

# N-Heterocyclic Carbene Ligands in Nonsymmetric Diiron Models of Hydrogenase Active Sites

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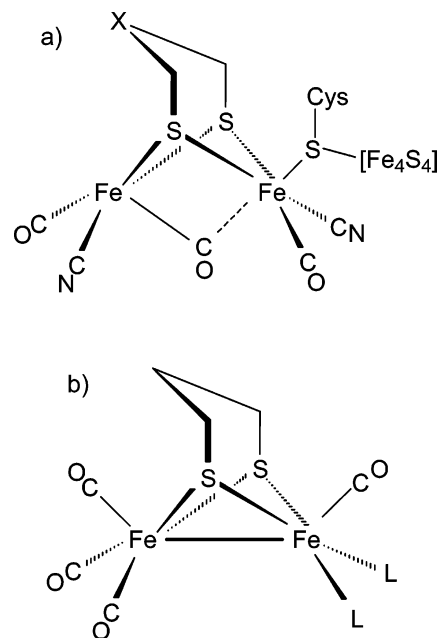
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Reaction of  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6]$  (**1**) at room temperature with the N-heterocyclic carbenes  $\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-L}$  ( $\text{I}_{\text{Me}} = 1\text{-methylimidazol-2-ylidene}$ ,  $\text{L} = \text{NMe}_2, \text{SMe}$ ) afforded the pentacarbonyl carbene derivatives  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-NMe}_2\}]$  (**2a**) and  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-SMe}\}]$  (**2b**). Reaction of **1** with  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  at room temperature provided the dimer  $[\{\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\text{CO})_5\}_2\{\mu\text{-(I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\}]$  (**3**) together with the chelated bis-NHC complex  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\}]$  (**4a**) as the major product. The analogous reaction of **1** with  $\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-I}_{\text{Me}}$  yielded the chelated bis-NHC complex  $[\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\text{CO})_4\{\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-I}_{\text{Me}}\}]$  (**4b**). Addition of  $\text{HBF}_4$  to compound **4a** afforded the stable bridging hydride complexes  $[\text{Fe}_2(\mu\text{-H})\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\}](\text{BF}_4)$  (**5a,b**) with NHC ligands in a basal/basal and basal/apical mode of coordination in **5a,b**, respectively. The molecular structures of **2a**, **3**, **4a,b**, and **5a** were confirmed by X-ray diffraction studies. Low-temperature NMR studies on the protonation of **4a** showed spectroscopic evidence for the formation of a very unstable terminal hydride and a bridging hydride species with a NHC ligand having a non classical mode of coordination via a C-4(5) bond. Cyclic voltammetry revealed that **4a** is a catalyst for proton reduction.

## Introduction

$[\text{FeFe}]$  hydrogenases are metalloenzymes that catalyze the reduction of protons to dihydrogen at very high rates.<sup>1</sup> The crystal structures of the active site, called H-cluster, have revealed its organometallic nature with a diiron subsite consisting of an asymmetrical complex bearing CO and  $\text{CN}^-$  ligands (Figure 1a).<sup>2</sup> Extensive research has been devoted to studies concerning synthetic models of the  $[\text{FeFe}]$  hydrogenases.<sup>3</sup> Most of the model compounds, obtained from the well-known diiron



**Figure 1.** Schematic representations of (a) the active site of  $[\text{FeFe}]$  hydrogenase from *D. desulfuricans* ( $\text{X} = \text{CH}_2, \text{NR}, \text{O}$ ) and (b) a nonsymmetrically disubstituted model complex, with  $\text{L} = \sigma\text{-donor}$  ligand.

complex  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6]$  (**1**) and related derivatives, use phosphine<sup>4</sup> or isonitrile<sup>5</sup> ligands as surrogates of the cyanide ligand, whose reactivity is complicated by side reactions at the

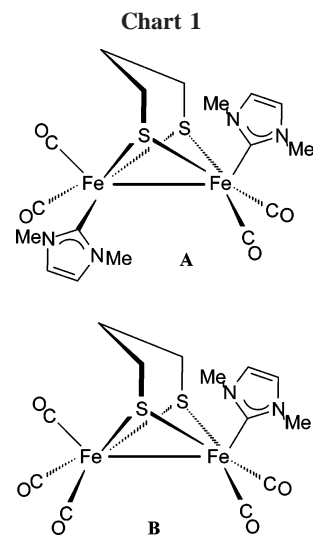
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nitrogen atom.<sup>5c,f</sup> Recent experimental and theoretical studies on the reactivity of **1**<sup>6</sup> and its diruthenium analogue<sup>7</sup> have provided new developments in the chemistry of these simple models. We have been interested in the synthesis and electrochemical studies of models of the [FeFe] hydrogenase for some time.<sup>8</sup> In this field, we<sup>8e</sup> and others<sup>9</sup> have recently described new diiron models with N-heterocyclic carbenes (NHCs) derived from imidazolium ions have received considerable attention as ligands in organometallic chemistry,<sup>10</sup> due to their distinctive electronic properties compared to those of other neutral two-electron donors: NHCs are strong  $\sigma$ -donor ligands having little or moderate  $\pi$ -accepting ability and are tunable both electronically and sterically.<sup>11</sup> Metal binding at the C(2) position is usually observed for transition-metal NHC com-



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plexes, but abnormal C(4/5) binding has also been reported.<sup>12</sup> In a previous work,<sup>8e</sup> we have obtained the symmetrically disubstituted complex  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{IME})_2]$  (**A**), where IMe = 1,3-dimethylimidazol-2-ylidene (Chart 1), having carbonyl vibrations similar to those of the dicyano compound  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{CN})_2]^{2-}$ .<sup>13</sup> This result indicates that the donor strength of the NHC ligand IMe is comparable to that of the cyanide ligand. Nevertheless, our studies have also shown that **A** is unstable in the presence of acids, probably because the reductive elimination of the imidazolium salt obtained after protonation of the iron center leads to catalyst deactivation. Such a cleavage of the M–C<sub>carbene</sub> bond has been reported in other transition-metal catalysts.<sup>14</sup>

Another purpose is to feature a diiron complex with well differentiated environments around each metal center, as observed in the active site of the [FeFe] hydrogenase. A recent theoretical study has shown that an interesting approach would consist of the synthesis of  $[\text{Fe}_2(\mu\text{-SRS})(\text{CO})_4(\text{L})_2]$  models where one iron center is bonded to two electron-donating ligands (L), whereas the other iron is bonded to strongly electron-accepting ligands (Figure 1b).<sup>15</sup>

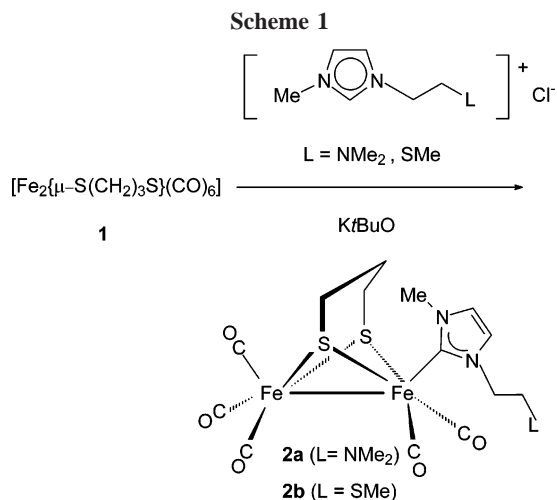
In this report we have investigated the reactivity of complex **1** with the potentially bidentate NHC ligands  $\text{IME}-(\text{CH}_2)_2\text{-L}$  ( $\text{IME} = 1\text{-methylimidazol-2-ylidene}$ ,  $\text{L} = \text{NMe}_2, \text{SMe}$ ) and  $\text{IME}-(\text{CH}_2)_n\text{-IME}$  ( $n = 1, 2$ ), with the aim of chelating one iron center and therefore stabilizing protonated forms. Chelated bis-NHC complexes are presumably more stable than monodentate NHC

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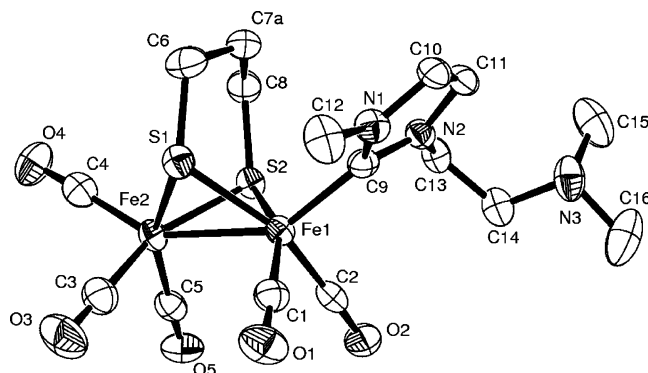


complexes, as reductive elimination of the imidazolium precursor is more difficult to obtain.<sup>16</sup>

## Results and Discussion

**Synthesis and Reactivity of the Neutral Complexes.** In an earlier work, the disubstituted and monosubstituted complexes **A** and **B** (Scheme 1) were obtained from the reaction of **1** with an excess of 1,3-dimethylimidazol-2-ylidene.<sup>8c</sup> The transmetalation of the NHC from a silver complex<sup>17</sup> was unsuccessful for this reaction. The free NHC ligand, generated by treatment of the corresponding imidazolium salt with the strong base KtBuO, was difficult to isolate and thus was kept in a THF solution prior to reacting with the metal complex. The free NHCs used in this report, bearing sterically small substituents at the nitrogen atoms, were also not isolated and were prepared by following the same procedure as described previously.<sup>8c</sup> Addition of 3.5 equiv of  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-L}$  (L = NMe<sub>2</sub>, SMe) to a THF solution of **1** at room temperature afforded the monosubstituted compounds  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-L}\}]$  (L = NMe<sub>2</sub> (**2a**), SMe (**2b**)), which were isolated after purification by silica gel chromatography as orange powders in 67% and 39% yields, respectively (Scheme 1).

