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Protophilicity, electrochemical property, and desulfurization of diiron dithiolate complexes containing a functionalized C₂ bridge with two vicinal basic sites

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ABSTRACT

Two diiron dithiolate complexes $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5L]$ (L = PPh₃, **2**; P(Pyr)₃, **3**) containing a functionalized C_2 bridge with two vicinal basic sites were prepared and characterized as models of the FeFe-hydrogenase active site. The molecular structures of 2 and its N-protonated form $[(2H_N)(OTf)]$ were determined by X-ray analyses of single crystals. In the solid state of $[(2H_N)(OTf)]$. Each asymmetric unit contains a molecule of $[(2H_N)(OTf)]$ and a molecule of water. The molecule of water is close to the iron atom of the [Fe(CO)₃] unit (Fe···O(H₂O), 4.199 Å). The complexes 2 and 3 are relatively protophilic. ³¹P NMR spectra and cyclic voltammograms show that they can be protonated by the mild acids CCl₃COOH and CF₃COOH. Electrochemical studies show that the first reduction peak of 3 at -1.51 V versus Fc⁺/Fc is 110 mV more positive than that (-1.62 V) found for the analogous diiron azadithiolate complex $[{(\mu-SCH_2)_2N(CH_2C_6H_5)}Fe_2(CO)_5P(Pyr)_3]$ (7). Protonation of **2** and **3** leads to the anodic shifts of 610– 650 mV for the Fe^lFe^l/Fe^lFe⁰ reduction potentials. The shifts are apparently larger than that (450 mV) for protonation of **7**. The reaction of the all-carbonyl complex $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5L]$ with two equivalents of bis(diphenylphosphino)methane (dppm) in refluxing toluene affords a desulfurized complex $[(\mu-S)(\mu-dppm)_2Fe_2(CO)_4]$ (6). The reaction process was studied. A dppm mono-dentate intermediate [$\{\mu$ -SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₅(κ ¹-dppm)] (**4**) and a dppm μ -bridging species [{µ-SC(NBn)CH(NHBn)S-µ}Fe₂(CO)₄(µ-dppm)] (5) have been isolated and spectroscopically characterized.

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1. Introduction

The chemistry of diiron dithiolate complexes has attracted intensive attention in recent years since their close resemblance in structure to the FeFe-hydrogenase active site (H-cluster) [1,2]. The DFT investigations suggest that the central atom in the dithiolate bridge of the H-cluster is a nitrogen (SCH₂NHCH₂S) or an oxygen atom (SCH₂OCH₂S) [3–5]. Both the theoretical calculations and the studies on the synthetic model complexes have shown that the internal base may act as a proton transfer relay in the [FeFe]-H₂ase active site (H-cluster) [6-9]. The protophilicity and the electrochemical property of diiron dithiolate complexes containing different internal bases have been extensively reported. Protonation of diiron azadithiolate complexes at the bridging-nitrogen atom has been verified spectroscopically and crystallographically [8-13], which results in considerable anodic shifts (370-420 mV) of the Fe^IFe^I-to-Fe^IFe⁰ reduction potentials for the diiron complexes. Double protonated forms of diiron azadithiolate complexes, both at the bridging-nitrogen atom and the iron center, have also been spectroscopically characterized in situ [14-16]. Recently, we have reported the crystal structure of a proton-hydride diiron complex $[(\mu-H)(\mu-pdt){Fe(CO)_3}{Fe(CO)(\kappa^2 p, p'-PNHP)}](OTf)_2 (PNP = Ph_2-PNHP)$ PCH₂N(*n*-Pr)CH₂PPh₂) [17]. In addition, there is one report on the double protonation at the σ -donor ligand (CN⁻) and the iron center, resulting in an unstable species [18]. The pyridyl group has been tethered to the central carbon of the propane-1,3-dithiolato (pdt) bridge of the diiron complex as an internal base and a hemi-labile ligand [19]. The protonation and deprotonation of the pyridyl group can control the extent of carbonylation of the diiron model complex.

