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Studies on the Condensation Pathway to and Properties of Diiron Azadithiolate Carbonyls

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Reaction of $Fe_2(SH)_2(CO)_6$ and HCHO, which gives $Fe_2[(SCH_2)_2NH](CO)_6$ in the presence of NH_3, affords the possible intermediate $Fe_2(SCH_2OH)_2(CO)_6$, which has been characterized crystallographically as its axial−equatorial isomer. $Fe_2(SCH_2OH)_2(CO)_6$ was shown to react with ammonia and amines to give $Fe_2[(SCH_2)_2NR](CO)_6$ (R = H, alkyl). Related hemithioacetal intermediates were generated by treatment of $Fe_2(SH)_2(CO)_6$ with RC(O)C(O)R (R = H, Ph, 4-F-C_6H_4) to give cycloadducts. The benzil derivative $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$, a C_2-symmetric species, was also characterized crystallographically. The acylated azadithiolate $Fe_2[(SCH_2)_2NAc](CO)_6$ was prepared by reaction of $Li_2Fe_2S_2(CO)_6$ with $(ClCH_2)_2NC(O)Me$. DNMR experiments show that the free energies of activation for rotation of the amide bond are the same for $Fe_2[(SCH_2)_2NAc](CO)_6$ and $Fe_2[(SCH_2)_2NAc](CO)_4(PMe_3)_2$, which implies that the ligands on the iron centers do not strongly affect the basicity of the nitrogen. As a control, we showed that the thioamide $Fe_2[(SCH_2)_2NC(S)Me](CO)_6$ does exhibit a significantly higher barrier to rotation, attributable to the increased double-bond character of the N−C(S) bond.

Introduction

Since diiron azadithiolates were first reported in 2001,[1] many derivatives of the type $Fe_2[(SCH_2)_2NR](CO)_{6-x}L_x$ have been described.[1−5] These efforts are motivated by the following considerations: (i) the possibility that the azadithiolate is the dithiolate cofactor in the Fe-only hydrogenases,[6] (ii) the possibility that such a ligand could play a functional role in the heterolytic activation of H_2,[7,8] and (iii) the amine is a versatile point of attachment for diverse substituents.[4,5] The functionalization of organometallic sulfides is an active area.[9]

Although many azadithiolato complexes have been described, relatively few studies have examined the parent $Fe_2[(SCH_2)_2NH](CO)_6$ (**1**H).[3] This species contains the specific dithiolate that is plausible biologically. Compound **1**H has been prepared by treatment of $Fe_2(SH)_2(CO)_6$ with formaldehyde and sources of ammonia. Alternatively, **1**H can be prepared by condensation of $Fe_2(SH)_2(CO)_6$ with hexamethylenetetramine.[3] These condensation pathways have been lightly studied, and proposed intermediates have not been well characterized. We previously proposed that formaldehyde adds to $Fe_2(SH)_2(CO)_6$ to give hydroxymethyl intermediates that condense with amine or ammonia. In this paper we describe the isolation of such hydroxyalkyl derivatives. The formation of azadithiolates via the apparent condensation of hydroxymethyl amines with $Fe_2(SH)_2(CO)_6$ has also been demonstrated.[5]

In this project we also sought to probe possible coupling of the azadithiolato functionality to the electronic properties of the attached diiron unit. We previously reported that **1**H was only weakly basic,[1] but we had not evaluated the character of the amine in derivatives where CO has been substituted. This aspect is biologically relevant, since in nature, the dithiolate is attached to a diiron center bound to two cyanide ligands, which are powerful σ-donors.

Results

Synthesis and Basic Properties of $Fe_2[(SCH_2)_2NH](CO)_6$. Compound **1**H was prepared by the addition of aqueous

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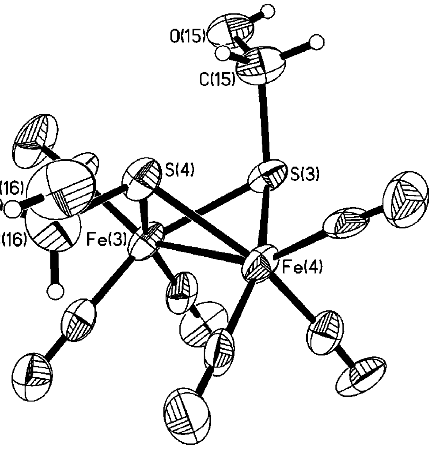
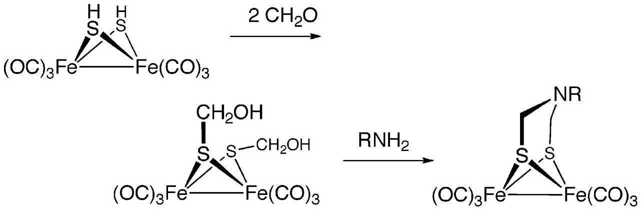


Figure 1. Structure of one of two molecules of $Fe_2(SCH_2OH)_2(CO)_6$ in the asymmetric unit, with thermal ellipsoids drawn at the 50% probability level.

