



# Synthesis and structural characterization of sulfur rich iron (II) carbonyl dimers: Facile reversible reaction with carbon monoxide

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## ARTICLE INFO

### Article history:

Received 27 June 2008

Received in revised form 30 June 2008

Accepted 30 June 2008

Available online 9 July 2008

### Keywords:

Iron(II) carbonyls

Hydrogenase models

Tridentate thiolate ligands

## ABSTRACT

The sulfur-rich iron carbonyl dimer complexes  $[\text{Fe}(\text{CO})_2(\text{S}^{\text{Si}}\text{S}_2)]_2$  (**2**), and  $[\text{Fe}(\text{CO})(\text{S}^{\text{Si}}\text{S}_2)]_2$  (**3**) have been prepared. The  $[2\text{Fe}-2\text{S}]$  cores of the new complexes are planar. The binding mode of the tridentate sulfur ligand in complex **2** is facial with a  $\text{S}(\text{thiolate})-\text{Fe}-\text{S}(\text{thiolate})$  angle of  $92^\circ$ , while in complex **3**, the  $\text{S}^{\text{Si}}\text{S}_2$  ligand binds the metal with a  $\text{S}(\text{thiolate})-\text{M}-\text{S}(\text{thiolate})$  angle of  $120^\circ$ . The Fe–Fe distance is reduced from 3.45 Å in complex **2** to 2.78 Å in the 32 electron dimer complex **3**. Complexes **2** and **3** are at equilibrium in solution and can be readily interconverted by addition or removal of CO.

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## 1. Introduction

Hydrogenase enzymes catalyze the oxidation of dihydrogen and the reduction of protons in nature. X-ray crystallography and IR spectroscopy of [Fe]-only hydrogenases have shown the active site to be comprised of a  $[2\text{Fe}-2\text{S}]$  subunit linked to a  $[4\text{Fe}-4\text{S}]$  cluster by a cystenyl-S bridge [1,2]. The two iron atoms in the  $[2\text{Fe}-2\text{S}]$  subunit are linked by a bridging dithiolate ligand and are ligated by the biologically uncommon ligands carbon monoxide (CO) and cyanide ( $\text{CN}^-$ ) [3].

A new class of Fe containing hydrogenases, Hmd hydrogenases ( $\text{H}_2$ -forming methylenetetrahydromethanopterin dehydrogenase), has been recently characterized by Thauer and coworkers [4]. This enzyme, previously thought to be metal free [5], catalyzes the transfer of a hydride ( $\text{H}^-$ ) from  $\text{H}_2$  to an organic pterin substrate in methanogenic bacteria. IR and Mössbauer spectroscopy of Hmd suggest that the active site is comprised of a monomeric Fe(II) dicarbonyl moiety [6,7]. The detailed structure of the Hmd active site is unknown, but spectroscopic data is consistent with the presence of two CO ligands, and a combination of S ligands and N/O ligands [8,9]. In this work, we describe our efforts to prepare monomeric iron dicarbonyl complexes as models for this active site.

The organosulfur ligands  $\text{S}'\text{S}_2$  ( $\text{S}'\text{S}_2 = \text{bis}(2\text{-mercaptophenyl})\text{-sulfide}$ ) and  $\text{S}'^{\text{Si}}\text{S}_2$  ( $\text{S}'^{\text{Si}}\text{S}_2 = \text{bis}(2\text{-mercapto-3-trimethyl-silylphenyl})\text{-sulfide}$ ) (Fig. 1) were initially developed by Sellmann and coworkers, who prepared a series of  $\text{MS}'\text{S}_2\text{L}$  complexes ( $\text{M} = \text{Ni}, \text{Pt}, \text{Fe}$ ) [10–12]. The tridentate ligands  $\text{S}'\text{S}_2$  and  $\text{S}'^{\text{Si}}\text{S}_2$  are structur-

ally flexible. In Ni group complexes the ligands adopt a planar configuration, forming distorted square planar  $[\text{M}(\text{S}'\text{S}_2)(\text{L})]$  complexes ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{L} = \text{monodentate ligands}$ ) with  $\text{S}_1(\text{thiolate})-\text{M}-\text{S}_3(\text{thiolate})$  angles close to  $180^\circ$ . In contrast the  $\text{S}'\text{S}_2$  assumes a facial binding mode in Fe complexes. The facial geometry affords complexes with  $\text{S}_1(\text{thiolate})-\text{M}-\text{S}_3(\text{thiolate})$  angles around  $90^\circ$ .