The afore-mentioned internal bases of the FeFe-Hase mimics, namely, the nitrogen atoms in the azapropanedithiolato bridge, the CN⁻ ligand, and the pyridyl group, can be protonated in organic solvents only in the presence of strong acids [8-19]. Studies on the diiron complexes featuring an internal basic site, which can be readily protonated by weak acids with a large influence on the Fe^IFe^I/Fe^IFe⁰ reduction potential, are of interest for design of ironbased electrochemical and photochemical catalysts for proton



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reduction to dihydrogen. In this work, we prepared and characterized two diiron dithiolate complexes [{µ-SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₅L] (L = PPh₃, **2**; P(Pyr)₃, **3**) containing a functionalized C₂ bridge with two vicinal basic sites. We found that the reaction of the complex $[\{\mu$ -SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₆] (1) with two equivalents of bis(diphenylphosphino)methane (dppm) in refluxing toluene afforded a desulfurized complex $[(\mu-S)(\mu-dppm)_2Fe_2 (CO)_4$ (6) via a dppm mono-dentate intermediate [{ μ -SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₅(κ^{1} -dppm)] (**4**) and a dppm μ bridging species $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_4(\mu-dppm)]$ (5). The complexes 2 and 3 can be protonated by mild acids CCl₃COOH and CF₃COOH in acetonitrile, resulting in a 610-650 mV anodic shift of the Fe^IFe^I/Fe^IFe⁰ reduction potentials. Here, we report the preparation and characterization of 2-6, the molecular structures of **2**, its protonated species $[(2H_N)(OTf)]$, and **6**, the protophilicity of **2** and **3**, as well as the electrochemical properties of **2** and **3** compared with the analogous diiron azadithiolate complex $[{(\mu-SCH_2)_2N(CH_2C_6H_5)}Fe_2(CO)_5P(Pyr)_3]$ (7).

2. Experimental

2.1. General procedures and materials

All reactions and operations related to organometallic complexes were carried out under dry, oxygen-free dinitrogen with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Commercially available chemicals, Me₃NO · 2H₂O, HOTf, CCl₃COOH, CF₃COOH, PPh₃, and dppm, were of reagent grade and used as received. Ligand P(Pyr)₃, diiron carbonyl complexes [{ μ -SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₆] (1) and [{(μ -SCH₂)₂N(CH₂C₆H₅)}Fe₂(CO)₅P(Pyr)₃] (7) were prepared following the literature methods [20–22].

Infrared spectra were recorded on JASCO FT/IR 430 spectrophotometer. Proton and ³¹P NMR spectra were collected with a Varian INOVA 400 NMR Instrument. Mass spectra were recorded on an HP1100 MSD mass spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.

2.2. Synthesis of [{ μ -SC(NBn)CH(NHBn)S- μ }Fe₂(CO)₅L] (L = PPh₃, **2**; P(Pyr)₃, **3**)

CO-Removing reagent Me₃NO · 2H₂O (0.11 g, 1.0 mmol) was added to a solution of **1** (0.58 g, 1.0 mmol) in MeCN (20 ml). The red solution was stirred for 5 min and the color turned dark red. Triphenylphosphine (0.27 g, 1.0 mmol) was added to the solution, and it was stirred for 30 min. The solvent was removed under reduced pressure. The residue was purified by chromatography on a silica gel column with hexane/CH₂Cl₂ (2:1, v/v) as eluent. The complex **2** was obtained as red powder from the collected red band after removal of solvent. Yield: 0.70 g (86%). *Anal.* Calc. for C₃₉H₃₁Fe₂N₂O₅PS₂: C, 53.99; H, 3.71; N, 3.15. Found. C, 53.78; H, 3.78; N, 3.07%. IR (KBr): v(CO) 2048 (s), 1988 (s), 1938 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 7.00–7.52 (25H, 5Ph), 4.54, 4.39 (2d, *J*_{H-H} = 15.8 Hz, 2H, C=NCH₂), 3.87, 3.59 (2d, *J*_{H-H} = 13.8 Hz, 2H, NHCH₂) 3.11 (s, 1 H, SCH), 2.10 (s, 1 H, NH) ppm. ³¹P NMR (CDCl₃): δ 60.24 ppm.

The complex **3** was prepared according to the abovedescribed protocol. Yield: 0.50 g (80%). IR (KBr): v(CO) 2059 (s), 2007 (s), 1991 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 7.13–7.27 (10H, 2Ph), 6.63, 6.21 (2s, 12H, 3Pyr), 4.79, 4.73 (2d, J_{H-H} = 14.4 Hz, J_{H-H} = 27.2 Hz, 2H, C=NCH₂), 3.94, 3.70 (2d, J_{H-H} = 8.8 Hz, 2H, NHCH₂), 3.28 (s, 1H, SCH), 2.21 (s, 1H, NH) ppm. ³¹P NMR (CDCl₃): δ 140.01 ppm.