The IR spectra of **2a,b** display patterns in the carbonyl region very similar to that of **B**<sup>8c</sup> (Table 1); this suggests that the new compounds **2a,b** are both monosubstituted NHC metal complexes. The <sup>1</sup>H NMR spectrum of **2a** displays two signals at 7.30 and 7.03 ppm for the imidazole protons and a singlet at 4.01 ppm for the N-Me protons, suggesting a fast rotation of the NHC ligand around the Fe-C bond in solution.<sup>8c</sup> The <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum of **2a** shows a signal due to C<sub>carbene</sub> at 184.75 ppm, in the typical high-frequency region for such a metalated carbon atom. The structure of **2a**, determined by an X-ray diffraction study, is in agreement with the spectroscopic data. The ORTEP diagram of **2a** is illustrated in Figure 2, with the most representative bond distances and angles being given in Table 2. The study confirms the presence of one NHC ligand, which lies in an apical position. The usual square-pyramidal geometry is observed for the iron centers, which are separated by a distance of 2.5352(7) Å, close to that observed in related complexes.<sup>18</sup> The Fe-C<sub>carbene</sub> distance (1.980(4) Å) is typical



**Figure 2.** ORTEP diagram of  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-NMe}_2\}]$  (**2a**), depicted with 50% thermal ellipsoids.

**Table 1. Comparative FTIR Data of Complexes 1–5 in the Carbonyl Stretching Frequency Region, Measured in CH<sub>3</sub>CN Solution**

compd	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_6]$ ( <b>1</b> )	2073, 2033, 1999
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4(\text{IMe})_2]$ ( <b>A</b> )	1967, 1926, 1888
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5(\text{IMe})]$ ( <b>B</b> )	2036, 1971, 1912
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-NMe}_2\}]$ ( <b>2a</b> )	2037, 1970, 1911
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-SMe}\}]$ ( <b>2b</b> )	2038, 1970, 1911
$[\{\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\}_2(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})]$ ( <b>3</b> )	2039, 1974, 1913
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})]$ ( <b>4a</b> )	1996, 1920, 1872
$[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-I}_{\text{Me}}\}]$ ( <b>4b</b> )	1994, 1921, 1869
$[\text{Fe}_2(\mu\text{-H})\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})]^+$ ( <b>5a,b</b> )	2092, 2032, 1946

**Table 2. Selected Bond Lengths (Å) and Angles (deg) in 2a and in the Dimer 3**

	<b>2a</b>	<b>3</b>
C(1)–Fe(1)	1.756(4)	1.757(4)
C(4)–Fe(2)	1.799(4)	1.794(4)
C(9)–Fe(1)	1.980(4)	1.983(3)
C(59)–Fe(51)		1.966(3)
S(1)–Fe(2)	2.2595(10)	2.2604(10)
S(1)–Fe(1)	2.2632(10)	2.2718(9)
S(2)–Fe(2)	2.2631(10)	2.2640(10)
S(2)–Fe(1)	2.2691(10)	2.2824(9)
Fe(1)–Fe(2)	2.5352(7)	2.5162(7)
Fe(51)–Fe(52)		2.5228(6)
S(51)–Fe(52)–Fe(51)		56.21(3)
S(52)–Fe(52)–Fe(51)		56.38(2)
S(1)–Fe(2)–Fe(1)	55.98(3)	56.49(3)
S(2)–Fe(2)–Fe(1)	56.10(3)	56.75(3)

of bonds having  $\sigma$  character.<sup>19</sup>

Attempts to synthesize the chelated complexes  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-L}\}]$  by substitution of more carbonyls in **2a,b** with pendant thioether or dimethylamine failed, even when these compounds were heated in refluxing toluene or in the presence of Me<sub>3</sub>NO as a decarbonylation agent. The thioether or dimethylamine groups are probably not nucleophilic enough to ensure directly the substitution of a second CO in **2a,b**, due to the presence of the strong  $\sigma$ -donor NHC ligand that enhances the Fe-CO  $\pi$ -back-donation. Such a substitution reaction with a thioether group was reported to occur in related hexacarbonyl complexes for which the CO ligands are more labile than in **2a,b**.<sup>20</sup> The failure of the  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-L}$  (L = NMe<sub>2</sub>, SMe) ligands to afford the desired chelated complexes led us to use bis-NHC ligands that are thought to be more reactive.

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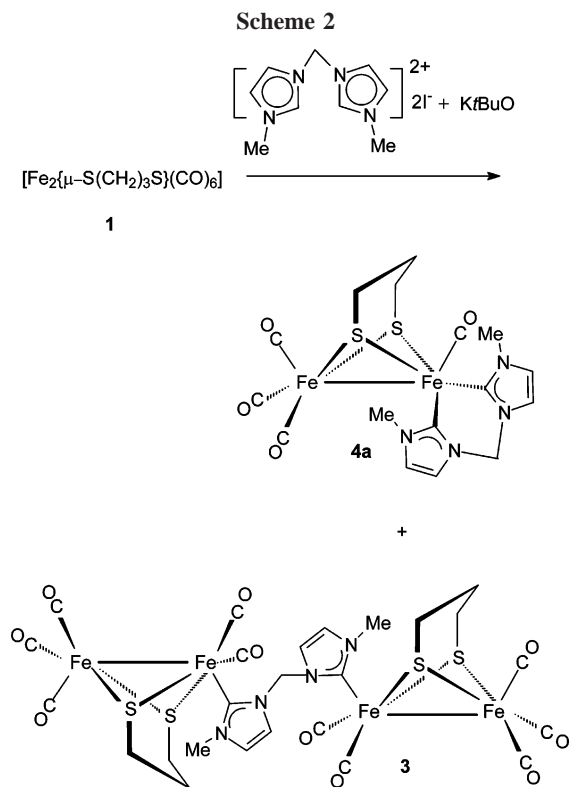
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(20) (a) Lawrence, J. D.; Li, H.; Rauchfuss, T. B. *Chem. Commun.* **2001**, 1482. (b) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082. (c) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Liu, Y.; Wang, H.-T.; Liu, X.-F.; Hu, Q.-M. *Organometallics* **2005**, *24*, 6126.





The reaction of **1** at room temperature with the bis-NHC ligand  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  yielded a mixture of the dimeric species  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_5]_2\{\mu\text{-}(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\}$  (**3**) and the targeted chelated bis-NHC compound  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\}]$  (**4a**) (Scheme 2).

Compounds **3** and **4a** were characterized by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. The IR spectrum of **3** displays strong bands in the carbonyl region at 2039, 1974, and 1913  $\text{cm}^{-1}$ , very close to those reported for the monosubstituted complex **B**, which suggests that **3** is also a monosubstituted complex. Crystals suitable for diffraction studies were grown from a hexane/dichloromethane mixture at  $-10\text{ }^\circ\text{C}$ . The molecular structure of **3** (Figure 3) reveals that it contains two  $\{\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_5\}$  moieties bridged by the  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  ligand. The iron centers display the expected square-based-pyramidal coordination environment. The NHC groups are both in apical positions, and the  $\text{Fe}\text{-C}_{\text{carbene}}$  distances, 1.983(3) and 1.966(3) Å, are typical of bonds having  $\sigma$  character.<sup>19</sup> The  $\text{Fe}\text{-Fe}$  distances (2.5162(7) and 2.5228(6) Å) are close to those found in other double-diiron complexes (2.4938(11)–2.5383(11) Å) with a bridging diphosphine ligand.<sup>20c</sup>

The  $\nu(\text{CO})$  bands for **4a** (1996, 1920, and 1872  $\text{cm}^{-1}$ ) are shifted to lower wavenumbers with respect to those of **3**, indicating the substitution of a second carbonyl ligand. The  $^1\text{H}$  NMR spectrum of **4a** shows two signals due to the imidazole protons at 7.04 and 6.88 ppm and one additional signal attributed to the *N*-methyl groups at 4.00 ppm, which is consistent with a basal/basal coordination mode of a chelating bis-NHC ligand. The protons of the methylene bridge exhibit an AB quartet at 5.80 ppm ( $^2J_{\text{AB}} = 12\text{ Hz}$ ). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows the signal of the  $\text{C}_{\text{carbene}}$  atoms at  $\delta$  197.79 ppm, in agreement with those of other NHC iron(I) complexes.<sup>11d,19</sup> The molecular structure of **4a** (Figure 4, Table 3) determined by X-ray diffraction is in agreement with the spectroscopic assignments and confirms that the chelating bis-carbene is in a basal/basal position. The bite angle  $\text{C}(59)\text{-Fe}(1)\text{-C}(9)$  of 87.39(12) $^\circ$  is comparable with those reported for complexes bearing chelating

bis-carbene ligands having a methylene linker.<sup>21</sup> The  $\text{Fe}\text{-C}_{\text{carbene}}$  bond distances (1.935(3), 1.921(3) Å) compare well with those of compound **3**. The six-membered metallacycle adopts a boatlike conformation. The  $\text{Fe}\text{-Fe}$  distance in **4a** (2.5774(6) Å) is longer than in **3** (2.5162(7) Å) and longer than in the reduced form of the  $[\text{FeFe}]$  hydrogenase enzymes (2.55 Å).<sup>2c</sup> A significantly shorter distance is found for the  $\text{Fe}\text{-C}$  bond length of the carbonyl of the  $\{\text{Fe}(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\text{CO}\}$  subunit (1.737(3) Å) relative to those of the carbonyls of the  $\{\text{Fe}(\text{CO})_3\}$  subunit (1.762(4)–1.789(4) Å) and to those obtained in the starting compound  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6]$  (**1**), which are in the range 1.793(3)–1.801(3) Å.<sup>13a</sup> This indicates an enhanced  $\text{Fe}\text{-CO}$   $\pi$ -back-donation afforded by the NHC ligands.