The iron complex  $[\text{Fe}(\text{CO})_2(\text{S}'\text{S}_2)]_2$  (**1**), a sulfur-rich diferrous dicarbonyl dimer, has been prepared by Sellmann and coworkers via reaction of the neutral  $(\text{S}'\text{SH})_2$  with  $[\text{Fe}(\text{CO})_3(\text{PhCH}=\text{CHCOMe})]$  [12]. The complex is comprised of two  $(\text{Fe}(\text{CO})_2\text{S}'\text{S}_2)$  fragments with facial coordination of the  $\text{S}'\text{S}_2$  ligand. The dimer is bridged by two of the thiolates, forming a centrosymmetric dimer (Fig. 2). The  $[2\text{Fe}-2\text{S}]$  core of complex **1** is planar, unlike the other reported diferrous carbonyl complexes, which exhibit the butterfly core present in the  $\text{Fe}_2$  hydrogenases [13–15]. The Fe–S distances in complex **1** are in the range typical of low-spin Fe(II) thiolate and thioether complexes. However, the Fe–Fe distance is 3.45 Å, significantly longer than that reported for the butterfly diferrous carbonyl complexes.

Sellmann and coworkers reported the preparation of monomeric iron(II) monocarbonyl complexes such as  $[\text{Fe}(\text{CO})_2\text{S}'\text{S}_2\text{PCy}_3]$  from the insoluble complex **1** [12]. Based on the facile ligand addition reactions, the existence of a formally 16 electron monomeric dicarbonyl species in equilibrium with **1** was proposed (Fig. 2). The proposed monomeric dicarbonyl species **1a** and **1b** likely have a solvent molecule bound to the open site resulting from dimer fragmentation.

Aiming to generate and isolate monomeric dicarbonyl or tricarbonyl Fe(II) complexes, to study  $\text{H}_2$  activation process, we have explored in greater detail the chemistry of the  $\text{S}'\text{S}_2$  and  $\text{S}'^{\text{Si}}\text{S}_2$  ligands. The organosulfur compound  $\text{S}'(\text{SH})_2$  (**4**) was initially synthesized

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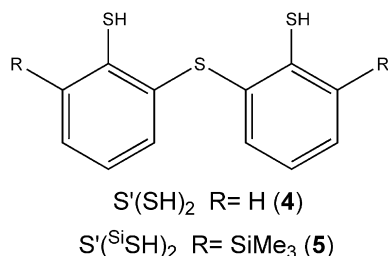


Fig. 1. Tridentate organosulfur ligands  $S'S_2$  and  $S'SiS_2$ .

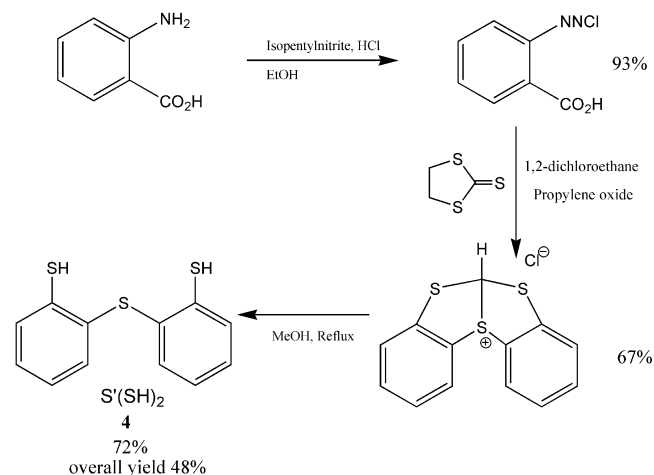
by Sellmann and coworkers through a four-step one-pot reaction involving lithiation of diphenyl sulfide, followed by treatment with elemental sulfur and finally reduction with  $LiAlH_4$ . Final treatment with HCl affords **4** in 20% overall yield after a tedious workup [10].