2.3. Synthesis of $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5PPh_3](OTf)$

HOTf (1.5 equivalents) was added to a solution of **2** (0.81 g, 1.0 mmol) in diethyl ether (50 ml). The red solution was stirred for 5 min and stood for 3 h. Protonated species [(**2**H_N)(OTf)] was precipitated as red powder from the solvent and washed three times with cold diethyl ether. Yield: 0.83 g (87%). *Anal.* Calc. for C₄₀H₃₂F₃Fe₂N₂O₈PS₃: C, 49.81; H, 3.34; N, 2.90. Found: C, 49.43; H, 3.42; N, 2.65%. IR (KBr): ν (CO) 2061 (s), 2009 (s), 1948 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 7.09–7.43 (25H, 5Ph), 4.77, 4.58 (2d, J_{H-H} = 13.2 Hz, 2H, C=NCH₂), 4.40–4.80 (br, 2H, NH₂), 4.10, 3.87 (2d, J_{H-H} = 12.8 Hz, 2H, NHCH₂), 3.59 (s, 1H, SCH) ppm. ³¹P NMR (CDCl₃): δ 59.10 ppm.

2.4. Synthesis of $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5(dppm)]$ (4)

Ligand dppm (0.39 g, 1.0 mmol) was added to a solution of **1** (0.58 g, 1.0 mmol) in toluene (20 ml). The mixture was refluxed for 0.5 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was chromatographed on an alumina column with hexane/CH₂Cl₂ (2:1, v/v) as eluent. The complex **4** was obtained as red powder from the collected red band after removal of solvent. Yield: 0.66 g (69%). IR (KBr): v(CO) 2045 (s), 1986 (vs), 1934 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 7.10–7.35 (30H, 6Ph), 4.52, 4.20 (2d, $J_{H-H} = 15.8$ Hz, 2H, $C=NCH_2$), 3.92, 3.61 (2d, $J_{H-H} = 13.2$ Hz, 2H, NHCH₂), 3.40 (s, 1H, SCH), 3.18 (d, $J_{H-H} = 8.0$ Hz, 2H, PCH₂P), 2.17 (s, 1H, NH) ppm. ³¹P NMR (CDCl₃): δ 53.18 (d, $J_{P-P} = 91.5$ Hz, coordinated dppm), -26.31 (d, $J_{P-P} = 91.5$ Hz, non-coordinated dppm) ppm. ESI-MS: m/z 937.1 [M+H]⁺.

2.5. Synthesis of $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_4(\mu-dppm)]$ (5)

The toluene solution (20 ml) of **1** (0.58 g, 1.0 mmol) and dppm (0.39 g, 1.0 mmol) was refluxed for 1.5 h. Complex **5** was obtained by chromatography of the residue on an alumina column with hexane/CH₂Cl₂ (1:1, v/v) as eluent. Yield: 0.60 g (66%). IR (KBr): vCO 1995 (s), 1964 (vs), 1931 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 7.11–7.55 (30H, 6Ph), 4.92, 4.73 (2br, 2H, C=NCH₂), 4.35, 4.01 (2br, 2H, NHCH₂), 4.10 (s, 2H, PCH₂P), 3.46 (s, 1H, SCH), 2.20 (br, 1H, NH) ppm. ³¹P NMR (CDCl₃): δ 57.23 (d, *J*_{P-P} = 59.9), 56.31 (br), 56.03 (br), 54.30 (d, *J*_{P-P} = 53.4) ppm. ESI-MS: *m/z* 909.1 [M+H]⁺.

2.6. Synthesis of $[(\mu-S)(\mu-dppm)_2Fe_2(CO)_4]$ (6)

Ligand dppm (0.78 g, 2.0 mmol) was added to a solution of **1** (0.58 g, 1.0 mmol) in toluene (20 ml). The solution was refluxed for 6 h. The complex **6** was precipitated as red powder from the solution and washed three times with acetone. Yield: 0.72 g (70%). *Anal.* Calc. for C₅₄H₄₄Fe₂O₄P₄S: C, 63.30; H, 4.33. Found: C, 63.27; N, 4.35%. IR (KBr): *v*CO 1967 (m), 1925 (s), 1898 (m), 1875 (w) cm⁻¹. ³¹P NMR (CH₂Cl₂): δ 44.20 ppm.