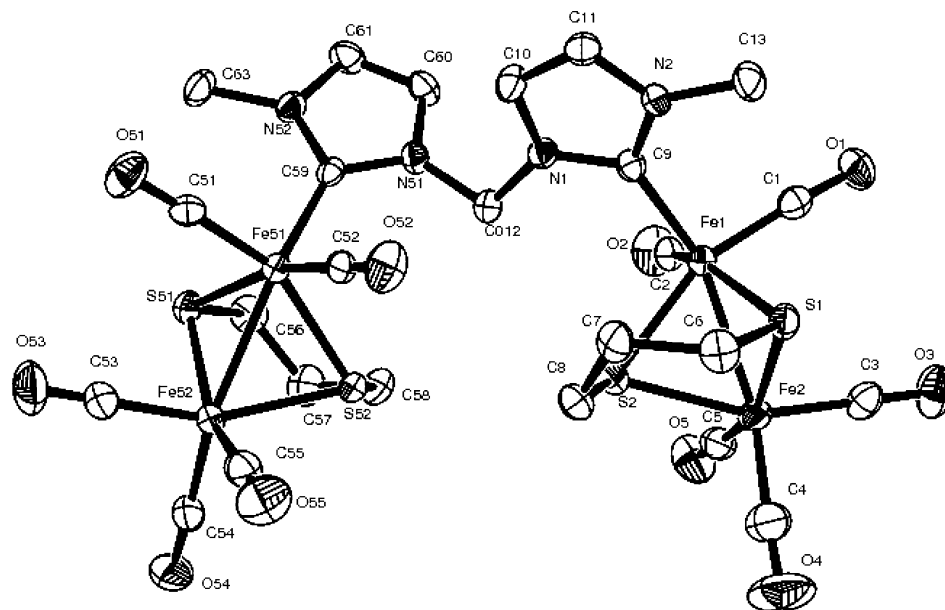
Low-temperature NMR experiments were performed, and no change appeared in the  $^1\text{H}$  NMR spectrum of **4a** even at  $-90\text{ }^\circ\text{C}$ , suggesting that only one isomer is present both in solution and in the solid state. This result reveals that no basal/apical site exchange operates in the  $\{\text{Fe}(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\text{CO}\}$  subunit. By comparison, the disubstituted compound  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{CN-tBu})_2]$  exists in four isomeric forms, depending on the mutual positions (basal or apical) of the substituting ligands.<sup>5c</sup> The  $\nu(\text{CO})$  bands observed in the IR spectrum of **4a** (1996, 1920, and 1872  $\text{cm}^{-1}$ ) are very close to those reported for the symmetrically disubstituted complex **A**<sup>8c</sup> (1967, 1926, and 1888  $\text{cm}^{-1}$ ), indicating the important electronic influence of the ligand  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  on both iron centers. The  $\nu(\text{CO})$  bands of **4a** (average  $\nu(\text{CO})$  1929  $\text{cm}^{-1}$ ) are also close to those observed for the reduced form of the enzyme *Desulfovibrio vulgaris* (1965, 1916, and 1894  $\text{cm}^{-1}$ ; average  $\nu(\text{CO})$  1925  $\text{cm}^{-1}$ ).<sup>2c,22</sup>

The ligand  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  was prepared by proton abstraction from the corresponding bis-imidazolium salt with  $\text{KtBuO}$  prior to metalation with **1**. IR spectroscopic measurements in the carbonyl region established that the **3/4a** ratio depends on reaction conditions. Employing 1 or 2 equiv of  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  afforded mainly the starting material and small amounts of **3** and **4a**. The use of 3 equiv of ligand was necessary to ensure the complete consumption of **1**. When a THF solution of the ligand  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  was added to the THF solution of **1**, compound **3** was obtained as the major product (see method A in the Experimental Section), whereas a slow addition of a THF solution of **1** to a THF solution of the ligand gave essentially **4a** (method B) along with a small amount of **3**, which could be eliminated by repeating washings with diethyl ether. Compound **4a** is stable in the solid state as well as in dichloromethane solution.

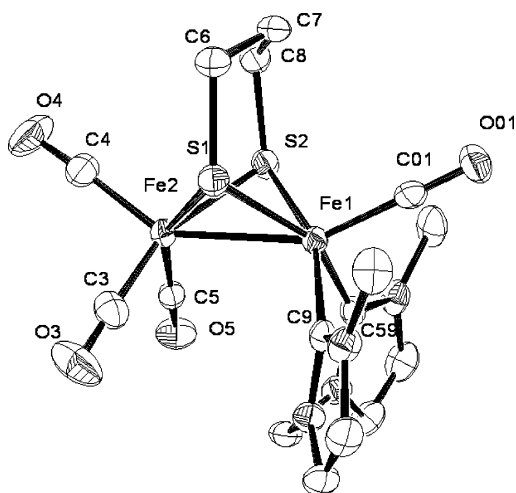
Similarly, slow addition of a THF solution of **1** to an excess of  $\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-I}_{\text{Me}}$  afforded the chelated bis-NHC complex  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-I}_{\text{Me}}\}]$  (**4b**). The  $\nu(\text{CO})$  bands for **4b** are nearly similar to those of **4a**, suggesting the same mode of coordination for the bis-NHC ligand in both compounds.  $^1\text{H}$  NMR resonances for the imidazole rings appear as two doublets at 5.99 and 5.87 ppm in  $\text{C}_6\text{D}_6$  and at 6.95 and 6.85 ppm in  $\text{CD}_2\text{Cl}_2$ . The protons of the ethylene bridge exhibit two AB quartets at 5.13 and 3.13 ppm. The structure of **4b**

(21) See recent examples: (a) Quezada, C. A.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *671*, 183. (b) Poyatos, M.; Mas-Marza, E.; Sanau, M.; Peris, E. *Inorg. Chem.* **2004**, *43*, 1793. (c) Jin, C.-M.; Twamley, B.; Shreeve, J. M. *Organometallics* **2005**, *24*, 3020. (d) Vogt, M.; Pons, V.; Heinekey, D. M. *Organometallics* **2005**, *24*, 1832. (e) Viciano, M.; Poyatos, M.; Sanau, M.; Peris, E.; Rossin, A.; Ujaque, G. P.; Lledos, A. *Organometallics* **2006**, *25*, 1120. (f) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Organometallics* **2006**, *25*, 4670. (g) Ahrens, S.; Zeller, A.; Taige, M.; Strassner, T. *Organometallics* **2006**, *25*, 5409.

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**Figure 3.** ORTEP diagram of  $[(\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_5)_2\{\mu\text{-}(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\}]$  (**3**), depicted with 50% thermal ellipsoids.

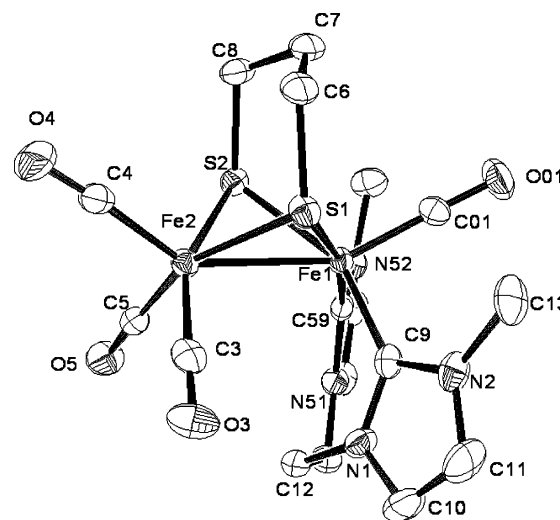


**Figure 4.** ORTEP diagram of  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\}]$  (**4a**), depicted with 50% thermal ellipsoids.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for Chelated Bis-NHC Complexes **4a,b** and **5a**

	<b>4a</b>	<b>4b</b>	<b>5a</b>
C(01)–Fe(1)	1.737(3)	1.732(2)	1.748(3)
C(4)–Fe(2)	1.789(4)	1.800(2)	1.810(3)
C(9)–Fe(1)	1.935(3)	1.950(2)	1.952(3)
C(59)–Fe(1)	1.921(3)	1.985(2)	1.951(3)
S(1)–Fe(1)	2.2452(9)	2.2437(6)	2.2565(8)
S(1)–Fe(2)	2.2812(9)	2.2674(6)	2.2808(8)
S(2)–Fe(1)	2.2447(9)	2.2604(6)	2.2652(8)
S(2)–Fe(2)	2.2726(9)	2.2651(7)	2.2769(8)
Fe(1)–Fe(2)	2.5774(6)	2.6253(4)	2.6054(6)
C(59)–Fe(1)–C(9)	87.39(12)	95.26(9)	87.81(11)
S(2)–Fe(2)–Fe(1)	54.70(2)	54.458(17)	54.79(2)
S(1)–Fe(2)–Fe(1)	54.63(2)	53.991(17)	54.52(2)

(Figure 5) is in agreement with the spectroscopic data and reveals that the chelating NHC ligand remains coordinated in a basal/basal position. Complexes **4a,b** show close structural parameters in terms of bond distances. The Fe–C<sub>carbene</sub> distances for the imidazole rings are 1.950(2) and 1.985(2) Å. As expected, the bite angle of the chelating bis-carbene ligand in **4b** (95.26(9)°) is larger than in **4a**, because of the substitution of the methylene by the ethylene bridge. Because **4b** was formed



**Figure 5.** ORTEP diagram of  $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-(CH}_2)_2\text{-I}_{\text{Me}}\}]$  (**4b**), depicted with 50% thermal ellipsoids.