Scheme 1



formaldehyde to a THF solution of $Fe_2(SH)_2(CO)_6$,[10] followed by the addition of ammonium carbonate. Yields were ca. 25%. The corresponding reaction of $Fe_2(SH)_2(CO)_6$, HCHO, and *t*-$BuNH_2$ proceeded more efficiently to give **1**Bu-*t* in 60% yield (Scheme 1). Qualitative tests demonstrated that **1**H and **1**Bu-*t* are relatively stable to heat and air; therefore, the modest yields appear not to reflect instability intrinsic to the complex. Compound **1**Bu-*t* was, however, decomposed by primary and secondary amines as well as by H_2S. In contrast, the corresponding propanedithiolate $Fe_2(S_2C_3H_6)(CO)_6$ is largely unaffected by H_2S and dilute solutions of amines. Ott et al. have shown that amines displace a CO ligand in $Fe_2(S_2C_3H_6)(CO)_6$.[5]

Characterization of $Fe_2(SCH_2OH)_2(CO)_6$. THF solutions of $Fe_2(SH)_2(CO)_6$ react with 2 equiv of aqueous formaldehyde. Reaction progress can be monitored by *in situ* IR spectroscopy with a focus on the highest energy ν_{CO} band. A major product is $Fe_2(SCH_2OH)_2(CO)_6$, but mass spectra suggest that the reaction affords additional products such as $Fe_2(SCH_2OH)(SCH_2OCH_2OH)(CO)_6$. ^1H NMR spectra proved problematic, although we observed equally intense singlets at δ 4.6 and 4.36, which are assigned to the axial−equatorial isomer, as is seen in other examples of $Fe_2(SR)_2(CO)_6$.[11,12] Attempts to remove the solvent resulted in loss of CH_2O, affording $Fe_2S_2(CO)_6$. Samples of $Fe_2(SCH_2OH)_2(CO)_6$ were shown to react with ammonia and primary amines to give the azadithiolates $Fe_2[(SCH_2)_2NR](CO)_6$ (R = H, Bu-*t*).

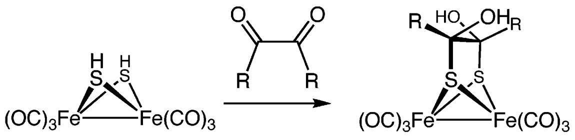
Although $Fe_2(SCH_2OH)_2(CO)_6$ was unstable, we were able to obtain single crystals from hexane (Figure 1, Table 1). Two independent but similar molecules comprise the asymmetric unit. The crystallographic analysis confirmed the previously anticipated[3] structure, wherein hydroxymethyl groups adopt the axial−equatorial orientation. Otherwise, the structure is unremarkable and quite similar to that of $Fe_2(SEt)_2(CO)_6$.[12] The individual molecules are interconnected by hydrogen bonding.

Table 1. Selected Distances (Å) and Angles (deg) for $Fe_2(SCH_2OH)_2CO)_6$

Fe(3)−Fe(4)	2.5063(14)	C(15)−S(3)	1.835(6)
Fe(3)−S(3)	2.260(2)	C(16)−S(4)	1.808(6)
Fe(4)−S(3)	2.2705(19)	C(15)−O(15)	1.403(6)
Fe(3)−S(4)	2.250(2)	C(16)−O(16)	1.396(6)
Fe(4)−S(4)	2.2577(18)		
Fe(3)−S(3)−Fe(4)	67.17(6)	C(15)−S(3)−Fe(4)	114.3(2)
Fe(3)−S(4)−Fe(4)	67.55(6)	S(4)−Fe(4)−S(3)	80.10(6)
C(16)−S(4)−Fe(3)	113.7(2)	S(4)−Fe(3)−S(3)	80.47(7)
C(16)−S(4)−Fe(4)	116.1(2)	O(15)−C(15)−S(3)	108.1(4)
C(15)−S(3)−Fe(3)	112.9(2)	O(16)−C(16)−S(4)	109.9(4)

Condensation of $Fe_2(SH)_2(CO)_6$ and Glyoxal. In an effort to isolate a more stable aldehyde adduct, we treated $Fe_2(SH)_2(CO)_6$ with glyoxal, $(CHO)_2$. This condensation produced a red product, assumed to be $Fe_2[S_2(CHOH)_2](CO)_6$, the polarity of which was evident from its low solubility in hexane. Its ^1H NMR spectrum exhibited three broadened signals, one of which is assigned to OH and the other two assigned to the C*H* on the meso and the chiral diastereoisomers, respectively. The IR spectrum of the mixture in the ν_{CO} region was very similar to those for other $Fe_2(SR)_2(CO)_6$ compounds. Careful chromatography produced samples that were enriched in one isomer, which isomerized over the course of several hours to the equilibrium mixture. We propose that the isomerization is associated with the reversibility of the aldehyde addition process. Consistent with this proposal, treatment of this isomeric mixture with aqueous formaldehyde and *t*-$BuNH_2$ gave **1**Bu-*t* in good yield.