2.7. X-ray crystal structure determination

Single crystals of **2**, [(**2**H_N)(OTf)], and **6** were obtained by recrystallization from dichloromethane/hexane. All of the single crystal X-ray diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 298 K using the ω -2 θ scan mode. Data processing was accomplished with the SAINT program. Intensity data were corrected for absorption by the SADABS program. The structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELX-97 program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by geometrical calculation and refined in a riding model, and the proton on the N atom of [(**2**H_N)(OTf)] was

Table 1

Crystallographic data and processing parameters for 2, $[(2H_N)(OTf)]$, and 6.

Complex	2	[(2 H _N)(OTf)]	6
Empirical formula	C40H33Cl2Fe2N2O5PS2	$C_{41}H_{34}Cl_2F_3Fe_2N_2O_9PS_3$	C54H44Fe2O4P4S
M _w	899.37	1065.45	1024.53
Crystal system	monoclinic	triclinic	triclinic
Space group	P2(1)/n	ΡĪ	ΡĪ
a (Å)	13.412(3)	11.5545(7)	12.242(2)
b (Å)	15.090(3)	12.2831(8)	12.453(2)
c (Å)	20.288(5)	19.086(1)	18.658(3)
α (°)	90.00	71.785	108.06(1)
β (°)	94.815(3)	86.715	97.30(1)
ν (°)	90.00	64.865	108.486(8)
$V(Å^3)$	4092(2)	2320.4(3)	2483.3(6)
Z	4	2	2
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.460	1.525	1.370
F(000)	1840	1088	1056
Crystal size (mm ³)	0.06 imes 0.49 imes 0.52	0.09 imes 0.13 imes 0.22	0.07 imes 0.10 imes 0.17
$\theta_{\text{Min}/\text{Max}}$ (°)	2.21/27.16	2.17/18.65	1.81/25.00
Reflections collected/unique	19849/7145	17183/7943	18416/8400
Parameters refined	472	584	586
Goodness-of-fit on F^2	1.057	1.011	0.932
Final $R_1 [I > 2\sigma(I)]$	0.0629	0.0437	0.0704
Final wR ₂	0.1833	0.1164	0.1341
Residual electron density (e Å ⁻³)	1.236, -1.094	0.651, -0.487	0.665, -0.543

located by the difference Fourier map. Crystal data and parameters for data collections and refinements of complexes **2**, $[(2H_N)(OTf)]$, and **6** are listed in Table 1. The quality of the single crystal of the complex **6** containing solvent was not good, resulting in the large R_{int} value (0.1613).

2.8. Electrochemistry

Acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was dried with molecular sieves and then freshly distilled from CaH₂ under N₂. A solution of 0.05 M *n*[NBu₄][PF₆] (Fluka, electrochemical grade) in CH₃CN was used as electrolyte, which was degassed by bubbling with dry argon for 10 min before measurement. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 100 mV/s. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire. All potentials are reported relative to the Fc⁺/Fc potential.

3. Results and discussion

3.1. Preparation and spectroscopic characterization of the complexes 2, 3, and $[(2H_N)(OTf)]$

The parent complex $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_6]$ (1) was prepared according to the literature method [20], which is an oil and very sensitive to air and moisture. More stable diiron complexes $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5PPh_3]$ (2) and $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2(CO)_5P(Pyr)_3]$ (3) were obtained by treating **1** with a phosphine ligand in the presence of the CO-removing reagent Me₃NO · 2H₂O in CH₃CN. The complexes **2** and **3** are stable in the solid state and in the solution. They were characterized by IR, ¹H and ³¹P NMR spectroscopy, and the elementary analysis. The complex **2** displays three ν (CO) bands at 2048, 1988, and 1938 cm⁻¹ in the IR spectrum, and the ν (CO) bands of **3** appear at 2059, 2007, and 1991 cm⁻¹. Comparison of the ν (CO) bands of

2 and **3** is clearly indicative of the weaker electron donating capability of the $P(Pyr)_3$ ligand as compared to the PPh₃ ligand. The ¹H





Fig. 1. The IR spectra of complexes 4 (bottom), 5 (middle), and 6 (top).

signals for the two CH_2 groups, the CH, and the NH group in the complex **3** are all move to down-field by 0.11–0.17 ppm compared to the corresponding signals of **2**. The complexes **2** and **3** display ³¹P signals at 60.2 and 140.0 ppm, respectively.