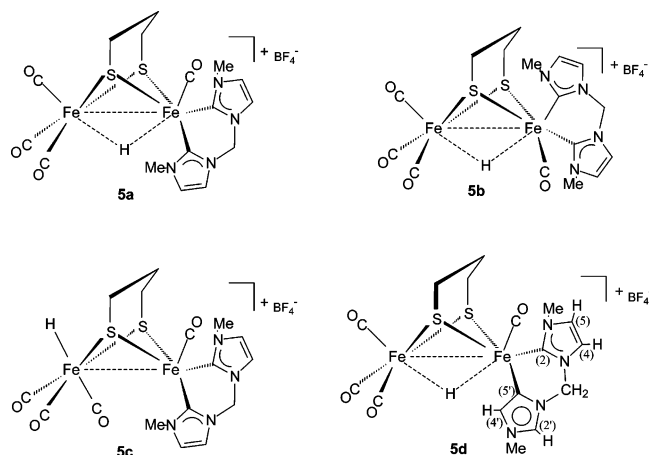
in low yield (11%), we have limited the protonation reaction and the electrochemistry studies to **4a**.

**Protonation Reaction of 4a.** An excess of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  was added at  $-25^\circ\text{C}$  to a solution of **4a** in  $\text{CH}_2\text{Cl}_2$ , which immediately turned from red to brown. The reaction product was precipitated by adding  $\text{Et}_2\text{O}$  to the reaction mixture, which led to a brown solid after filtration. The IR spectrum of this compound displays three  $\nu(\text{CO})$  bands at 2092, 2032, and 1946  $\text{cm}^{-1}$ . This average shift of  $\nu(\text{CO})$  values of 110  $\text{cm}^{-1}$  to higher wavenumbers, in comparison to the values for the neutral complex **4a**, is typical of protonation at the metal–metal bond.<sup>4a,d,5f,23</sup> The  $^1\text{H}$  NMR spectrum of the brown solid dissolved in  $\text{CD}_2\text{Cl}_2$  reveals that it contains a mixture (90/10 ratio) of two isomers, as indicated by signals at  $-12.16$  ppm (**5a**, major) and at  $-15.10$  ppm (**5b**) (Chart 2).

Crystallization of the above brown solid in  $\text{CH}_2\text{Cl}_2$  at  $-10^\circ\text{C}$  afforded crystals of **5a**. Indeed, the  $^1\text{H}$  NMR spectrum of these crystals in  $\text{CD}_2\text{Cl}_2$  revealed only the presence of the hydride signal at  $-12.16$  ppm, attributed to **5a**. These crystals

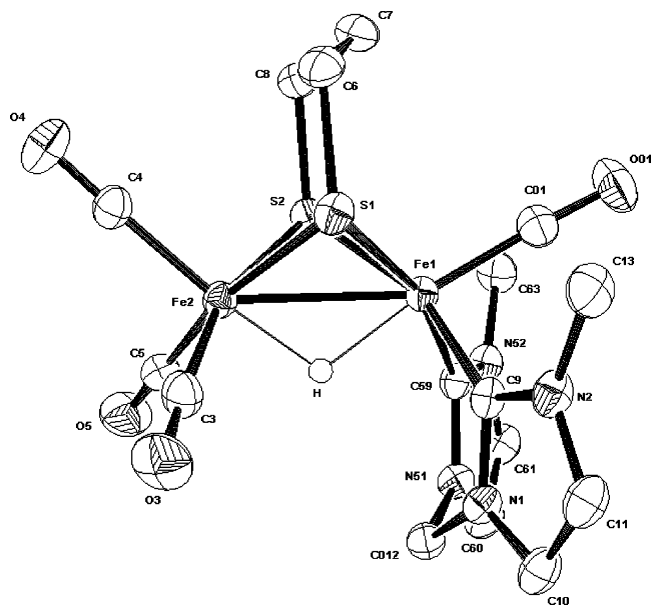
(23) Dong, W.; Wang, M.; Liu, X.; Jin, K.; Li, G.; Wang, F.; Sun, L. *Chem. Commun.* **2006**, 305.

Chart 2

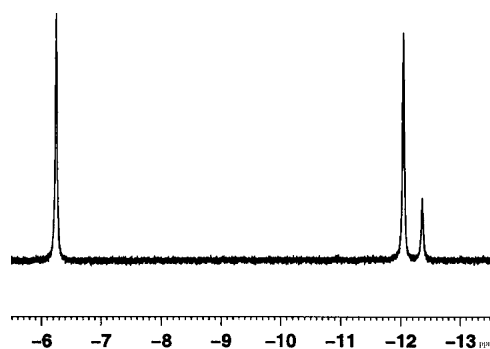


were suitable for a X-ray diffraction study, and the structure of **5a** in the solid-state could be described as a bridging hydride with a chelating NHC ligand located on one iron in a basal/basal position (Figure 6). The presence of a hydride between the two iron atoms in **5a** was demonstrated by an X-ray diffraction study. Indeed, during the last steps of the anisotropic refinement, only a few electron density peaks slightly greater than the background noise were observed. Most of them were located around the counterion BF<sub>4</sub><sup>-</sup> and the molecule of CH<sub>2</sub>Cl<sub>2</sub> (cocrystallized solvent molecule). The strong disorder observed in both molecules explains perfectly the residual electronic density. However, one electronic density peak lasts within the structure of the coordination complex molecule. This electronic density peak can be confidently attributed to one H atom for the following reasons: this peak is the only one to be greater than the background noise around the molecule, and its replacement by H slightly improves the refinement. The position of this peak, between the two iron atoms, agrees with the expected position of H in such hydride complexes.<sup>4b,5f,23</sup> Finally, the presence of this supplementary hydrogen atom, proved by <sup>1</sup>H NMR measurements, agrees with the neutrality of charges within the crystal structure. Each iron center displays a distorted-octahedral geometry, in agreement with previously reported (Fe<sup>II</sup>(μ-H)Fe<sup>II</sup>) complexes.<sup>4b,5f,23</sup> They are both displaced from their pyramidal base toward the apical direction, by 0.3224(4) Å for Fe<sub>1</sub> from plane1 (S1–S2–C9–C59), and by 0.2356(4) Å for Fe<sub>2</sub> from plane2 (S1–S2–C3–C5). The H–plane1 and H–plane2 distances (1.38(4) and 1.32(4) Å, respectively) are almost the same. The Fe–Fe distance (2.6054(6) Å) is elongated by approximately 0.03 Å compared to the Fe–Fe bond in the neutral complex **4a**. The chelate bite angle is 87.81(11)°, nearly similar to that of **4a**. The Fe<sub>1</sub>–H and Fe<sub>2</sub>–H distances (1.710 and 1.562 Å, respectively) are comparable to those of other (Fe<sup>II</sup>(μ-H)Fe<sup>II</sup>) complexes.<sup>4b,5f,23</sup>

In the <sup>1</sup>H NMR spectrum of **5a** the *N*-methyl groups appear as a singlet at 3.80 ppm and the imidazole protons are at 7.59 and 6.94 ppm. The protons of the methylene bridge exhibits an AB quartet at 6.47 ppm. The <sup>13</sup>C NMR spectrum of **5a** displays one carbene signal at 182.89 ppm and three signals at 217.83, 206.00, and 202.22 ppm (intensity 1/1/2, respectively) in the CO region. The low-field resonance at 217.83 ppm is assigned to the carbonyl of the {Fe(I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub>)CO} subunit. No change is observed in the <sup>1</sup>H NMR spectrum in the range –80 to +25 °C. These data show that this compound is rigid on the NMR time scale. Similar behavior was observed for the bridging hydride complex [Fe<sub>2</sub>(μ-H){μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>4</sub>(CN)(PMe<sub>3</sub>)].<sup>5f</sup> After 2 h in CD<sub>2</sub>Cl<sub>2</sub> solution, **5a** gave a new <sup>1</sup>H NMR pattern,



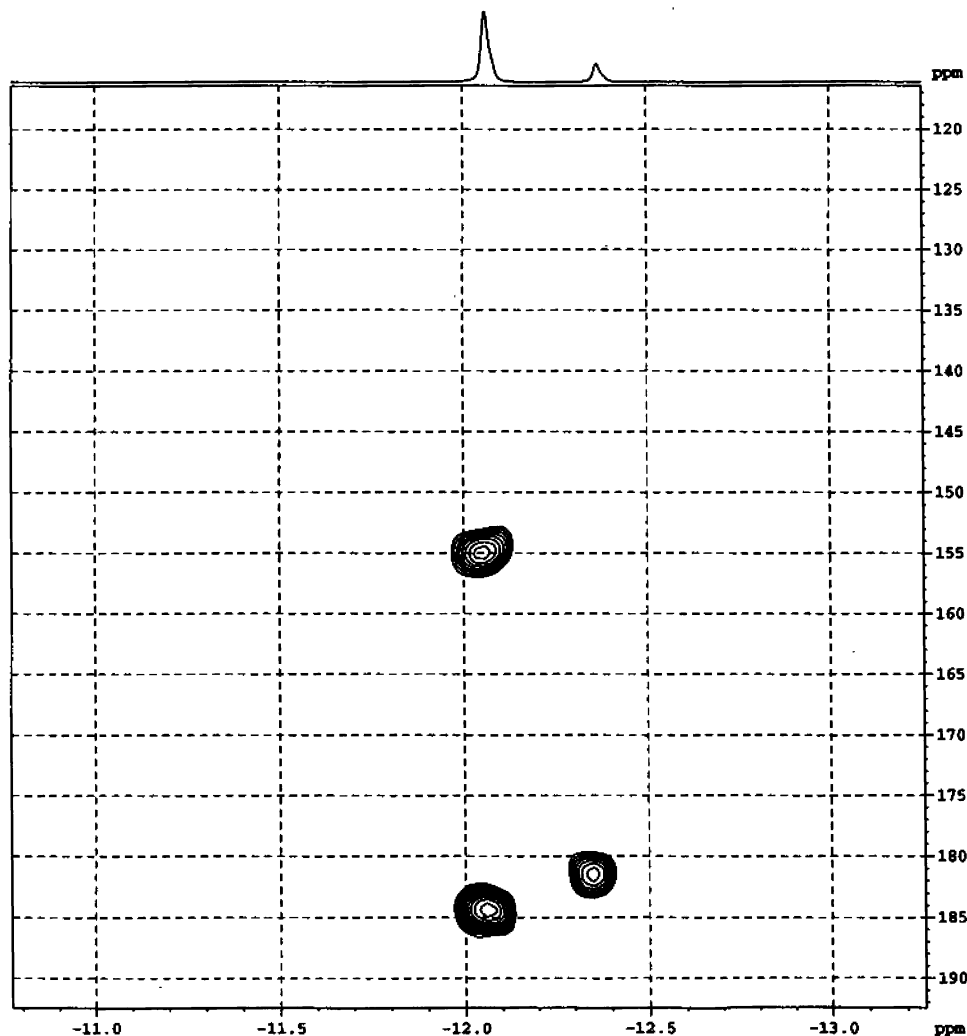
**Figure 6.** ORTEP diagram of [Fe<sub>2</sub>(μ-H){μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>4</sub>{I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub>}(BF<sub>4</sub><sup>-</sup>)·CH<sub>2</sub>Cl<sub>2</sub> (**5a**), depicted with 50% thermal ellipsoids. The counterion (BF<sub>4</sub><sup>-</sup>) and CH<sub>2</sub>Cl<sub>2</sub> (cocrystallized solvent molecule) are omitted for clarity.