Condensation of $Fe_2(SH)_2(CO)_6$ with Benzil. Treatment of $Fe_2(SH)_2(CO)_6$ with benzil gave the yellow-brown adduct $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$ (eq 1). The reaction is slower than the addition of formaldehyde to $Fe_2(SH)_2(CO)_6$, but the product proved more readily purified than other derivatives. The ^1H NMR spectrum of the product exhibited a D_2O-exchangeable signal at δ 2.83. The compound also appears to be unstable in polar solvents such as CD_3CN solution. We also spectroscopically characterized the corresponding adduct of 4,4′-difluorobenzil, $Fe_2[S_2C_2(OH)_2(C_6H_4\text{-}4\text{-}F)_2](CO)_6$. The ^1H and ^{19}F NMR spectra indicate that this compound is structurally analogous to the benzil derivative.



(1)

R = H, Ph, C_6H_4F

The structure $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$ was examined by single-crystal X-ray diffraction (Figure 2, Table 2). The molecule consists of the usual Fe_2S_2 butterfly core with idealized C_2 symmetry. The hydroxyl groups, the H atoms of which were refined, are mutually trans. The S_2C_2 ligand backbone is twisted as a result of the steric influence of the Ph groups. The protons of the CO−H groups are oriented toward the CO ligand, but any interaction between the OH groups and the axial CO ligands must be weak because the ν_{CO} bands in the IR spectrum are unremarkable. The IR spectrum of this compound in solution is almost identical with that for $Fe_2(S_2C_2H_4)(CO)_6$. The IR spectrum of a KBr pellet containing the compound displayed six sharp ν_{CO} bands, consistent with its low symmetry.

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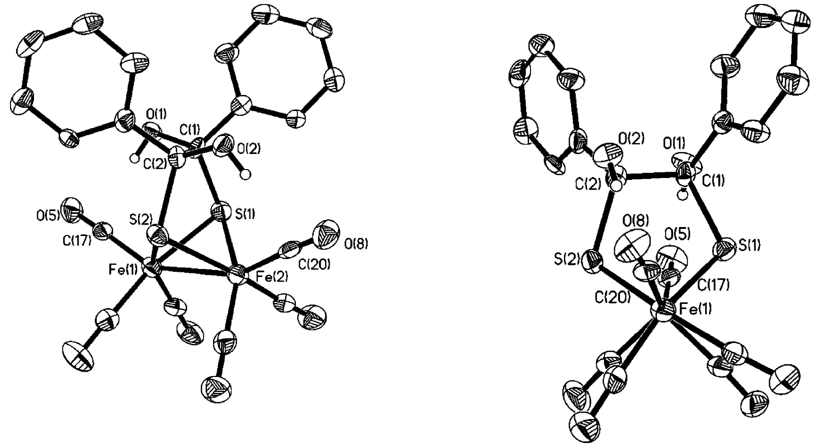

Figure 2. Two perspectives of the structure of $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$ with thermal ellipsoids drawn at the 50% probability level. Phenyl hydrogen atoms were omitted for clarity.

Table 2. Selected Distances (Å) and Angles (deg) for $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$

Fe(1)−Fe(2)	2.4941(19)	C(1)−S(1)	1.866(9)
Fe(1)−S(2)	2.251(3)	C(1)−O(1)	1.407(9)
Fe(1)−S(1)	2.259(3)	C(2)−O(2)	1.393(9)
Fe(2)−S(1)	2.252(3)	C(1)−C(2)	1.560(12)
Fe(2)−S(2)	2.256(3)	C(17)−Fe(1)	1.798(10)
C(2)−S(2)	1.901(9)	C(20)−Fe(2)	1.790(9)
Fe(2)−S(1)−Fe(1)	67.13(9)	O(1)−C(1)−S(1)	108.4(6)
Fe(1)−S(2)−Fe(2)	67.20(8)	C(2)−C(1)−S(1)	110.1(6)
S(2)−Fe(1)−S(1)	79.49(10)	C(1)−C(2)−S(2)	108.0(6)
S(1)−Fe(2)−S(2)	79.54(10)	C(20)−Fe(2)−S(2)	99.9(3)
C(2)−S(2)−Fe(1)	109.0(3)	C(20)−Fe(2)−S(1)	110.2(3)
C(2)−S(2)−Fe(2)	101.1(3)	C(1)−S(1)−Fe(2)	108.3(3)
O(2)−C(2)−S(2)	107.9(6)	C(1)−S(1)−Fe(1)	102.0(3)