A more convenient synthesis of  $S'(SH)_2$  was developed by Nakayama and coworkers, who have used this compound in the synthesis of thioether crowns [16–18]. This synthesis is based on the dipolar cycloaddition reaction of ethylene trithiocarbonate with two equivalents of benzyne. The diazonium salt which serves as the benzyne precursor is generated by reaction of anthranilic acid with isopentyl nitrite in acidic media (Scheme 1). This reaction takes minutes and proceeds in near quantitative yield. Caution: The diazonium chloride is shock sensitive; as such it should be handled with care and used promptly after generation.

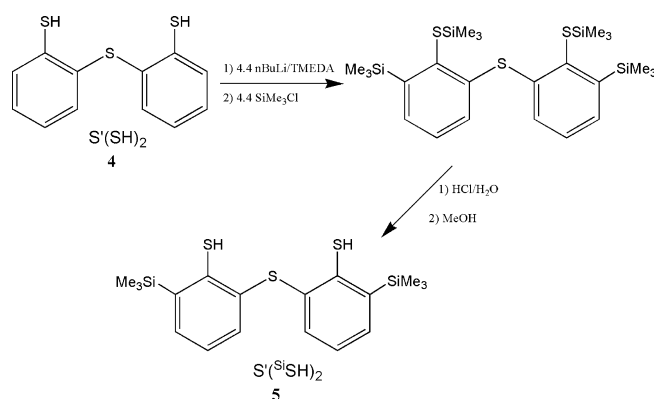
We obtain the polycyclic sulfonium salt in 70% yield as a foul smelling yellow/orange powder, which can be recrystallized from hot acetic acid to afford a colorless crystalline solid. We found it more expedient to carry out the subsequent hydrolysis in refluxing methanol using the impure sulfonium salt, which affords ligand **4** as a colorless powder in an overall yield of 48% (Scheme 1).

The bulkier  $S'(SiSH)_2$  ligand (**5**) was prepared by reaction of **4** with four equivalents of  $nBuLi/TMEDA$ , followed by treatment of the resulting tetra-anion with four equivalents of  $Me_3Si-Cl$ . This reaction affords bis-(2-thiotrimethylsilane-3-trimethylsilylphenyl-sulfide). Treatment with acid and methanol affords  $S'(SiSH)_2$  (**5**) in very high yields (Scheme 2).

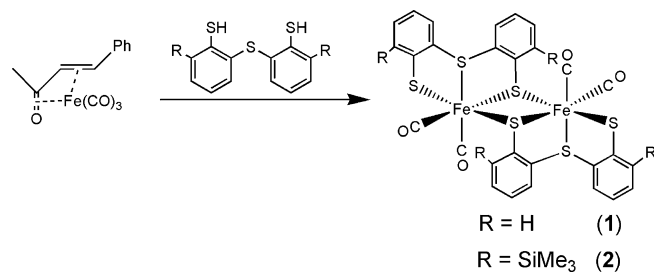
As reported by Sellmann and coworkers, we find that reaction of  $[Fe(CO)_3(PhCH=CHCOMe)]$  with  $S'(SH)_2$  (**4**) affords the dimer  $[Fe(CO)_2(S'S_2)]_2$  (**1**) (Scheme 3). Complex **1** was previously reported to be insoluble in common organic solvents. No NMR spectrum was reported for complex **1**. We find that crystalline samples of **1** can be dissolved in THF and  $CH_2Cl_2$  in concentrations up to 0.2 mmol. THF solutions of **1** are stable at low temperatures (243 K) for days, but decompose over the course of hours at 273 K. The  $^1H$  NMR spectrum of complex **1** in THF- $d_8$  shows the presence of two aromatic rings in different environments, consistent with the solid state structure of **1**. The IR spectrum of **1** in THF solutions shows two bands in the  $\nu(CO)$  region at 2035 and 1996  $cm^{-1}$ , very similar to the frequencies previously reported for **1** in the solid state. These observations suggest that complex **1** also forms a centrosymmetric dimer in solution.



Scheme 1.



Scheme 2.



Scheme 3.