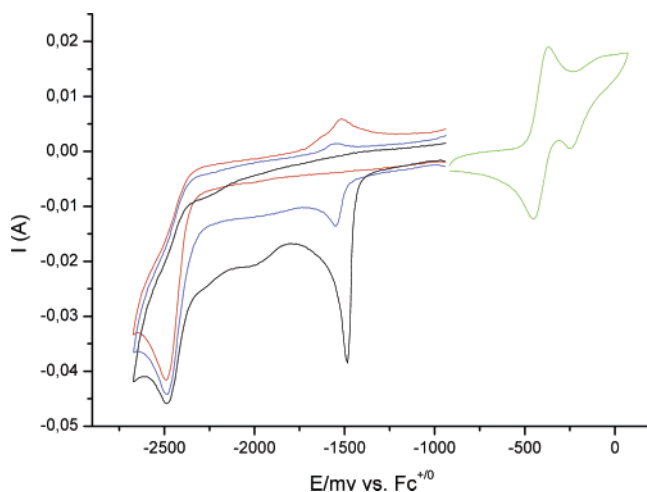
**Figure 7.** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum in the hydride region after addition of HBF<sub>4</sub> to compound **4a** at low temperature, recorded at –90 °C.

which is attributed to the formation of the hydride **5b**. After 7 days in the CD<sub>2</sub>Cl<sub>2</sub> solution compound **5b** became the major product (60%). The most significant feature of the <sup>1</sup>H NMR data of **5b** compared to **5a** is the nonequivalency of the two imidazol-2-ylidene rings: **5b** exhibits two signals at 4.04 and 3.87 ppm for the *N*-methyl group and four signals for the imidazole protons between 7.70 and 7.05 ppm. The <sup>13</sup>C NMR spectrum of **5b** displays four signals of equal intensity for the carbonyl ligands and two signals for the C<sub>carbene</sub> at 183.72 and 182.23 ppm. We propose that **5b** is a bridging hydride complex having a chelating NHC ligand in a basal/apical position, while **5a** is the isomer having the chelating NHC ligand in a basal/basal position (Chart 2). Different isomeric species have been also reported for other diiron μ-hydride compounds in relation to basal or apical orientations of isonitrile or phosphane ligands. The mixture of isomers **5a,b** is stable at least for 7 days in CD<sub>2</sub>Cl<sub>2</sub>, even in the presence of strong acid (HBF<sub>4</sub> and CF<sub>3</sub>CO<sub>2</sub>H). Reductive elimination of imidazolium salt from the chelated NHC complex is more difficult than that from the corresponding monodentate bis-NHC compound **A**, which decomposes rapidly in the presence of acid.

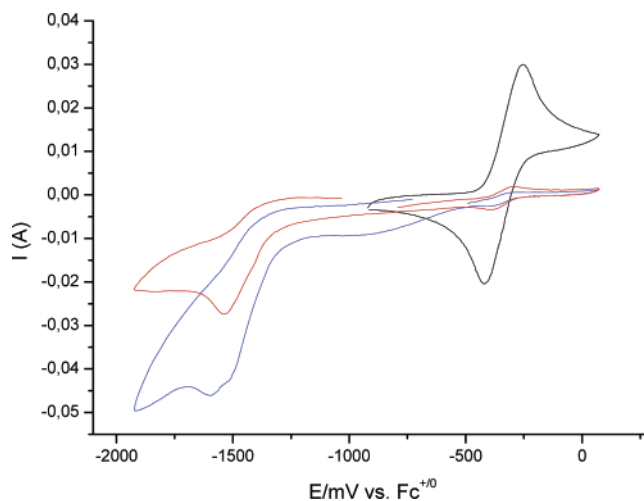
**Protonation Reaction of 4a in Situ.** The monitoring of the protonation reaction of **4a** with HBF<sub>4</sub>·Et<sub>2</sub>O by <sup>1</sup>H NMR spectroscopy at low temperatures (–90 °C) reveals, surprisingly,



**Figure 8.** Partial contour plot of the  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum, recorded at  $-80\text{ }^\circ\text{C}$ , in the hydride region, showing the correlations between hydride and  $\text{C}_{\text{carbene}}$  in **5d** (major) and **5a**. No correlation was observed for **5c**.



**Figure 9.** Cyclic voltammograms ( $\nu = 0.1\text{ V s}^{-1}$ ) of complex **4a** (5.0 mg,  $1.0 \times 10^{-2}$  mmol) in  $\text{N}_2$ -purged  $\text{CH}_3\text{CN}$  solution +  $\text{Bu}_4\text{NPF}_6$  electrolyte (toward more negative potentials, red line; toward more positive potentials, green line) and this solution after addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (1.5  $\mu\text{L}$ ,  $0.6 \times 10^{-2}$  mmol, blue line; 3  $\mu\text{L}$ ,  $1.2 \times 10^{-2}$  mmol, black line).

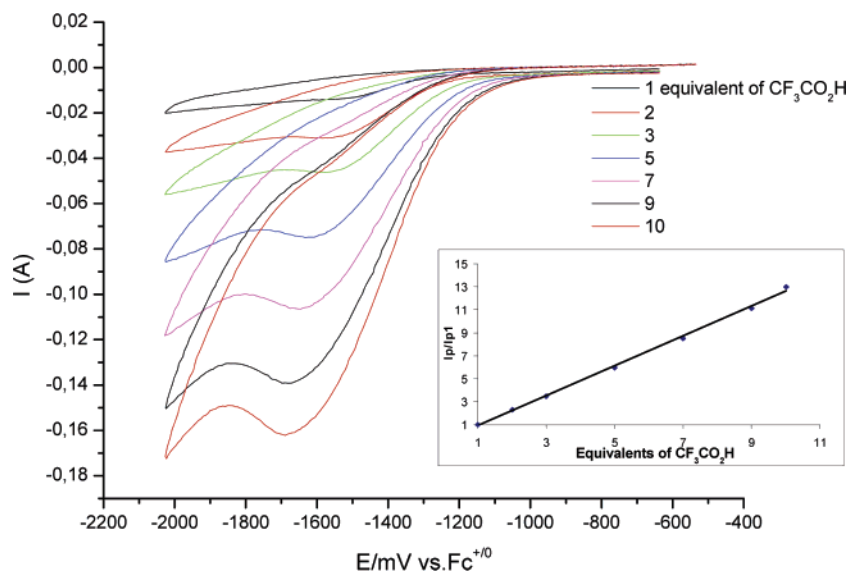


**Figure 10.** Cyclic voltammograms ( $\nu = 0.1\text{ V s}^{-1}$ ) of complex **4a** (5.0 mg,  $1.0 \times 10^{-2}$  mmol) in  $\text{N}_2$ -purged  $\text{CH}_2\text{Cl}_2$  solution +  $\text{Bu}_4\text{NPF}_6$  electrolyte (reversible oxidation, black line) and this solution after addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (3  $\mu\text{L}$ ,  $1.2 \times 10^{-2}$  mmol, red line; 5  $\mu\text{L}$ ,  $2 \times 10^{-2}$  mmol, blue line).

the presence of two new hydride species, **5c** (42%,  $\delta_{\text{H hydride}} -6.26$  ppm) and **5d** (39%,  $\delta_{\text{H hydride}} -12.06$  ppm), in addition to **5a** (19%,  $\delta_{\text{H hydride}} -12.36$  ppm, at  $-90\text{ }^\circ\text{C}$ ). An important

feature of this  $^1\text{H}$  NMR spectrum is the hydride signal at  $-6.26$  ppm (**5c**), which is at much lower field than the other hydride signals (Figure 7). Unfortunately, the extreme instability of **5c** even at  $-90\text{ }^\circ\text{C}$  precluded its full characterization. Unlike all





**Figure 11.** Dependence of current heights of electrocatalytic waves for **4a** in the presence of 1–10 equiv of  $CF_3CO_2H$  in  $N_2$ -purged  $CH_2Cl_2$  solution +  $Bu_4NPF_6$  electrolyte and plot of the catalytic peak current ( $I_p/I_{p1}$ , where  $I_{p1}$  is the intensity of the current after addition of 1 equiv of  $CF_3CO_2H$ ) as a function of the acid concentration.