Protonation of **2** in diethyl ether with addition of 1.5 equivalents HOTf afforded the N-protonated species $[(2H_N)(OTf)]$ as red precipitate in a good yield (87%) after being washed with cold diethyl ether and recrystallization in hexane/CH₂Cl₂. In comparison to the v(CO) bands of **2**, the v(CO) bands of $[(2H_N)(OTf)]$ is shifted to higher frequencies by ca. 15 cm⁻¹ in average, indicating that protonation of the amino-N atom on the C₂ bridge has apparent influence on the electron density of the iron atoms. This shift value of the v(CO) bands is comparable to those reported for N-protonation of other analogous diiron complexes [8–15]. The proton resonance

of the SCH group directly attached to the protonated-N atom is moved down-field by ca. 0.31 ppm in the ¹H NMR spectrum of [($2H_N$)(OTf)]. The spectroscopic evidence strongly supports the protonation of the N atom in the complex **2**. Upon addition of an equivalents of aniline to the solution of [($2H_N$)(OTf)], the ³¹P signal at 58.0 ppm for the N-protonated species completely disappeared, and in the same time the signal at 60.2 ppm for the complex **2** appeared as the only peak in the ³¹P NMR spectrum, indicating a reversible protonation and deprotonation process between **2** and [($2H_N$)(OTf)] (Scheme 1).

3.2. CO-displacement of 1 by dppm

The reaction of the complex 1 with an equivalents of bis(diphenylphosphino)methane (dppm) in refluxing toluene for 0.5 h afforded the complex $[{\mu-SC(NBn)CH(NHBn)S-\mu}Fe_2 (CO)_5(\kappa^1$ -dppm)] (4), in which dppm acts as a simple monodentate ligand. When the toluene solution of 4 was further refluxed for 1 h, an intramolecular CO-displacement occurred to form a μ -dppm bridging complex [{ μ -SC(NBn)CH(NHBn)S- μ }Fe₂- $(CO)_4(\mu$ -dppm)] (5). The complex with a chelating dppm ligand was not detected during the reaction by ³¹P NMR monitoring, which is different from the reaction of $(\mu-pdt)$ [Fe₂(CO)₆] and dppm [23,24]. If another equivalents of dppm was added to the toluene solution of **5**, an unexpected complex $[(\mu-S)(\mu-dppm)_2Fe_2(CO)_4]$ (6) was obtained after 4.5 h reflux. The complex 6 was formed by simultaneous CO-displacement and desulfurization of 5 (Scheme 2). Sulfur-containing organic compound PhCH₂N=CHC(S)NHCH₂Ph was detected in the reaction solution by HPLC-MS analysis. The first two steps for the reaction of 1 and dppm to form the complexes **4** and **5** are just similar to the reaction of $(\mu$ -pdt)[Fe₂(CO)₆] and dppm [23,24], while the third step, desulfurization reaction, is special for 1. The complex (µ-pdt)[Fe₂(CO)₄(µ-dppm)], in analogy to **5**, did not react with dppm even in refluxing toluene for 72 h. The results show that the $[\mu$ -SC=NBnCH(NHBn)(μ -S)] bridge in **1** is apparently less stable than the pdt bridge. The complexes 4-6 were characterized by IR, MS, ¹H and ³¹P NMR spectroscopy, and the molecular structure of 6 was determined by X-ray diffraction study.

Except for the additional ¹H signals of dppm, the complex **4** displays a similar ¹H NMR spectrum with that of **2**. In addition to the signals at 7.10–7.35 ppm for phenyl groups of dppm and the C₂ bridge, a typical doublet at 3.18 ppm (J = 8.0 Hz) for the CH₂ group of dppm is found in the ¹H NMR spectrum of **4**. Two doublets, at 53.2 ppm for the coordinate phosphorus and -26.3 ppm for the non-coordinate one, appear in the ³¹P{1H} NMR spectrum of **4**. As the free phosphorus of dppm in **4** is coordinated to the other iron atom by replacement of a CO ligand, the ¹H signal for the



Fig. 2. Molecular structures of 2 (left) and $(2H_N)^+/H_2O$ with the thermal ellipsoids at 30% probability.