Monitoring of solutions of **1** by  $^1H$  NMR spectroscopy at 273 K shows the gradual formation of a new species, as a new set of aromatic resonances evolves over time. A new species is also observed

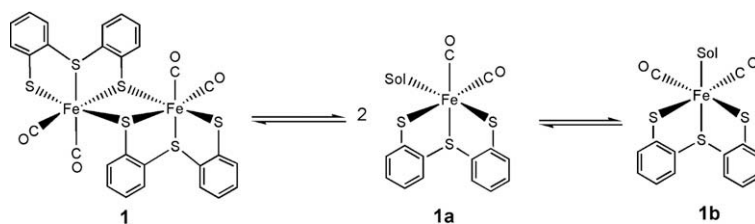


Fig. 2. Proposed solution equilibrium of complex **1**.

in the IR spectrum, with  $\nu(\text{CO})$  at  $2049\text{ cm}^{-1}$ . Complete decomposition occurs over several hours, to afford an apparently paramagnetic species, which is NMR silent. We propose that the transient species that we have observed corresponds to the monomeric fragmentation product of dimer **1**, as postulated by Sellmann and coworkers.

Reaction of  $[\text{Fe}(\text{CO})_3(\text{PhCH}=\text{CHCOMe})]$  with ligand  $\text{S}'(\text{Si}^{\text{Si}}\text{H})_2$  (**5**) in diethyl ether affords the dimer  $[\text{Fe}(\text{CO})_2(\text{S}'\text{Si}_2)]_2$  (**2**) (Scheme 3). Complex **2** can be isolated from the reaction mixture by precipitation from concentrated solutions. The IR spectrum of **2** in the  $\nu(\text{CO})$  region (KBr) consists of two intense bands at  $2029$  and  $1988\text{ cm}^{-1}$ , suggesting a structure similar to that of complex **1** (Table 1).

Crystals of complex **2** suitable for X-ray diffraction were obtained from concentrated diethyl ether solutions. Complex **2** is dimeric, comprised of two  $(\text{Fe}(\text{CO})_2\text{S}'\text{Si}_2)$  fragments with facial coordination of the  $\text{S}'\text{Si}_2$  ligand. The Fe atoms adopt a distorted octahedral geometry, bridged by two thiolate ligands. The bridging thiolates that form the  $[\text{2Fe}-\text{2S}]$  core act as four electron donors, producing a centrosymmetric 36 electron diamagnetic dimer. The  $[\text{2Fe}-\text{2S}]$  core of complex **2** is planar like complex **1**. The Fe–Fe distance in **2** is  $3.45\text{ \AA}$ , the same as complex **1**. These bond lengths are over 35% longer than the typical distances of the butterfly Fe–Fe dimers (around  $2.6\text{ \AA}$ ). The Fe–S distances lie between  $2.29$  and  $2.35\text{ \AA}$ , typical of low-spin Fe(II) thiolate and thioether complexes (Fig. 3).

Although the introduction of the bulky trimethylsilyl moieties does not prevent dimerization, this substitution on the ligand backbone increases solubility. In contrast to complex **1**, complex **2** is soluble in a range of organic solvents. The IR spectrum of **2** in  $\text{CH}_2\text{Cl}_2$  exhibits two bands in the  $\nu(\text{CO})$  region at  $2034$  and  $1995\text{ cm}^{-1}$ , which is very similar to the spectrum of complex **1**. An additional band of variable intensity was observed at  $1975\text{ cm}^{-1}$ , which was ultimately found to increase when the solution was concentrated *in vacuo*. This new species is tentatively assigned as a monocarbonyl complex **3**. The spectrum of complex **2** was restored when the solution was placed under an atmosphere of CO (Fig. 4). As noted above, the existence of a 16 electron monomer in equilibrium with **1** was proposed by Sellmann and coworkers (Fig. 2) [12]. Thus, the presence of an additional species in equilibrium with **2** was expected, but the effect of CO on this equilibrium suggests that **3** is a monocarbonyl complex, formulated as the dimeric complex  $[\text{Fe}(\text{CO})(\text{S}'\text{Si}_2)]_2$ . Upon removal of all CO, complex **3** can be isolated (Scheme 4). This decarbonylation reaction occurs quantitatively at room temperature in minutes.