the other bridging hydride complexes reported in this paper, no correlation between the hydride and the  $C_{\text{carbene}}$  was observed in the  $^1H$ – $^{13}C$  HMBC 2D experiment. This could suggest that **5c** is the intermediate  $[Fe(H)(CO)_3\{\mu-S(CH_2)_2S\}Fe(CO)\{I_{Me}-CH_2-I_{Me}\}](BF_4)$ , having a terminal hydrido ligand localized on the  $Fe(CO)_3$  subunit (Chart 2). This hypothesis is also supported by the protonation in situ of a bis-phosphine analogue of **4a**,  $[Fe_2\{\mu-S(CH_2)_2S\}(CO)_4\{Ph_2P(CH_2)_2PPh_2\}]$ , which showed spectroscopic evidence for the presence of a terminal hydride on this  $Fe(CO)_3$  subunit.<sup>24</sup> The synthesis of the diferrous terminal hydride complex  $[Fe(H)(PMe_3)_2(\mu-CO)\{\mu-S(CH_2)_2S\}Fe(CO)(PMe_3)_2](PF_6)$  has been recently reported; its  $^1H$  NMR spectrum exhibits a signal at  $-4.6$  ppm, which has been assigned to the terminal hydrido ligand.<sup>25</sup> The corresponding  $\mu$ -hydride compound  $[Fe_2\{\mu-S(CH_2)_2S\}(\mu-H)(CO)_2(PMe_3)_4](PF_6)$  displays a signal at  $\delta -20.6$  ppm, which has been attributed to the bridging hydride. The structures of both of these compounds were determined crystallographically.<sup>25</sup> Moreover, it has been reported that the protonation of  $[Fe_2\{\mu-(SCH_2)_2N(C_6H_4-p-NO_2)\}(CO)_2(PMe_3)_2]$ <sup>23</sup> affords a  $\mu$ -S protonated species with a signal at  $\delta 3.05$  ppm assigned to the proton at the bridging sulfur atom; therefore, we can exclude here for **5c** the hypothesis of such a protonation reaction at the bridging sulfur atom. At  $-80$  °C the hydride signal at  $-6.26$  ppm (**5c**) collapses, whereas the signals for **5a** and **5d** increase.

The NMR data suggested an unusual coordination mode for the NHC ligands in **5d**.  $^1H$ – $^{13}C$  HMBC 2D measurements for **5d** recorded at  $-80$  °C exhibit two signals attributable to the  $C_{\text{carbene}}$  atoms at 184 and 155 ppm, which we assigned to C(2) and C(5'), respectively (Figure 8).

The  $^1H$  NMR spectrum of **5d** displays two sets of signals for the imidazole protons: two singlets at 7.45 and 6.95 ppm, corresponding as expected to H(5) and H(4), and the well-separated signals at 6.36 and 8.63 ppm, assigned to H(4') and H(2') (Chart 2). These observations are consistent with the presence of one NHC ligand having a normal metal binding at C(2) ( $\delta 184$  ppm), whereas the second NHC ligand is C(5')-bound ( $\delta 155$  ppm for C(5')) via an abnormal binding mode of

coordination.<sup>12</sup> Two AX doublets due to methylene protons are observed at 6.73 and 6.06 ppm. The carbon signals for C(4) and C(5) and for C(2') and C(4') are observed at 123 and 122 ppm and at 134 and 127 ppm, respectively. The unusual C(4/5) binding mode was previously reported for bidentate functionalized NHC ligands<sup>12a</sup> and more recently for a monodentate NHC.<sup>12c–f</sup> Compound **5d** is unstable and gives rise between  $-80$  and  $-50$  °C to the thermodynamically more stable hydride **5a**, with a normal binding at C(2).

**Electrochemical Study.** The electrochemistry of **4a** was studied by cyclic voltammetry (CV) in  $CH_3CN$  and  $CH_2Cl_2$  in the presence of  $Bu_4NPF_6$  as supporting electrolyte (Figures 9 and 10). **4a** exhibits a chemically irreversible two-electron reduction at  $-2.42$  V vs  $Fc^{+/0}$  in  $CH_3CN$ . A similar CV behavior was observed for the symmetrically disubstituted complex **A**.<sup>8c</sup> The reversible diffusion-controlled, one-electron oxidation of **4a** at  $E_{1/2}^{ox} = -0.41$  V in  $CH_3CN$  is attributed to the couple  $Fe^I/Fe^0/Fe^{II}$ . Upon addition of  $HBF_4 \cdot Et_2O$  to a  $CH_3CN$  solution of **4a**, a new reduction peak appeared at  $E_p^{red} = -1.48$  V, a potential about 1.0 V less negative than for the reduction of **4a**, which is consistent with protonation of the Fe–Fe bond.<sup>4d,5e,f</sup> The current of the reduction peak observed at  $-1.54$  V in a  $CH_2Cl_2$  electrolyte increases linearly with increasing acid ( $CF_3CO_2H$ ) concentration (Figure 11), which is a diagnostic for catalytic proton reduction.<sup>26</sup>

Similar features were observed in the electrocatalytic proton reduction by  $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(PMe_3)_2]$ <sup>4d</sup> and  $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(CN)(PMe_3)]^-$ <sup>5e,f</sup> in presence of strong acids in the same range of potentials as for **4a**: i.e. at  $-1.5$  and  $-1.4$  V, respectively. Detailed electrochemical studies of NHC–propanedithiolate–diiron complexes will be described elsewhere.

## Conclusions

A chelating bis-NHC ligand ( $I_{Me}-CH_2-I_{Me}$ ) was easily introduced at one iron center in the diiron–hexacarbonyl–propanedithiolate compound  $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_6]$  by facile carbonyl displacement at room temperature. This reaction

(24) Unpublished results.

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afforded an asymmetrically disubstituted model complex of the subsite of [FeFe] hydrogenase enzymes. Only one isomer was observed in solution and in the solid state for the neutral chelated complex. The protonation reaction of this compound affords two bridging hydride isomers in relation to the basal/basal or basal/apical mode of coordination of the chelating bis-NHC ligand. Crystallization afforded only the basal/basal isomer. These compounds are stable in solution, unlike the corresponding monodentate NHC complex, which allowed their electrochemical study in the presence of acids. The neutral chelated complex catalyzes proton reduction at  $-1.5$  V vs  $\text{Fc}^{+/0}$ . This complex is a potentially interesting starting compound for further catalyst tuning through the substitution of the remaining carbonyl ligands. The protonation reaction was studied by NMR spectroscopy at low temperature and reveals the existence of new hydride intermediates: a very unstable terminal hydride species and a bridging hydride compound with the bis-NHC ligand in normal C(2) and abnormal C(5) binding modes. We have shown that the bis-NHC ligand  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}$  afforded a stable chelated complex even in the presence of strong acids and, therefore, this ligand can be considered as a credible alternative to cyanide, phosphine, and isonitrile ligands in the synthesis of models of the all-iron hydrogenase active site.

### Experimental Section

Reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All reagents were used as purchased (Sigma-Aldrich). The solvents were predried using conventional methods and were distilled prior to use. Deuterated dichloromethane was stored under argon over molecular sieves before use. NMR spectra were recorded on a Bruker AMX 3-400 or a Bruker DRX 500 spectrometer with chemical shifts reported in  $\delta$  values relative to residual protonated solvents for  $^1\text{H}$  NMR spectra and to the solvent for  $^{13}\text{C}$  NMR spectra. Infrared spectra were recorded in the range  $2300\text{--}1600\text{ cm}^{-1}$  in  $\text{CH}_3\text{CN}$  solution with a FT-IR NEXUS Nicolet spectrometer. Elemental analyses were performed by the Service Central d'Analyses du CNRS. The imidazolium salts  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-NMe}_2\cdot\text{HCl}$ ,  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-SMe}\cdot\text{HCl}$ ,  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\cdot 2\text{HI}$ , and  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-I}_{\text{Me}}\cdot 2\text{HBr}$  were prepared according to literature methods.<sup>27</sup> The starting material  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_6]$  (**1**) was prepared by minor variations of the procedure of Seyferth and co-workers.<sup>28</sup> Electrochemical experiments, including cyclic voltammetry and bulk electrolysis, were carried out as described previously.<sup>8a</sup>

**Preparation of  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-NMe}_2\}]$  (**2a**).** Potassium *tert*-butoxide (2.25 g, 20.0 mmol) and THF (100 mL) were added to the imidazolium chloride salt  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-NMe}_2\cdot\text{HCl}$  (2.53 g, 13.4 mmol) to give a light yellow solution. After 3 h, the reaction mixture was filtered through Celite 545 and eluted with THF. After evaporation of the solvent, the free carbene was extracted in toluene ( $3 \times 40$  mL) at room temperature. The combined filtrates were concentrated to 70 mL in a 250 mL round-bottom flask. The complex  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_6]$  (**1**; 1.02 g, 2.64 mmol) was dissolved in this solution, and the resulting mixture was stirred at room temperature until the starting material disappeared, as indicated by IR. The resulting deep red solution was filtered through Celite 545 under argon. The solvent was removed under vacuum. The crude solid was then chromatographed on silica gel. A red band was eluted with a dichloromethane/acetonitrile (50/50) mixture. Evaporation of the solution gave 900 mg (yield 67%, based on diiron complex) of **2a**.

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IR ( $\text{CH}_3\text{CN}$ ):  $\nu_{\text{CO}}$  2037, 1970, 1911  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 298 K):  $\delta$  7.30, 7.03 (2s, 2H,  $\text{NCH}=\text{CHN}$ ), 4.50 (s broad, 2H,  $\text{NCH}_2\text{-}$ ), 4.01 (s, 3H,  $\text{NCH}_3$ ), 2.70 (t,  $J_{\text{HH}} = 8.0$  Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{N(CH}_3\text{)}_2$ ), 2.31 (s, 6H,  $\text{N(CH}_3\text{)}_2$ ), 2.2–1.4 (m broad, 6H,  $\text{S(CH}_2\text{)}_3\text{S}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz, 298 K):  $\delta$  216.98, 212.43 (CO), 184.75 ( $\text{C}_{\text{carbene}}$ ), 125.07 ( $\text{NCH}=\text{CHNCH}_3$ ), 123.07 ( $\text{NCH}=\text{CHNCH}_3$ ), 60.36 ( $\text{NCH}_2\text{-}$ ), 50.57 ( $\text{CH}_2\text{N(CH}_3\text{)}_2$ ), 45.82 ( $\text{N(CH}_3\text{)}_2$ ), 40.21 ( $\text{NCH}=\text{CHNCH}_3$ ), 30.87, 30.44, 24.19 ( $\text{S(CH}_2\text{)}_3\text{S}$ ). Mp: 112 °C. Anal. Calcd for  $\text{C}_{16}\text{H}_{21}\text{Fe}_2\text{N}_3\text{O}_5\text{S}_2$ : C, 37.60; H, 4.14; N, 8.22. Found: C, 37.30; H, 4.26; N, 8.15.