Acylated Derivatives of $Fe_2[(SCH_2)_2NH](CO)_6$. The complex $Fe_2[(SCH_2)_2NC(O)Me](CO)_6$ (**1**Ac) was initially prepared by the condensation of $MeC(O)NH_2$ and $Fe_2(SCH_2OH)_2(CO)_6$. FD−MS and NMR confirmed the formation of **1**Ac, but the reproducibility and yield were poor. More successful was the alkylation of $Li_2Fe_2S_2(CO)_6$ with $(ClCH_2)_2NAc$.[13] We tested the possible conversion of **1**Ac into **1**H, but **1**Ac was stable in hot (55 °C) 12 M HCl. Thiation of **1**Ac with Lawesson's reagent[14] afforded the expected thioamide $Fe_2[(SCH_2)_2NC(S)Me](CO)_6$. The IR spectra of the amide and thioamide were virtually indistinguishable in the ν_{MCO} region. We found that **1**Ac reacted with PMe_3 to give $Fe_2[(SCH_2)_2NAc](CO)_4(PMe_3)_2$, which was characterized spectroscopically.

DNMR Studies of $Fe_2[(SCH_2)_2NC(X)Me](CO)_6$ (X = S, O). The ^1H NMR spectrum of **1**Ac was examined over the range −80 to +100 °C. Only one methyl signal was observed at all temperatures, which indicates the absence of isomers. The signals for the methylene groups, however, changed significantly as a function of temperature (Figure 3). At −80 °C, two doublets of doublets for SCH_2N were observed. When the sample was warmed, these signals broadened, coalescing into two singlets at room temperature. At ~100 °C in $CD_3C_6D_5$ solution, the two CH_2 singlets coalesced into a broad singlet. Two dynamic processes are relevant to these observations. First, the "flipping" of the FeS_2C_2N ring, which is seen also for $Fe_2(pdt)(CO)_6$ and **1**H, has a low barrier of ca. 10 kcal/mol.[15] More interesting is the rotation about the N−C(O) bond, which has a high barrier. For acetamide, the barrier is ca. 18 kcal/mol.[16]

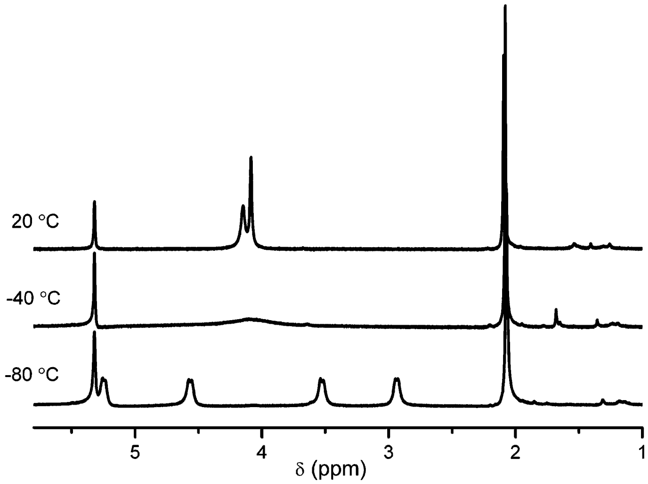

Figure 3. 500 MHz ^1H NMR spectra of $Fe_2[(SCH_2)_2NAc](CO)_6$ at various temperatures (CD_2Cl_2 solution).

The DNMR spectrum for $Fe_2[(SCH_2)_2NAc](CO)_4(PMe_3)_2$ was similar to that for the hexacarbonyl parent. In particular, the coalescence temperatures for $Fe_2[(SCH_2)_2NAc](CO)_4(PMe_3)_2$ and $Fe_2[(SCH_2)_2NAc](CO)_6$ are nearly identical, which is significant because for each compound the $\Delta\delta$ values for the two CH_2 singlets are within 10%. This observation suggests that the donor ligand does not affect the N−C(O) π-bond. As a control experiment, we evaluated the DNMR properties of $Fe_2[(SCH_2)_2NC(S)Me](CO)_6$. The overall pattern for the low-temperature chemical shifts are similar to those for the parent amide, although rotation about the N−C(S)Me bond is subject to a higher barrier, as coalescence is >100 °C.

Discussion

The condensation route from $Fe_2(SH)_2(CO)_6$ to $Fe_2[(SCH_2)_2NH](CO)_6$ was shown to be consistent with the intermediacy of hydroxymethyl derivatives. The reactivity of MSH complexes toward aldehydes has been previously discussed only lightly, although the reaction of thiols with aldehydes is well-known in organic chemistry and biochemistry.[17] The compounds $Fe_2(SCH_2OH)_2(CO)_6$ and $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$ are rare structurally characterized examples of the $M-SCR_2OH$ functionality.