The IR spectrum of isolated **3** in the carbonyl stretching region (KBr) consists of one intense band at  $1980\text{ cm}^{-1}$ . In  $\text{CH}_2\text{Cl}_2$  solution

**Table 1**

Crystal data and structure refinement for  $[\text{Fe}(\text{CO})_2(\text{S}'\text{Si}_2)]_2$  (**2**)

Empirical formula	$\text{C}_{40}\text{H}_{48}\text{Fe}_2\text{O}_4\text{S}_6\text{Si}_4$
Formula weight	1009.2
Temperature	$130(2)\text{ K}$
Wavelength	$0.71073\text{ \AA}$
Crystal size, color	$0.10 \times 0.10 \times 0.10\text{ mm}$ , red
Crystal system, space group	Monoclinic, $C 2/c$
Unit cell dimensions	$a = 24.9970(11)\text{ \AA}$ , $\alpha = 90^\circ$ $b = 12.1490(6)\text{ \AA}$ , $\beta = 110.9431(18)^\circ$ $c = 16.3120(9)\text{ \AA}$ , $\gamma = 90^\circ$
Volume	$4626.5(4)\text{ \AA}^3$
Z, Calculated density	4, $1.449\text{ mg/m}^3$
Absorption coefficient	$1.040\text{ mm}^{-1}$
$F(000)$	2096
Crystal size	$0.10 \times 0.10 \times 0.10\text{ mm}$
Reflections for indexing	106
Theta range for data collection	$2.13\text{--}27.49^\circ$
Index ranges	$-32 \leq h \leq 32$ , $-15 \leq k \leq 15$ , $-21 \leq l \leq 21$
Reflections collected/unique	9449/5101 [ $R_{\text{int}} = 0.1407$ ]
Completeness to theta = $25.00$	98.8%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.9031 and 0.9031
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5101/0/253
Goodness-of-fit (GoF) on $F^2$	$S = 0.914$
$S = \sqrt{(\sum(w * D * D) / (n - p))}$ , where $D = (F_o * F_o - F_c * F_c)$	
Final R indices [ $I > 2\sigma(I)$ ]	$*R_1 = 0.0607$ , $wR_2 = 0.1238$
R indices (all data)	$R_1 = 0.2090$ , $*wR_2 = 0.1818$
$R_1 = \sum   F_o  -  F_c   / \sum  F_o $ , $wR_2 = \sqrt{(\sum(w * D * D) / \sum(w * F_o * F_o))}$ , where $D = (F_o * F_o - F_c * F_c)$	
Weighting scheme calc $w = 1 / [\sigma^2(F_o^2) + (0.0669P)^2 + 0.0000P]$ , where $P = (F_o^2 + 2F_c^2) / 3$	
Largest difference peak and hole	$0.508$ and $-0.646\text{ e \AA}^{-3}$

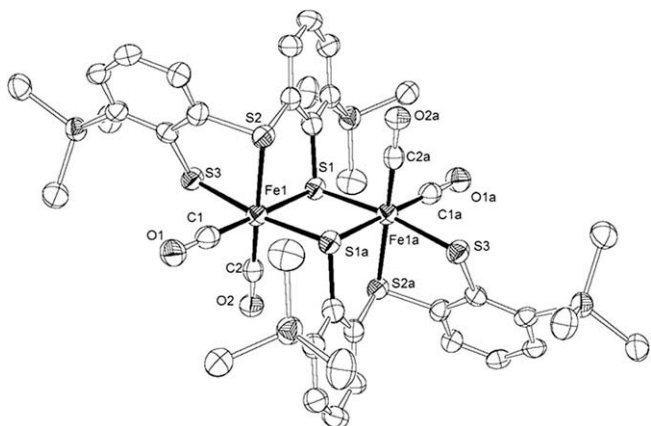
a single band is observed at  $1975\text{ cm}^{-1}$ . The isolated complex is therefore identical to the species previously observed in equilibrium with **2** in solution (Fig. 4).

The  $^1\text{H}$  NMR spectrum of complex **3** exhibits two sets of resonances of equal intensities for the aromatic (12 H) and the trimethylsilane hydrogen atoms (36 H), indicative of the presence of two aromatic rings in different environments. This pattern is consistent with a centrosymmetric dimer structure in solution (Fig. 5).