**Preparation of  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\{\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-SMe}\}]$  (**2b**).** Potassium *tert*-butoxide (2.53 g, 22.5 mmol) and THF (60 mL) were added to the imidazolium salt  $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-SMe}\cdot\text{HCl}$  (2.8 g, 15 mmol). After 2 h of vigorous stirring, the reaction mixture was filtered through Celite 545 and eluted with THF. The combined filtrates were concentrated to 50 mL in a round-bottom flask to give a THF solution of the free carbene ( $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-SMe}$ ). This solution was transferred into a THF solution of compound **1** (1.16 g, 3 mmol), and this mixture was stirred at room temperature for 2 h. The solvent was then removed under vacuum to give a brown-red oil, which was filtered through silica gel. A red fraction was collected by elution with a  $\text{CH}_2\text{Cl}_2$ /hexane (60/40) mixture. Slow evaporation of the solvent gave an orange powder of compound **2b** (600 mg, yield 39%).

IR ( $\text{CH}_3\text{CN}$ ):  $\nu_{\text{CO}}$  2038, 1970, 1911  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 298 K):  $\delta$  7.19, 7.06 (2s, 2H,  $\text{NCH}=\text{CHN}$ ), 4.70 (s broad, 2H,  $\text{NCH}_2\text{-}$ ), 4.02 (s, 3H,  $\text{NCH}_3$ ), 2.97 (t,  $J_{\text{HH}} = 8.0$  Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{SCH}_3$ ), 2.32 (s, 3H,  $\text{SCH}_3$ ), 2.2–1.4 (m broad, 6H,  $\text{S(CH}_2\text{)}_3\text{S}$ ). Mp: 120 °C. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{Fe}_2\text{N}_2\text{O}_5\text{S}_3$ : C, 35.04; H, 3.53; N, 5.45. Found: C, 34.80; H, 3.68; N, 5.24.

**Preparation of  $[\{\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_5\}_2\{\mu\text{-(I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})\}]$  (**3**) and  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_4\{\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\}]$  (**4a**).** Method A. Potassium *tert*-butoxide (3.10 g, 27.6 mmol) and THF (100 mL) were added to methylenebis(*N*-methylimidazolium) iodide,  $\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}}\cdot 2\text{HI}$  (3.40 g, 7.89 mmol). After 3 h of vigorous stirring at room temperature, the reaction mixture was filtered through Celite 545 and eluted with THF. The combined filtrates were concentrated to 80 mL in a round-bottom flask to give a THF solution of the free carbene ( $\text{I}_{\text{Me}}\text{-(CH}_2\text{)}_2\text{-I}_{\text{Me}}$ ). This solution was transferred to a THF solution of the complex  $[\text{Fe}_2\{\mu\text{-S(CH}_2\text{)}_3\text{S}\}(\text{CO})_6]$  (1.00 g, 2.59 mmol) at room temperature. The resulting mixture was stirred at room temperature for 1 h. The solution was evaporated to dryness in vacuo. The resulting red solid was dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and applied to a silica gel column. The first red band was eluted with a dichloromethane/hexane (50/50) mixture. Slow evaporation of the solvent gave an orange powder of compound **3** (195 mg, yield 15%). A second red band eluted with dichloromethane/hexane (90/10) gave complex **4a** (160 mg, yield 7%) as a red powder after slow evaporation of the solvents.

Compound **3**: IR ( $\text{CH}_3\text{CN}$ )  $\nu_{\text{CO}}$  2039, 1974, 1913  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, acetone)  $\delta$  7.55 (s, 2H, 2  $\text{NCH}=\text{CHN}$ ), 7.27 (s, 2H, 2  $\text{NCH}=\text{CHN}$ ), 7.16 (s broad, 2H,  $\text{NCH}_2\text{N}$ ), 4.14 (s, 6H, 2  $\text{CH}_3$ ), 2.30–1.70 (m, 12 H, 2 ( $\text{S(CH}_2\text{)}_3\text{S}$ )); mp 200 °C. Anal. Calcd for  $\text{C}_{25}\text{H}_{24}\text{Fe}_4\text{N}_4\text{O}_{10}\text{S}_4$ : C, 33.66; H, 2.71; N, 6.28. Found: C, 33.90; H, 2.92; N, 6.00.

Compound **4a**: IR ( $\text{CH}_3\text{CN}$ )  $\nu_{\text{CO}}$  1996, 1920, 1872  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.04 (d, 2H,  $J_{\text{HH}} = 2$  Hz, 2  $\text{NCH}=\text{CHN}$ ), 6.88 (d, 2H,  $J_{\text{HH}} = 2$  Hz, 2  $\text{NCH}=\text{CHN}$ ), 5.82 (d,  $\text{H}_A$ ,  $J_{\text{AB}} = 12$  Hz,  $\text{NCH}_2\text{N}$ ), 5.77 (d,  $\text{H}_B$ ,  $J_{\text{AB}} = 12$  Hz,  $\text{NCH}_2\text{N}$ ), 4.00 (s, 6H, 2  $\text{CH}_3$ ), 2.43 (dt, 2H,  $J_{\text{gem-H,H}_e} = 12.5$  Hz,  $J_{\text{HH}} = 4.5$  Hz,  $\text{S-CH}_a\text{H}_e\text{CH}_2\text{CH}_d\text{H}_e\text{S}$ ), 2.02 (m, 1H,  $\text{SCH}_2\text{CHHCH}_2\text{S}$ ), 1.97 (m, 1H,  $\text{SCH}_2\text{CHHCH}_2\text{S}$ ), 1.76 (dt, 2H,  $J_{\text{gem-H,H}_e} = 13$  Hz,  $J_{\text{HH}} = 4.5$  Hz,  $\text{S-CH}_a\text{H}_e\text{CH}_2\text{CH}_d\text{H}_e\text{S}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  223.88 (CO), 215.99 broad (CO), 197.79 ( $\text{C}_{\text{carbene}}$ ), 123.49 and 119.89 ( $\text{NCH}=\text{CHN}$ ), 62.65 ( $\text{NCH}_2\text{N}$ ), 38.35 ( $\text{CH}_3$ ), 31.30, 25.77 ( $\text{S(CH}_2\text{)}_3\text{S}$ ); mp 190 °C. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{Fe}_2\text{N}_4\text{O}_4\text{S}_2$ : C, 37.98; H, 3.58; N, 11.06. Found: C, 37.82; H, 3.68; N, 10.87.

Table 4. Crystallographic Data

	2a	4a	4b	5a·CH <sub>2</sub> Cl <sub>2</sub>	3
empirical formula	C <sub>17</sub> H <sub>23</sub> Fe <sub>2</sub> N <sub>3</sub> - O <sub>5.25</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>18</sub> Fe <sub>2</sub> N <sub>4</sub> - O <sub>4</sub> S <sub>2</sub>	C <sub>17</sub> H <sub>20</sub> Fe <sub>2</sub> N <sub>4</sub> - O <sub>4</sub> S <sub>2</sub>	C <sub>17</sub> H <sub>21</sub> BCl <sub>2</sub> F <sub>4</sub> Fe <sub>2</sub> - N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>25</sub> H <sub>24</sub> Fe <sub>4</sub> N <sub>4</sub> - O <sub>10</sub> S <sub>4</sub>
formula wt	539.20	506.16	520.19	678.91	892.12
temp (K)	150(2)	170(2)	170(2)	170(2)	170(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	8.4095(5)	12.5398(7)	12.8669(5)	13.9259(6)	12.5655(7)
<i>b</i> (Å)	11.8025(8)	10.9309(7)	10.3183(4)	13.7185(5)	16.9556(10)
<i>c</i> (Å)	12.8638(10)	14.5834(6)	15.4042(5)	16.7211(6)	15.7778(9)
α (deg)	114.724(7)	90.00	90.00	90.00	90.00
β (deg)	92.134(5)	91.601(5)	91.751(3)	124.231(4)	92.214(5)
γ (deg)	96.054(5)	90.00	90.00	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	1148.58(14)	1998.19(19)	2044.18(13)	2641.1(2)	3359.0(3)
<i>Z</i>	2	4	4	4	4
calcd density (Mg/m <sup>3</sup> )	1.530	1.683	1.690	1.707	1.764
abs coeff (mm <sup>-1</sup> )	1.477	1.691	1.656	1.519	2.000
<i>F</i> (000)	544	1032	1064	1368	1800
cryst size (mm)	0.15 × 0.15 × 0.35	0.24 × 0.13 × 0.05	0.30 × 0.17 × 0.07	0.48 × 0.30 × 0.16	0.50 × 0.18 × 0.11
θ <sub>min</sub> –θ <sub>max</sub> (deg)	3.47–23.26	3.70–26.37	3.30–26.37	3.46–24.71	2.73–26.37
no. of rflns collected	14 497	15 813	25 717	30 889	25536
no. of unique data, <i>R</i> (int)	3190, 0.0306	4082, 0.0469	4166, 0.0313	4481, 0.0289	6857, 0.0401
transmissn (max–min)	0.8086–0.6255	0.9202–0.6870	0.8929–0.6365	0.7931–0.5292	0.8100–0.4346
no. of data/restraints/params	3190/0/290	4082/0/255	4166/0/264	4481/0/357	6857/0/424
GOF on <i>F</i> <sup>2</sup>	1.046	1.018	1.095	1.053	0.923
final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> 1 = 0.0421 w <i>R</i> 2 = 0.1110	<i>R</i> 1 = 0.0393 w <i>R</i> 2 = 0.0800	<i>R</i> 1 = 0.0328 w <i>R</i> 2 = 0.0798	<i>R</i> 1 = 0.0403 w <i>R</i> 2 = 0.1042	<i>R</i> 1 = 0.0377 w <i>R</i> 2 = 0.0782
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0491 w <i>R</i> 2 = 0.1169	<i>R</i> 1 = 0.0594 w <i>R</i> 2 = 0.0875	<i>R</i> 1 = 0.0418 w <i>R</i> 2 = 0.0841	<i>R</i> 1 = 0.0432 w <i>R</i> 2 = 0.1068	<i>R</i> 1 = 0.0582 w <i>R</i> 2 = 0.0851
largest diff peak, hole (e Å <sup>-3</sup> )	0.959, –0.302	0.451, –0.274	0.860, –0.276	0.898, –0.603	0.583, –0.365
refinement method			full-matrix least squares on <i>F</i> <sup>2</sup>		

#### Preparation of [Fe<sub>2</sub>{μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>4</sub>{I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub>}] (4a).