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Among complexes containing the M−SCR_2OH linkage, the unstable species $Fe_2(SCMe_2CH_2C(OH)(Me)S)(CO)_6$ was previously generated via the addition of $Fe_2(SH)_2(CO)_6$ to the α,β-unsaturated ketone $Me_2C{=}CHC(O)Me$.[18] Another example of this functionality resulted from the addition of hydroxide to η^5-thiophene complexes.[19]

The dynamics for $Fe_2[(SCH_2)_2NAc](CO)_6$ and $Fe_2[(SCH_2)_2NAc](CO)_4(PMe_3)_2$ proved to be similar. This observation indicates that donor ligands on Fe do not substantially influence the nitrogen of the azadithiolate ligand. This finding in turn suggests that the ligands on the diiron subunit do not strongly interact with the nitrogen of the azadithiolate. Consistent with this observation, we observe that ν_{CO} varies little as one changes the substituents on nitrogen from H to Ac.

Experimental Section

Unless otherwise indicated, reactions were conducted using Schlenk techniques at room temperature. ^1H and ^{31}P NMR spectra were recorded on an 11.7 T instrument. IR data are reported in cm^{-1}. Chromatography was conducted in air. Other methods used in this laboratory have been recently described.[20]

Revised Preparation of $Fe_2S_2(CO)_6$. The following procedure represents a further optimization of the literature method.[21] A three-neck, 2 L round-bottomed flask was fitted with a mechanical stirrer, a N_2-inlet adapter, and a septum connected to a bubbler. After being flushed with N_2, the flask was charged with 50 mL (0.378 mol) of $Fe(CO)_5$, followed by 250 mL of MeOH, and finally 150 mL of freshly prepared aqueous KOH (~50%). After it was stirred for 30 min, the homogeneous solution was cooled to 0 °C, and 65.33 g of S_8 was delivered over the course of 5 min. The turbid black mixture was stirred for 1 h and then was treated with 625 mL of H_2O, 1500 mL of pentane (or hexanes), and finally 169 g (3.16 mol) of NH_4Cl. *Caution! Evolution of H_2S.* The ice bath was then removed, and the reaction mixture was stirred at room temperature for 14−16 h, after which time bubbling had slowed significantly. The resulting reaction mixture consisted of a dark red pentane layer and a black oily aqueous phase. The pentane layer was filtered through a pad of ca. 400 mL of Celite, which was then rinsed with ca. 500 mL of pentane. The oily aqueous phase was extracted with 1−2 L of pentane until all of the extracts were no longer red, and this pentane extract was also passed through the Celite. The combined deep red pentane fractions were washed with an approximately equal volume of water, dried over Na_2SO_4, and evaporated. The solid residue was then transferred to a 150 mL Schlenk flask fitted with a water-cooled cold finger sublimation apparatus. Sublimation was conducted at room temperature with a static vacuum maintained at ca. 0.01 mmHg. The red sublimate was periodically removed. The sublimation requires days for completion, but attempts to accelerate the process by warming the sample resulted in decreased yields. Yield: 30 g (46% based on $Fe(CO)_5$). IR (cyclohexane): ν_{CO} 2083 (m), 2043 (s), 2007 (m), 1991 (m), 1969 (w), 1956 (w).

$Fe_2[(SCH_2)_2NH](CO)_6$ (1H). (a) Aminomethylation Reagent. In a 150 mL flask, a slurry of 2.23 g (3.09 mmol) of $(NH_4)_2CO_3$ in 30 mL of THF was warmed to 60 °C and then treated over the course of 5 min with 25 mL (30.8 mmol) of 37% aqueous HCHO, resulting in a colorless solution. Following the addition, the solution was heated at 60 °C for 1 h and then cooled to room temperature.

(b) $Fe_2[(SCH_2)_2NH](CO)_6$. In an adaptation of the procedure of Seyferth, a solution of 1.07 g (3.11 mmol) of $Fe_2S_2(CO)_6$ in 20 mL of THF, cooled to −78 °C, was treated with 7.0 mL (7.0 mmol) of a 1.0 M THF solution of $LiEt_3BH$. After 15 min, 1.0 mL (12.9 mmol) of CF_3CO_2H was added to give a red-orange solution. After a further 15 min, the reaction solution was warmed to room temperature. The entire aminomethylation solution was transferred dropwise via cannula into the $Fe_2(SH)_2(CO)_6$ solution over the course of 15 min. After it was stirred for 16−20 h, the brown-red solution was evaporated, and the brown oily solid was extracted into ca. 200 mL of hexanes with vigorous stirring and sonication. The extracts were filtered and evaporated to dryness. The residue was then extracted into 8 mL of hexanes and chromatographed on a 4 × 30 cm silica gel column. Elution with hexanes gave three bands in the following order: unreacted $Fe_2S_2(CO)_6$ (50−100 mg), an unidentified red oil, and the product. Yield: 0.49 g (44%). IR (hexanes): $\nu_{CO} = 2075$ (m), 2035 (s), 2007 (s), 1989 (s), 1979 (s).

