Bu)_2$ (2). A solution of 3.0 g of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ in 60 mL of CH_2Cl_2 was treated with 1.9 mL of *t*-BuNC (2.1 equiv) and stirred for 2 days at room temperature. The solution was then evaporated to dryness under a N_2 stream. The resulting solid was dissolved in a minimal amount of CH_3CN and applied to a silicic acid column. Elution with CH_3CN affords the desired product as a red solution. Complex **2** was isolated by concentration of the CH_3CN solution. Yield: 2.15 g (55%). Anal. Calcd for $C_{17}H_{24}N_2O_4S_2Fe_2$: C, 41.15; H, 4.88; N, 5.65; S, 12.92. Found: C, 40.16; H, 4.69; N, 6.02; S, 12.12. ^1H NMR (500 MHz, CD_2Cl_2, δ): 1.95 (t, 4H, SCH_2, $J = 8$ Hz), 1.69 ppm (mult, 2H, CH_2), 1.44 (s, 18H, CN-*t*-C_4H_9). Low-temperature NMR experiments are described in the Results section. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2145 (sh), 2133 (m); ν_{CO} 1997 (m), 1972 (s), and 1933 (m). Cyclic voltammetry (CH_3CN): irreversible reduction at -1.56 V and oxidation at 0.76 V (vs NHE).

Solid-State Structure of 2. Suitable crystals were grown from a concentrated acetonitrile solution and mounted on glass capillaries in oil. Diffraction measurements were made on a red block crystal of dimensions 0.14 × 0.07 × 0.07 mm in a nitrogen stream at 130 K on a Nonius KappaCCD diffractometer using graphite-monochromated radiation ($\lambda = 0.710\,73$ Å). Crystal-to-detector distance was 30 mm, and exposure time was 50 s for all sets. The scan width was 2°. Data collection was 99.1% complete to 26.37° in θ. A total of 18 533 partial and complete reflections were collected covering the indices $h = -20$ to 20, $k = -18$ to 18, and $l = -10$ to 10. A total of 2285 reflections were symmetry independent, and the $R_{int} = 0.0780$ indicated good data quality. Indexing and unit cell refinement indicated an orthorhombic *P* lattice. The space group was found to be *Pnma* (No. 62) with cell parameters $a = 16.3690(4)$ Å, $b = 15.2380(12)$ Å, $c = 8.7430(12)$ Å, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 90°$. The cell volume was 2180.8(3) Å^3, and the calculated density was 1.511 g/cm^3, with $Z = 4$. The data were integrated and scaled using hkl-SCALEPACK. Solution by direct methods produced a complete heavy atom phasing model closely related to the proposed structure. All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The X-ray data are summarized in Table 1. Important bond distances and angles are listed in Table 2.

Protonation of Complex 2. A solution of 0.125 g (0.25 mmol) of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CN\text{-}t\text{-}Bu)_2$ in 10 mL of CH_2Cl_2 was treated with 40 μL (0.45 mmol) of triflic acid at -42 °C and allowed to warm to room temperature over the course of 1 h. Monitoring by infrared spectroscopy indicated complete conversion to $\{Fe_2(\mu\text{-}H)(\mu\text{-}S_2C_3H_6)(CO)_4(CN\text{-}t\text{-}Bu)_2\}^+[OTf]^-$ (**3**). Attempts to isolate **3** by concentration of CH_2Cl_2 or CH_2Cl_2/Et_2O solutions lead to an oily precipitate. A satisfactory combustion analysis could not be obtained. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2187 (m); ν_{CO} 2076 (m), 2060 (s), and 2028 (m). An optimal sample for NMR spectroscopy was obtained by in situ protonation using 0.015 g (0.03 mmol) of **2** and 5 μL (0.06 mmol) of triflic acid in 1 mL of CD_2Cl_2 at -42 °C. ^1H NMR (750 MHz, CD_2Cl_2, δ): -14.25 (17%); -14.29 (30%); -16.49 (49%); -18.71 (4%). Four associated *t*-Bu resonances were identified in the range of 1.5−1.7 ppm and tentatively assigned to the isomers of **3** (see Discussion). The resonances due to the propyl bridge in **3** are an overlapping set of complex multiplets and could not be definitively assigned.

Addition of water to solutions of **3** resulted in immediate reversion to **2**.

H/D Exchange Reaction of $\{Fe_2(\mu\text{-}H)(\mu\text{-}S_2C_3H_6)(CO)_4(CN\text{-}t\text{-}Bu)_2\}^+[OTf]^-$ (3) with D_2. A CD_2Cl_2 solution of neutral complex **2** was protonated in CD_2Cl_2 in a medium-pressure J-Young NMR tube using the method described above. The tube was then frozen, evacuated, and back-filled with 98 psi D_2. The sample was irradiated with visible light using a 450 nm cutoff filter and monitored periodically by ^1H NMR spectroscopy. Resonances attributed to HD gas at 4.58 ppm (1:1:1 pattern, $J = 43$ Hz) and H_2 at 5.60 ppm were observed to gradually increase in intensity over the course of several days. Extensive decomposition of complex **3** accompanies this reaction. UV irradiation (Hg arc lamp) of solutions of **3** leads to rapid decomposition with no formation of HD. In acetonitrile or acetone solutions, complex **3** decomposes rapidly even in the absence of light to a complex mixture of products.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Support was also provided by the University of Washington Royalty Research Fund.

Supporting Information Available: A crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC034334B

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