**Method B.** The free bis-carbene I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub> was prepared as described above (method A) from KO-*t*-Bu (2.02 g, 18 mmol) and I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub>·2HI (1.30 g, 6.00 mmol) in THF. Then, the complex [Fe<sub>2</sub>{μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>6</sub>] (1; 0.772 g, 2.00 mmol) was dissolved in 80 mL of THF and then cautiously added dropwise over 45 min to the THF solution of the free bis-carbene at room temperature. After evaporation of the solvent under vacuum, the residue was filtered through a Florisil pad and eluted with THF. The solvent was then removed, and the residue was washed with ether (2 × 10 mL) until the small amount of compound 3 disappeared, as indicated by IR spectroscopy. The product 4a was obtained as a red powder. The powder was dissolved in a THF/hexane (50/50) mixture, and slow evaporation of the solvents led to the deposition of a red crystalline material of 4a (259 mg, yield 26%).

#### Preparation of [Fe<sub>2</sub>{μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>4</sub>{I<sub>Me</sub>-(CH<sub>2</sub>)<sub>2</sub>-I<sub>Me</sub>}] (4b).

Compound 4b was prepared by a procedure similar to that of 4a (method B) from I<sub>Me</sub>-(CH<sub>2</sub>)<sub>2</sub>-I<sub>Me</sub>·2HBr (2.80 g, 7.95 mmol), KO-*t*-Bu (2.70 g, 23.9 mmol), and the complex [Fe<sub>2</sub>{μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>6</sub>] (0.990 g, 2.56 mmol). The product was obtained as orange crystals: yield 150 mg, 11%.

IR (CH<sub>3</sub>CN): ν<sub>CO</sub> 1994, 1921, 1869 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.99 (d, 2H, *J*<sub>HH</sub> = 2 Hz, 2 NCH=CHN), 5.87 (d, 2H, *J*<sub>HH</sub> = 2 Hz, 2 NCH=CHN), 5.15 (d, H<sub>A</sub>, *J*<sub>AB</sub> = 8.0 Hz, NCH<sub>2</sub>-CH<sub>2</sub>N), 5.12 (d, H<sub>B</sub>, *J*<sub>AB</sub> = 8.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 3.84 (s, 6H, 2 NCH<sub>3</sub>), 3.16 (d, H<sub>A'</sub>, *J*<sub>A'B'</sub> = 8 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 3.12 (d, H<sub>B'</sub>, *J*<sub>A'B'</sub> = 8.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>N), 2.40–1.80 (m, 6H, S(CH<sub>2</sub>)<sub>3</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 227.43 (CO), 222.99 broad (CO), 192.39 (C<sub>carbene</sub>), 124.68 and 121.75 (NCH=CHN), 49.60 (NCH<sub>2</sub>-CH<sub>2</sub>N; one CH<sub>2</sub> not observed), 39.82 (CH<sub>3</sub>), 30.73, 29.70, 26.00 (S(CH<sub>2</sub>)<sub>3</sub>S). Mp: 215 °C. Anal. Calcd for C<sub>17</sub>H<sub>20</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 39.25; H, 3.88; N, 10.77. Found: C, 38.62; H, 3.61; N, 10.57.

**Preparation of [Fe<sub>2</sub>{μ-H}{μ-S(CH<sub>2</sub>)<sub>3</sub>S}(CO)<sub>4</sub>{I<sub>Me</sub>-CH<sub>2</sub>-I<sub>Me</sub>}]<sup>2+</sup>-(BF<sub>4</sub>)<sup>-</sup> (5a,b).** HBF<sub>4</sub>·Et<sub>2</sub>O (*M*<sub>r</sub> = 161.9 g mol<sup>-1</sup>, 54%, *d* = 1.19, 30 μL, 1.19 × 10<sup>-1</sup> mmol) was added at –25 °C to a solution of 4a (0.048 g, 9.56 × 10<sup>-2</sup> mmol) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture turned immediately from red to brown and after 15 min of stirring was then concentrated to 10 mL. Addition of Et<sub>2</sub>O (80 mL)

led to the precipitation of a brown solid. The precipitate was washed with Et<sub>2</sub>O (3 × 20 mL), and a brown solid was obtained after filtration (40 mg, yield 70%). It contains two isomers, 5a,b (90/10 ratio), as indicated by <sup>1</sup>H NMR analyses (CD<sub>2</sub>Cl<sub>2</sub>). IR (CH<sub>3</sub>CN): ν<sub>CO</sub> 2092, 2032, 1946 cm<sup>-1</sup>.

Compound 5a: <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.59 (s, 2H, 2 NCH=CHN), 6.94 (s, 2H, 2 NCH=CHN), 6.70 (d, H<sub>A</sub>, *J*<sub>AB</sub> = 13 Hz, NCH<sub>2</sub>N), 6.23 (d, H<sub>B</sub>, *J*<sub>AB</sub> = 13 Hz, NCH<sub>2</sub>N), 3.80 (s, 6H, 2 CH<sub>3</sub>), 2.84 (m, 2H, SCH<sub>2</sub>H<sub>c</sub>CH<sub>2</sub>CH<sub>a</sub>H<sub>c</sub>S), 2.60 (m, 1H, SCH<sub>2</sub>CHHCH<sub>2</sub>S), 2.30 (m, 1H, SCH<sub>2</sub>CHHCH<sub>2</sub>S), 2.28 (m, 2H, SCH<sub>2</sub>H<sub>c</sub>CH<sub>2</sub>CH<sub>a</sub>H<sub>c</sub>S), –12.16 (s, 1H, Fe–H–Fe); <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 217.83 (CO), 206.00 (CO), 202.22 (2 CO), 182.89 (C<sub>carbene</sub>), 124.81 and 123.21 (NCH=CHN), 63.05 (NCH<sub>2</sub>N), 38.18 (CH<sub>3</sub>), 30.16, 22.93 (S(CH<sub>2</sub>)<sub>3</sub>S).

Compound 5b: <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.70, 7.55, 7.15, 7.05 (4 s, 4H, 2 NCH=CHN), 6.48 (d, 1H, *J*<sub>HH</sub> = 13 Hz, NCH<sub>2</sub>N), 5.90 (d, 1H, *J*<sub>HH</sub> = 13 Hz, NCH<sub>2</sub>N), 4.04 (s, 3H, CH<sub>3</sub>), 3.87 (s, 3H, CH<sub>3</sub>), 2.55–2.10 (m, 6H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), –15.10 (s, 1H, Fe–H–Fe); <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 215.22, 205.66, 203.18, 202.71 (4 CO), 183.72 and 182.23 (C<sub>carbene</sub>), 124.29, 123.74 (2 NCH=CHN), 124.29 (2 NCH=CHN), 62.79 (NCH<sub>2</sub>N), 38.68, 38.33 (2 CH<sub>3</sub>), 28.33, 23.76, 23.29 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S). Anal. Calcd for C<sub>16</sub>H<sub>19</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 30.08; H, 3.12; N, 8.25. Found: C, 30.26; H, 3.03; N, 8.27.

**Protonation of 4a in Situ.** A Solution of 4a (5.0 mg, 1.0 × 10<sup>-2</sup> mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.7 mL) was transferred to an NMR tube and was cooled to –95 °C. A slight excess of HBF<sub>4</sub>·Et<sub>2</sub>O (3 μL, 1.2 × 10<sup>-2</sup> mmol) was added to the NMR tube and the spectrum recorded at –90 °C. The low solubility of 4a precluded the collection of all of the NMR data. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 5a, δ<sub>H</sub> hydride –12.36 ppm, 19%; 5c, δ<sub>H</sub> hydride –6.26 ppm, 42%; 5d, δ<sub>H</sub> hydride –12.06 ppm, 39%. <sup>1</sup>H NMR at –80 °C: 5a, δ<sub>H</sub> hydride –12.36 ppm, 20%; 5c, δ<sub>H</sub> hydride, –6.30 ppm, 4%; 5d, δ<sub>H</sub> hydride –12.05 ppm, 76%. See the Results and Discussion for the chemical shift of the NHC ligand for 5d.

**X-ray Crystallography.** Single-crystal X-ray diffraction data were collected at 170 K on an X-CALIBUR-2 CCD four-circle diffractometer (Oxford Diffraction) with graphite-monochromated

Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures of **2a**, **3**, **4a,b**, and **5a** were solved by direct methods and successive Fourier difference syntheses with the Sir97 program<sup>29</sup> and refined on  $F^2$  by weighted anisotropic full-matrix least-squares methods using the SHELXL97 program.<sup>30</sup> Both of these programs were used within the WINGX package.<sup>31</sup> No absorption correction was needed, owing to the low absorption coefficients of these complexes. The ORTEP

program<sup>32</sup> was used for crystal-structure drawings. Crystallographic data for **2a**, **3**, **4a,b**, and **5a** are given in Table 4.

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**Supporting Information Available:** CIF files giving crystallographic data for compounds **2a**, **3**, **4a,b**, and **5a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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