$Fe_2(SCH_2OH)_2(CO)_6$. By the procedure as outlined above, $Fe_2(SH)_2(CO)_6$ (1.46 mmol) was generated in situ at −78 °C from 0.502 g (1.46 mmol) of $Fe_2S_2(CO)_6$ in 20 mL of THF, 3.2 mL of a 1.0 M THF solution of $LiEt_3BH$, and 0.40 mL (5.19 mmol) of CF_3CO_2H. The cold reaction mixture was treated with 0.24 mL (2.96 mmol) of 37% aqueous CH_2O, and the reaction solution was then warmed to room temperature. After the reaction mixture was stirred for ca. 16 h, solvent was removed, leaving a deep red oil that was washed with 10 mL of hexanes to remove unreacted $Fe_2S_2(CO)_6$. The red oil was extracted into 5 mL of Et_2O, and this solution was diluted with 50 mL of hexanes to precipitate colorless solids. The filtrate was evaporated to dryness, and the extraction−precipitation procedure was repeated. The orange-red $Fe_2(SCH_2OH)_2(CO)_6$ was finally extracted into 20 mL of hexanes, and this solution was filtered. When the filtrate was allowed to stand at room temperature, crystals appeared. FD−MS (*m*/*z*): 343.8 ($Fe_2S_2(CO)_6$, 15%), 376 ($Fe_2(SH)(SCH_2OH)(CO)_6$, 50%), 406 ($Fe_2(SCH_2OH)_2(CO)_6$, 100%), 436 ($Fe_2(SCH_2OH)(SCH_2OCH_2OH)(CO)_6$, 10%). IR (THF): ν_{CO} 2071 (w), 2034 (s), 1994 (m).

$Fe_2[(SCH_2)_2NBu\text{-}t](CO)_6$ (1Bu-*t*). A solution of $Fe_2(SH)_2(CO)_6$ was first generated from 0.215 g (0.624 mmol) of $Fe_2S_2(CO)_6$ in 10 mL of THF, 1.26 mL (1.26 mmol) of 1.0 M $LiEt_3BH$ in THF, and 0.13 mL (1.69 mmol) of CF_3CO_2H. This solution was treated with 0.10 mL (1.23 mmol) of 37% aqueous CH_2O, and after ca. 1 h, the reaction solution was treated with 0.07 mL (0.66 mmol) of *t*-$BuNH_2$, causing the red solution to deepen in color. After 20 min, the solvent was removed, and the residue was extracted with ~30 mL of hexanes. The extracts were concentrated to ~5 mL and chromatographed on a 4 × 30 cm silica gel column. Elution with hexanes gave unreacted $Fe_2S_2(CO)_6$ (23 mg) and $Fe_2[(SCH_2)_2NBu\text{-}t](CO)_6$. Yield: 0.144 g (52%; 58% conversion). IR (hexanes): ν_{CO} 2074 (m), 2036 (s), 2003 (s), 1995 (s), 1982 (m). ^1H NMR (CD_3CN): δ 3.30 (br, 4H, CH_2), 0.98 (s, 9H, CH_3).

$Fe_2[S_2(CHOH)_2](CO)_6$. A solution of 0.18 g (0.52 mmol) of $Fe_2(SH)_2(CO)_6$ in 20 mL of THF was treated with 1.0 mL of 40% aqueous (w/w) glyoxal. After this reaction mixture was stirred overnight, the solvent was evaporated, leaving a red oily residue. The residue was washed with 10 mL of hexane and then extracted with 5 mL of CH_2Cl_2. The extract was chromatographed on silica gel with CH_2Cl_2, and a red band consisting of a mixture of cis and trans isomers was obtained. Yield: 0.13 g (60%). ^1H NMR (CD_3CN): δ 4.91 (s, 2H, C*H*, trans), 4.82 (s, 2H, C*H*, cis), 4.63 (b, 2H, O*H*, cis and trans). IR (CH_3CN): 3633, 3540, 2077, 2040, 1999. HR-EIMS (*m*/*z*): found (calcd) 403.804 413 (403.804 639). Anal. Found (calcd): C, 24.30 (23.79); H, 1.07 (1.00). When this mixture was carefully rechromatographed on silica gel, initially with 2:1 CH_2Cl_2−hexane and then pure CH_2Cl_2 as eluent, fractions enriched in trans isomer and cis isomer could be obtained. A solution of the two enriched isomers in CH_3CN solution was observed to equilibrate in 7 h (for enriched cis isomer).