Fig. 3. Diagram of the dimeric structure of [(2H_N)(OTf)] encircling two water molecules by hydrogen bonds (ellipsoids at 30% probability).

CH₂ group of dppm ligand is moved from 3.18 to 4.10 ppm. There are two doublets at 57.23 ppm ($J_{P-P} = 59.9$) and 54.30 ppm ($J_{P-P} = 53.4$) as well as two broad signals at 56.31 and 56.03 ppm in the ³¹P spectrum of **5**, indicative of existence of two conformation isomers for the complex **5** in solution in an approximate equal ratio. The isomerization caused by swing of the μ -bridging dppm ligand is similar as that found for (μ -pdt)(μ -PNP)[Fe(CO)PMe₃]-[Fe(CO)₂] in our previous studies [25]. Because of the non-symmetric bridge of **5**, the chemical shifts should be different for the two phosphorus centers of the μ -dppm ligand. Therefore four ³¹P signals are observed, and the two broad signals at 56.31 and 56.03 ppm result from the overlap of two doublets. The complex **6** displays only one ³¹P signal at 44.2 ppm for four coordinate phosphorus atoms, indicating that **6** has a symmetric molecular structure.

Table 2	
Selected bond lengths (Å) and angles (°) for 2 and [(2H _N)(OTf)]	· H ₂ O.

Complex	2	$(2H_N)^{+}$
Bond lengths		
Fe(1)-Fe(2)	2.527(1)	2.5109(7)
Fe(1)-S(1)	2.256(1)	2.2651(9)
Fe(1)-S(2)	2.269(2)	2.274(1)
Fe(2)-S(1)	2.249(1)	2.250(1)
Fe(2)-S(2)	2.266(1)	2.263(1)
Fe(2)-P(1)	2.253(1)	2.260(1)
S(1)-C(6)	1.847(4)	1.816(3)
S(2)-C(7)	1.803(5)	1.788(3)
N(1)-C(6)	1.437(6)	1.474(4)
N(1)-C(8)	1.468(6)	1.502(4)
N(2)-C(7)	1.260(6)	1.250(4)
N(2)-C(9)	1.456(6)	1.455(5)
N(1)…N(2)	2.728	2.704
Bond angles		
S(1)-Fe(1)-S(2)	80.64(5)	81.14(3)
S(1)-Fe(2)-S(2)	80.87(5)	81.72(3)
P(1)-Fe(2)-Fe(1)	151.23(4)	151.05(3)
C(6) - N(1) - C(8)	114.7(4)	114.6(3)
C(7)-N(2)-C(9)	121.3(4)	121.5(3)
N(1)-C(6)-C(7)	110.8(4)	109.8(3)
N(1)-C(6)-S(1)	111.1(3)	112.0(3)
C(7)-C(6)-S(1)	107.9(3)	110.2(2)
N(2)-C(7)-S(2)	125.2(4)	127.5(3)
N(2)-C(7)-C(6)	119.4(4)	118.3(3)
C(6)-C(7)-S(2)	115.3(3)	114.1(2)

The complex **4** displays three v(CO) bands in the region of 2061–1948 cm⁻¹ (Fig. 1), which are shifted by ca. 50 cm⁻¹ in average to lower frequency as compared to the v(CO) bands of the complex **1**. The subsequent intramolecular CO/phosphine replacement results in a further red-shift of the v(CO) bands to 1995–1931 cm⁻¹. The complex **6** with two μ -bridging dppm ligands exhibits four v(CO) bands in the region of 1967–1875 cm⁻¹. The IR, MS, ¹H and ³¹P NMR data give clear evidence for the formation of phosphine mono-, di-, and tetra-substituted complexes **4**, **5**, and **6**, in the different stages of the CO-displacement of **1**.

3.3. Molecular structures of 2, $[(2H_N)(OTf)]$, and 6

To obtain unambiguous evidence for the N-protonation of **2**, the molecular structures of **2** and its N-protonated species $[(2H_N)(OTf)]$ were determined by X-ray analyses of single crystals, which are depicted in Figs. 2 and 3. The selected bond lengths and angles are summarized in Table 2. The central 2Fe2S skeletons of **2** and $(2H_N)^+$ are both in the butterfly framework and each Fe atom is coordinated in the pseudo-square-pyramidal geometry similar to previously reported 2Fe2S models [9–14,23,26]. The protonation of **2** occurs at the nitrogen atom [N(1)] of the secondary amine. The N…N distance (2.704 Å) is proper for intramolecular N–H…N interaction, which can considerably promote the stability of the N-protonated species. After protonation, both the bond lengths of N(1)–C(6) and N(1)–C(8) are elongated by 0.037 and 0.034 Å, respectively, while the bond length of N(2)–C(7) is shortened by 0.01 Å.