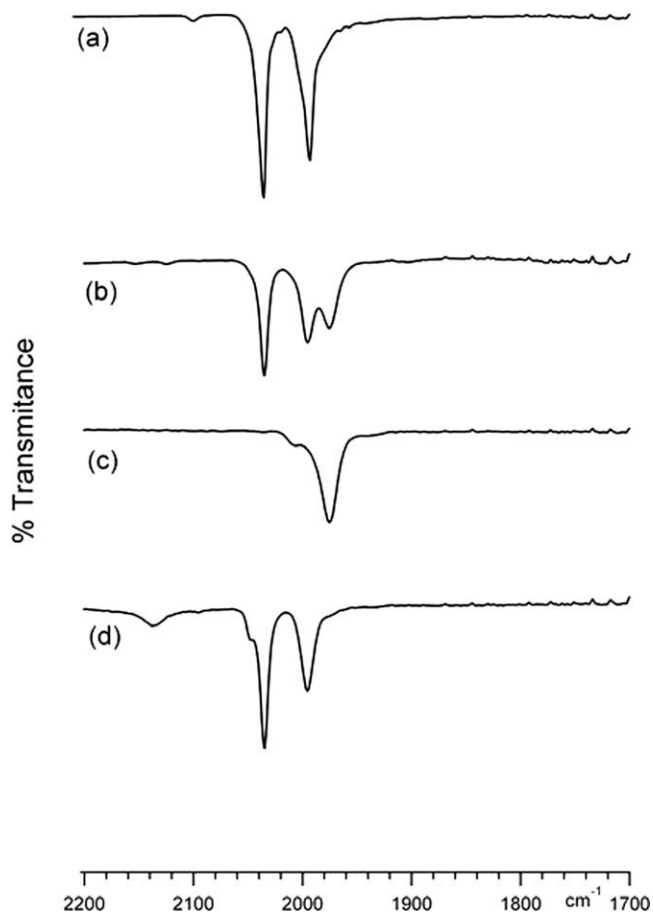
Small green crystals of complex **3** were obtained by cooling dilute diethyl ether solutions. X-ray diffraction studies of several samples did not afford data of sufficient quality for a complete structure determination, but the dimeric formulation was confirmed. A notable decrease of the iron iron distance is observed, from  $3.45\text{ \AA}$  in **2** to  $2.78\text{ \AA}$  in **3**. The two halves of complex **3** consist of formally sixteen electron Fe(II) moieties, thus electron counting formalisms require a *formal* Fe=Fe double bond.

The decarbonylation with concomitant bond formation observed for the formation of complex **3** from **2** is not unprecedented. For example, the singly bonded molybdenum dimer  $[\text{CpMo}(\text{CO})_3]_2$  loses two CO ligands upon heating, affording a  $[\text{CpMo}(\text{CO})_2]_2$  dimer with a formal triple bond [19]. The formation of the  $[\text{CpMo}(\text{CO})_2]_2$  dimer in refluxing xylene was shown to occur via odd-electron intermediates arising from the homolysis of the Mo–Mo bond in the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  precursor. Soft nucleophiles add to the metal–metal triple bond in this dimer complex, but the reverse reaction with CO to afford  $[\text{CpMo}(\text{CO})_3]_2$  was not observed [20]. Facile reaction of CO with the Fe=Fe double bond is observed in complex **3**, with regeneration of complex **2** observed in minutes when complex **3** is placed under 1 atm of CO (Scheme 4). This transformation has been monitored by IR spectroscopy (Fig. 4).

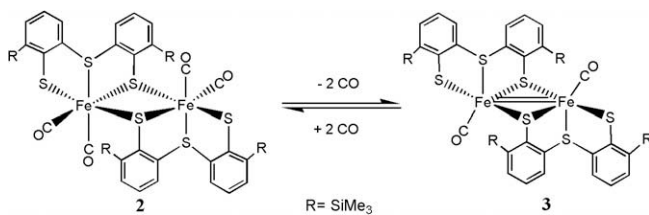
The two new complexes,  $[\text{Fe}(\text{CO})_2(\text{S}'\text{Si}_2)]_2$  (**2**) and  $[\text{Fe}(\text{CO})(\text{S}'\text{Si}_2)]_2$  (**3**), are rare examples of ferrous carbonyl complexes [21]. They are stable in the solid state at room temperature under inert atmospheres for long periods. In solution, both **2** and **3** are stable,