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$Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$. A solution of $Fe_2(SH)_2(CO)_6$ was generated in situ from 0.498 g (1.45 mmol) of $Fe_2S_2(CO)_6$, 15 mL of THF, 3.0 mL (3 mmol) of a 1.0 M THF solution of $LiEt_3BH$, and 0.23 mL (2.99 mmol) of CF_3CO_2H. This solution was treated with a solution of 0.304 g (1.45 mmol) of benzil in 5 mL of THF at −78 °C. After 1 h, the cold bath was removed, and stirring was continued at room temperature for ∼14 h before solvent was removed from the deep yellow-brown solution using a hot water bath. While still warm, the dark brown oily residue was washed with ca. 40 mL of hexanes. The combined hexane extracts were filtered through Celite and reduced in volume by half, whereupon a mustard yellow solid precipitated. The solid was washed with ca. 35 mL of hexanes. When they were cooled to 0 °C, the combined hexane extracts afforded crystals. Yield: 0.2 g (24%). The sample decomposed at 139 °C. ^1H NMR (CD_2Cl_2): 7.36 (m, C_6H_5), 2.83 (s, O*H*). Anal. Found (calcd): C, 42.98 (43.19); H, 1.94 (2.17); N, 0.09 (0.00). IR (hexanes): ν_{CO} 2077 (m), 2041 (s), 2006 (m), 2002 (sh). IR (THF): ν_{OH} 3577 (w), 3509 (w) cm^{-1}; ν_{CO} 2071 (s), 2035 (s), and 1996 (s) cm^{-1}. IR (KBr): ν_{OH} 3503 cm^{-1}; ν_{CO} 2087 (m), 2035 (s), 2015 (s), 1999 (s), 1990 (s), 1978 (s) cm^{-1}. FD-MS: 556 (M^+).

$Fe_2[S_2C_2(OH)_2(C_6H_4\text{-}4\text{-}F)_2](CO)_6$. The preceding procedure, but using 4,4′-difluorobenzil in place of benzil, afforded an orange-yellow hygroscopic powder. Yield: 0.24 g (47%). ^1H NMR (CD_2Cl_2): δ 7.33 (t, 4H, *o*-C_6H_4-4-F), 7.04 (t, 4H, *m*-C_6H_4-4-F), 2.89 (s, 2H, OH). ^{19}F NMR (CD_2Cl_2): δ −114 (s). IR (CH_2Cl_2): ν_{CO} 2077 (m), 2041 (s), 2003 (b, m) cm^{-1}; ν_{OH} 3683 (w), 3530 (w) cm^{-1}. FD-MS: 592 (M^+).

$Fe_2[(SCH_2)_2NAc](CO)_6$ (1Ac). A solution of $Li_2Fe_2S_2(CO)_6$ in ca. 45 mL of THF was treated with 1.2 mL (10.9 mmol) of $AcN(CH_2Cl)_2$. The reaction mixture was maintained at −78 °C for 1 h before being warmed to room temperature, at which point stirring was continued for 4 h before the solvent was removed. The dark brown-red oil was washed with 10 mL of hexanes and extracted with ca. 50 mL of CH_2Cl_2. The extract was filtered through Celite, concentrated, and chromatographed, with CH_2Cl_2 as eluent. The deep red second band was evaporated, and the resulting orange-red oil was triturated with hexanes to give a dark orange solid. Yield: 1.43 g (38%). Mp: 121 °C dec. IR (CH_2Cl_2): ν_{CO} 2078 (m), 2040 (s), 2006 (m), 1999 (sh), 1669 (m) cm^{-1}. ^1H NMR (CD_3CN): δ 4.16 (bs, 2H, CH_2), 4.14 (s, 2H, CH_2), 2.06 (s, 3H, CH_3). ^1H NMR (toluene-d_8): δ 3.57 (bs, 2H, CH_2), 3.00 (s, 2H, CH_2), 1.43 (s, 3H, CH_3). FD−MS (*m*/*z*): 428.9 (M^+). Anal. Found (calcd): C, 27.94 (28.00); H, 1.55 (1.65); N, 3.20 (3.27).