Fig. 3 shows that two molecules of water are caged by two $[(2H_N)(OTf)]$ molecules through hydrogen bonds. In the solid state of $[(2H_N)(OTf)]$, each asymmetric unit contains a molecule of $[(2H_N)(OTf)]$ and a molecule of water. The molecule of water is close to the iron atom of the $[Fe(CO)_3]$ unit with the $Fe(1)\cdots O(H_2O)$ distance of 4.199 Å. It is proposed that H_2O is coordinated to the distal iron atom in the H_{ox} state of the natural H-cluster [2,24]. The bond lengths and angles related to hydrogen bonds are given in Table S1 (see Supplementary data).

The molecular structure of **6** was also determined by single crystal X-ray analyses, which is shown in Fig. 4, and selected bond lengths and angles are given in Table 3. The central iron atoms of **6** are coordinated in the trigon-bipyramidal geometry, consistent with the structure of $[(\mu-CO)(\mu-dppm)_2Fe_2(CO)_4]$ [27]. Each iron atom is coordinated with two terminal carbonyls, which are



Fig. 4. Molecular structure of 6 with the thermal ellipsoids at 30% probability.

Table 3							
Selected	bond	lengths	(Å) a	nd ang	gles (°) for 6	i.

Bond lengths			
Fe(1)-Fe(2)	2.838(2)	Fe(1)-P(1)	2.229(2)
Fe(1)-S(1)	2.267(2)	Fe(1)-P(3)	2.204(2)
Fe(2)-S(1)	2.240(2)	Fe(2)-P(2)	2.230(2)
		Fe(2)–P(4)	2.215(2)
Bond angles			
Fe(1)-S(1)-Fe(2)	77.98(8)	P(3)-Fe(1)-Fe(2)	93.16(9)
S(1)-Fe(1)-Fe(2)	50.60(7)	P(4)-Fe(2)-Fe(1)	93.25(9)
S(1)-Fe(2)-Fe(1)	51.42(7)	P(1)-Fe(1)-S(1)	97.22(9)
P(1) - Fe(1) - P(3)	174.3(1)	P(2)-Fe(2)-S(1)	93.1(1)
P(2) - Fe(2) - P(4)	172.4(1)	P(3)-Fe(1)-S(1)	85.23(9)
P(1)-Fe(1)-Fe(2)	92.40(9)	P(4)-Fe(2)-S(1)	84.8(1)
P(2)-Fe(2)-Fe(1)	91.19(9)		

Table 4

Redox potentials of complexes 3 and 7 vs. Fc⁺/Fc.^a

Complex	$E_{\rm pa}$ (V) Fe ^I Fe ^I /Fe ^{II} Fe ^I	$E_{\rm pc}$ (V) Fe ^I Fe ^I /Fe ⁰ Fe ^I
2	+0.60	-1.66
[(2 H _N)(OTf)]	-	-1.01
3	+0.83	-1.51
[(3 H _N)(OTf)]	-	-0.90
7	+0.59	-1.62
[(7 H _N)(OTf)]	-	-1.17

^a [NBu₄][PF₆] (0.05 M) in CH₃CN under Ar; scan rate 0.1 V s⁻¹.

essentially co-planar with the bridging-sulfur atom. This plane is perpendicular to the plane defined by the four phosphorus atoms and the two iron atoms. The Fe(1)–Fe(2) bond length of 2.8383(16) Å in **6** is notably longer than that (2.742 Å) in $[(\mu-CO)(\mu-dppm)_2Fe_2(CO)_4]$, resulting from the replacement of the μ -CO bridge by μ -S bridge [28].

3.4. Cyclic voltammograms of the complexes 2, 3, and 7

To compare the electrochemical property and the protophilicity of **2** and **3** with the azadithiolate-bridging complex, [{(μ -



Fig. 5. Cyclic voltammograms of 3 (1.0 mM) in the presence of CF₃COOH in CH₃CN.