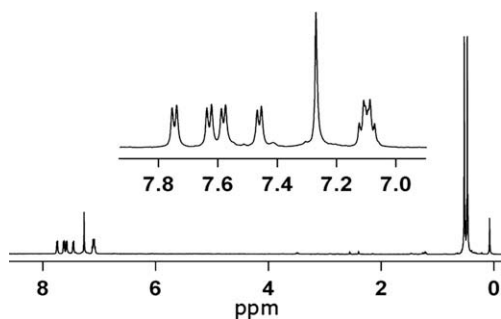
**Fig. 3.** ORTEP diagram (50% thermal ellipsoids) of  $[\text{Fe}(\text{CO})_2(\text{S}'\text{Si}_2)]_2$  (**2**). The Fe–Fe distance is  $3.45\text{ \AA}$ .



**Fig. 4.** Infrared spectra in the  $\nu(\text{CO})$  region. (a) Complex **2** in KBr: 2029, 1988  $\text{cm}^{-1}$ ; (b) complex **2** dissolved in  $\text{CH}_2\text{Cl}_2$ : 2034, 1995, 1975  $\text{cm}^{-1}$ . (c) Complex **3** in  $\text{CH}_2\text{Cl}_2$ : 1975  $\text{cm}^{-1}$ ; (d) complex **3** under 1 atm of CO shows complete formation of complex **2** after 10 minutes, with bands at 2034, 1995  $\text{cm}^{-1}$ .



**Scheme 4.** Reversible formation of complex **3**.



**Fig. 5.** 500 MHz  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$ .

but quite air sensitive, turning brown in minutes to form materials which are NMR silent and lack any evidence for bound CO. The

reactivity of the complexes **2** and **3** with acids has been studied. When treated with equimolar amounts of acetic acid, the complexes are stable for days before decomposing to intractable materials. Treatment with the stronger acids trifluoroacetic acid or *p*-toluenesulfonic acid leads to immediate decomposition.

We find that the complex  $[\text{Fe}(\text{CO})_2(\text{S}'\text{S}_2)]_2$  (**1**) is more soluble than previously reported, giving moderately stable solutions at low temperatures in THF. Decomposition to intractable products occurs at room temperature, likely through the intermediacy of a solvated monomer. Using the tripodal  $\text{S}_3$  ligand **5**, two new dithiolate bridged iron carbonyl dimers,  $[\text{Fe}(\text{CO})_2(\text{S}'\text{SiS}_2)]_2$  (**2**) and  $[\text{Fe}(\text{CO})_2(\text{S}'\text{SiS}_2)]_2$  (**3**) have been synthesized. These new complexes are stable at room temperature in solution. Complexes **2** and **3** can be reversibly interconverted by adding or removing CO (Scheme 4).

## 2. Experimental

Reactions involving metal complexes were carried out in the absence of oxygen using standard Schlenk line techniques. All solvents were dried over suitable drying agents and distilled prior to use.  $\text{Fe}_2(\text{CO})_9$  (Strem), isopentyl nitrite (Aldrich), anthranilic acid (Aldrich), ethylene trithiocarbonate (Aldrich) and propylene oxide (Aldrich), were used as received.  $\text{S}'(\text{SH})_2$  and  $\text{S}'(\text{SiSH})_2$  were prepared using slight modification of the literature procedures, as detailed below [11,16–18].  $[\text{Fe}(\text{CO})_2(\text{S}'\text{S}_2)]_2$  was prepared by reaction of  $[\text{Fe}(\text{CO})_3(\text{PhCH}=\text{CHCOMe})]$  [22] with  $\text{S}'\text{SH}_2$ .

### 2.1. 9aH-9,10-dithia-4b-thioniaindenof[1,2-a]indene chloride

A mixture of 14 g of ethylene trithiocarbonate and 38 g of 2-carboxybenzenediazonium chloride and propylene oxide (35 mL) in 1.2 L of 1,2-dichloroethane was heated under reflux for 2 h. Caution: The diazonium chloride is shock sensitive; as such it should be handled with care and used promptly after generation. The resulting solution was evaporated under reduced pressure. This material was obtained in 67–72% yield and was used without further purification.