$Fe_2[(SCH_2)_2NC(S)Me](CO)_6$. A solution of 0.504 g (1.17 mmol) of $Fe_2[(SCH_2)_2NAc](CO)_6$ in 15 mL of THF was treated with a slurry of 1.91 g (4.71 mmol) of Lawesson's reagent in 35 mL of THF. The reaction mixture was heated to reflux and monitored by TLC (CH_2Cl_2) until conversion was complete. After ca. 19 h of reflux, solvent was removed from the cooled reaction mixture, and the resulting brown solid was chromatographed on silica gel, with CH_2Cl_2 as eluent. The dark red band was concentrated to leave a dark orange solid that was washed with hexanes. Yield: 0.45 g (85%). Upon attempted measurement of its melting point, the sample decomposed at 140 °C. IR (CH_2Cl_2): ν_{CO} 2080, 2042, 2008 cm^{-1}; $\nu_{C=S}$ 1121 cm^{-1}. IR (hexanes): ν_{CO} 2080, 2043, 2012, 2005, 1988 cm^{-1}. ^1H NMR (CD_3CN): δ 4.79 (bs, CH_2), 4.40 (s, CH_2), 2.59 (s, CH_3). ^1H NMR (toluene-d_8): δ 4.14 (bs, CH_2), 3.10 (s, CH_2), 1.98 (s, CH_3). FD-MS (*m*/*z*): 445 (M^+). Anal. Found (calcd): C, 27.26 (26.99); H, 1.34 (1.59); N, 2.91 (3.15).

$Fe_2[(SCH_2)_2NC(O)Me](CO)_4(PMe_3)_2$. A solution of 0.199 g (0.463 mmol) of $Fe_2[(SCH_2)_2NAc](CO)_6$ in 5 mL of toluene was treated with 0.55 mL (5.41 mmol) of PMe_3 in 10 mL of toluene and heated to reflux. After it was refluxed for 1.5 h, the cherry red solution was cooled to room temperature and filtered, and the solvent was removed to give a dark red oil. Trituration with hexanes gave the dark red solid. Yield: 0.177 g (73%). IR (toluene): ν_{CO} 1988 (w), 1978 (w), 1952 (s), 1908 (m) 1668 (w) cm^{-1}. ^1H NMR (CD_3CN): δ 3.94 (s, CH_2), 2.02 (s, NC(O)CH_3), 1.50 (d, PCH_3). ^1H NMR (toluene-d_8): δ 4.01 (bs, CH_2), 3.45 (s, CH_2), 1.80 (s, NC(O)CH_3), 1.12 (d, PCH_3). ^{31}P NMR (CD_3CN): δ 25.04. FD-MS (*m*/*z*): 525 (M^+).

Table 3. Crystallographic Data for $Fe_2(SCH_2OH)_2(CO)_6$ and $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$

	$Fe_2(SCH_2OH)_2(CO)_6$	$Fe_2[SC(OH)Ph]_2(CO)_6$
chem formula	$C_8H_6Fe_2O_8S_2$	$C_{20}H_{12}Fe_2O_8S_2$
temp (K)	193(2)	193(2)
cryst size (mm)	0.32 × 0.32 × 0.10	0.22 × 0.04 × 0.02
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.828(3)	6.2738(14)
b (Å)	12.874(5)	21.591(5)
c (Å)	13.045(5)	16.124(4)
α (deg)	97.935(6)	90
β (deg)	101.023(6)	100.483(5)
γ (deg)	94.432(6)	90
V (Å^3)	1433.1(9)	2147.7(9)
Z	4	4
calcd density (Mg m^{-3})	1.882	1.720
μ(Mo Kα) (mm^{-1})	0.71073	0.71073
max/min transmissn	0.8022/0.3224	0.9535/0.7797
no. of measd/indep rflns	10 704/10 355	4059/3936
no. of data/restraints/params	10 355/134/366	3936/106/289
GOF on F^2	0.630	0.949
R_{int}	0.0000	0.0000
R1 ($I > 2\sigma$) (all data)[a]	0.0513 (0.1672)	0.0829 (0.2765)
wR2 ($I > 2\sigma$) (all data)[b]	0.0922 (0.1020)	0.0986 (0.1359)
max peak/hole (e/Å^3)	1.010/−0.827	0.651/−0.487

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{\sum[w(|F_o| - |F_c|)^2]/\sum[wF_o^2]\}^{1/2}$, where $w = 1/\sigma^2(F_o)$.

X-ray Crystallography. Crystals were mounted using Paratone-N oil (Exxon) to a thin glass fiber. Data, collected at 198 K on a Siemens CCD diffractometer, were filtered to remove statistical outliers. The integration software (SAINT) was used to test for crystal decay as a bilinear function of X-ray exposure time and sin θ. The data were solved using SHELXTL by direct methods; atomic positions were deduced from an E map or by an unweighted difference Fourier synthesis. H atom U's were assigned as $1.2U_{eq}$ for adjacent C atoms. Non-H atoms were refined anisotropically. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the final cycle. For crystallographic data, see Table 3.

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Supporting Information Available: Figures giving NMR spectra for the species synthesized in this study and CIF files giving crystallographic data for $Fe_2(SCH_2OH)_2(CO)_6$ and $Fe_2[S_2C_2(OH)_2Ph_2](CO)_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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