 $SCH_2)_2N(CH_2C_6H_5)$ Fe₂(CO)₅P(Pyr)₃] (**7**) was prepared. The cyclic voltammograms (CVs) of **2**, **3**, and **7** were studied in CH₃CN using 0.05 M [NBu₄][PF₆] as electrolyte. The redox potentials versus Fc⁺/Fc are summarized in Table 4. The first reduction peaks of **2** and **3** appear at -1.66 and -1.51 V, respectively, using ferrocene as an internal standard. The approximately equal current height in the CVs of complexes **2** and **3** and ferrocene with an identical molar concentration suggests that the primary reduction of complexes **2** and **3** is a one-electron process (Fe^IFe^I/Fe^IFe⁰). The reduction potential of **3** is 110 mV more positive than that (-1.62 V) found for the analogous diiron azadithiolate complex **7**. The oxidation peaks, at +0.60 and +0.83 V for **2** and **3**, respectively, and +0.59 V for **7**, are attributed to the Fe^IFe^I to Fe^{II}Fe^I process [29,30].

Upon addition of one equivalents of HOTf to the CH₃CN solution of 3, a new peak is observed at -0.90 V in the CV, attributed to the reduction of the protonated species [(3H_N)(OTf)] (Fig. S1, Supplementary data). Essentially identical CVs were obtained for protonation of **2** with a new peak at -1.01 V. In comparison, the reduction peak of [(7H_N)(OTf)] appears at -1.11 V (Fig. S1). Protonation of 2 and 3 leads to the 610-650 mV anodic shifts of the reduction peaks, while after protonation, the reduction peak of 7 is shifted by 450 mV. It shows that protonation of the internal base of 2 and 3 exhibits a larger influence on the reduction potential of the iron atoms compared to that displayed by the protonation of the azadithiolato bridge of 7. It is noteworthy that the complexes 2 and 3 can be protonated by mild acids CCl₃COOH and CF₃COOH (Fig. 5). In contrast, no new peak is detected in the CV when CF₃COOH is added to the solution of **7** (*Fig.* S2). The protonation of **2** and **3** is further verified by in situ ³¹P NMR spectroscopy with stepwise addition of CCl₃COOH to the CDCl₃ solution of 2 or 3 (Fig. S3). The results indicate that the complexes 2 and 3 are more protophilic than the diiron azadithiolate the complex 7. In fact, in organic solvents the internal bases of the FeFe-Hase mimics reported so far can be protonated only in the presence of strong acids, such as HClO₄ [11,13], HBF₄ [12,16,19], and HOTf [10,14,18].

4. Conclusion

The ³¹P NMR spectra and CVs show that the complexes **2** and **3** with a C_2 bridge containing two basic sites are more protophilic than other internal bases in the FeFe-Hase mimics reported so far. The omplexes **2** and **3** can be protonated by CCl₃COOH and CF₃COOH in organic solvent. Protonation and deprotonation

processes between 2 and [(2H_N)(OTf)], as well as 3 and $[(3H_N)(OTf)]$, are instant and reversible. The protonated species $[(2H_N)(OTf)]$ is relatively stable because of the proper distance for intramolecular N-H-N interaction, which is structurally characterized. It is noteworthy that each asymmetric unit of $[(2H_N)(OTf)]$ containing a molecule of water close to the iron atom of the $[Fe(CO)_3]$ subunit $(Fe(1) \cdots O(H_2O) 4.199 \text{ Å})$, which reminds us of H₂O coordinating to the distal iron atom in the H_{ox} state of the natural H-cluster. The reduction potential of the complex 3 is 110 mV more positive than that of the analogous azadithiolate complex **7**, and protonation of the internal base of **2** and **3** exhibits a larger influence on the reduction potential of the iron atoms than that displayed by the protonation of the azadithiolato bridge of **7**. In addition, a desulfurization reaction is found in the reaction of the complex **1** and two equivalents of dppm ligand to afford the complex **6** in refluxing toluene. The reaction undergoes by three steps via a dppm mono-dentate intermediate **4** and a dppm ubridging species 5.

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Appendix A. Supplementary data

CCDC 693477, 693476 and 693475 contain the supplementary crystallographic data for complexes **2**, $[(2H_N)(OTf)]$, and **6**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.01.006.

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