### 2.2. Bis(*o*-mercaptophenyl) sulfide (**4**)

Sulfonium salt (18 g) from above was heated at reflux in 500 mL of methanol for 2 h. The solution was evaporated and the residue was dissolved in 2 M NaOH (1.1 L) and  $\text{CH}_2\text{Cl}_2$  (1.5 L). The alkaline layer was acidified with concentrated hydrochloric acid and extracted with  $\text{CH}_2\text{Cl}_2$ . The extracts were washed with water and then dried over  $\text{MgSO}_4$ . Evaporation of the solvent afforded 9.8 g of **4** as a white solid (72% yield).

### 2.3. Bis(2-mercapto-3-trimethylsilylphenyl)-sulfide (**5**)

3.25 g (13 mmol) of **4** was suspended in 100 mL of hexane at 195 K. Twenty three milliliter of a 2.5 M *n*BuLi solution (56 mmol) was added slowly, followed by 15 mL of TMEDA. The suspension was allowed to warm to room temperature, and stirring was continued for 72 h. The yellow suspension was then cooled to 195 K, and 7.5 mL of  $\text{SiMe}_3\text{Cl}$  (59 mmol) was slowly added. After 1 h at 195 K, the suspension was allowed to warm to room temperature, and stirring was continued for 24 h. The colorless suspension was treated with 25 mL of  $\text{H}_2\text{O}$  and volatile components removed *in vacuo*. The resulting red-brown residue was dissolved in 250 mL of  $\text{Et}_2\text{O}$ , and washed with  $3 \times 100$  mL of 5% hydrochloric acid, followed by washing with  $2 \times 50$  mL of brine. After drying over  $\text{Na}_2\text{SO}_4$ , removal of all volatiles produced a yellow residue which was dissolved in 75 mL of methanol and heated to reflux for 12 h. Removal of the methanol *in vacuo* yielded a red-yellow

residue of  $S^{(Si)H}_2$ . Chromatography of the residue on a silica gel column (particle size 40–63  $\mu\text{m}$ ; 4 cm  $\times$  25 cm) eluting with hexane afforded the product as a colorless viscous oil which solidified upon standing. Yield: 4.2 g (80%).

#### 2.4. $[Fe(CO)_2(S^{Si}S_2)]_2$ (**2**)

An ethereal solution (10 mL) containing 37 mg (0.14 mmol) of  $[Fe(CO)_3(PhCH=CHCOMe)]$  and 58 mg (0.14 mmol) of  $S^{Si}S_2$  was stirred briefly, then set aside for 3 days. The red-brown crystals which formed were washed twice with small portions of cold ether (yield 60%). IR  $\nu(CO)$ : 2028, 1987  $\text{cm}^{-1}$  (KBr).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ) 8.02 (d, 2H), 7.82 (d, 2H), 7.43 (d, 2H), 7.36 (t, 2H), 7.17 (d, 2H), 6.98 (t, 2H), 0.36 (s, 18H) and 0.14 (s, 18H). Anal. Calc. for  $\text{C}_{40}\text{H}_{48}\text{O}_4\text{Fe}_2\text{S}_6\text{Si}_2$ : C, 47.67; H, 4.76; S, 19.07. Found: C, 47.71; H, 5.03; S, 18.84%.

#### 2.5. $[Fe(CO)(S^{Si}S_2)]_2$ (**3**)

An ethereal solution (10 mL) containing 100 mg (0.4 mmol) of  $[Fe(CO)_3(PhCH=CHCOMe)]$  and 160 mg (0.4 mmol) of  $S^{Si}S_2$  was degassed. The red solution was stirred overnight, with the color changing to green. After the head space gases were removed 5 mL of pentane was layered on top of the ether solution. The green precipitate formed was decanted and washed with 2  $\times$  5 mL portions of pentane (yield 55%). IR (KBr)  $\nu(CO)$ : 1980  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ) 7.79(d, 2H), 7.68(d, 2H), 7.62(d, 2H), 7.49(d, 2H), 7.14(t, 2H), 7.11(t, 2H), 0.51(s, 18H), and 0.47 (s, 18H). Anal. Calc. for  $\text{C}_{38}\text{H}_{48}\text{O}_2\text{Fe}_2\text{S}_6\text{Si}_2$ : C, 47.87; H, 5.07; S, 20.18. Found: C, 47.73; H, 5.21; S, 19.95%.

#### Acknowledgement

This work was supported by the US National Science Foundation.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.038.

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