six signals of equal intensity. (Chemical shifts are provided in the Experimental Section.)

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE84-11630. We thank Mr. Steven L. Mullen and Professor Alan G. Marshall for FT/ICR mass spectra. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by the National Science Foundation, Grant 79-10019).

Supplementary Material Available: Listings of anisotropic thermal parameters, intra-ring bond distances, and intra-ring bond angles (18 pages); listings of structure factor amplitudes (132 pages). Ordering information is given on any current masthead page.

Novel Anionic Rearrangements in Hexacarbonyldiiron Complexes of Chelating Organosulfur Ligands

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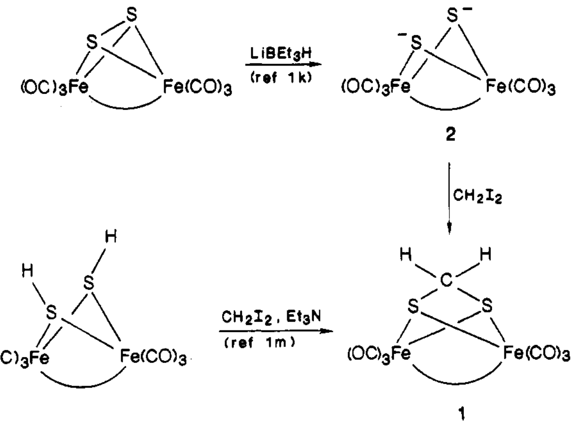
Bridging organosulfur chelate ligands of type –SCHRS– (R = H, Ph), $-SCH_2CH_2S-$, $-S(CH_2)_3S-$, and $-SCH_2\text{-}o\text{-}C_6H_4CH_2S-$ in their $Fe_2(CO)_6$ complexes are deprotonated by lithium diisopropylamide. The resulting anion in the case of the $-SCH_2CH_2S-$ ligand undergoes β-elimination to produce $(\mu\text{-LiS})(\mu\text{-}CH_2{=}CHS)Fe_2(CO)_6$, but the anions derived from the other ligands undergo an intramolecular rearrangement which involves nucleophilic attack by the carbanion at an iron atom with displacement of an electron pair onto one of the sulfur atoms. Addition of an organic halide then results in alkylation of a sulfur atom. In the case of $(\mu\text{-}SCH_2S)Fe_2(CO)_6$ this sequence results in formation of an $Fe_2(CO)_6$ complex of an alkyl dithioformate, $(HC(S)SR)Fe_2(CO)_6$. Complexes of the latter type also can be deprotonated. A similar anionic rearrangement then results in formation of novel $RR'S\text{–}CS\text{–}[Fe(CO)_3]_2$ complexes after alkylation of the intermediate sulfur-centered anion with R′X. The structures of three products of such reactions were determined by X-ray crystallography. $(\mu\text{-}CH_3C(O)CH_2SCHS)Fe_2(CO)_6$ (**10**) crystallizes in the space group $P\bar{1}$ ($a = 10.296$ (2) Å, $b = 11.306$ (2) Å, $c = 6.617$ (1) Å, $\alpha = 100.45$ (1)°, $\beta = 93.36$ (1)°, $\gamma = 103.38$ (1)°, $V = 732.9$ Å^3, and $Z = 2$). On the basis of 2073 observations and 194 parameters varied the structure has converged at $R = 0.042$ and $R_w = 0.055$. $(\mu\text{-}C_2H_5SCHC_6H_4CH_2S)Fe_2(CO)_6$ (**19**) crystallizes in $P2_1/n$ ($a = 15.003$ (2) Å, $b = 7.530$ (1) Å, $c = 16.599$ (2) Å, $\beta = 92.11$ (1)°, $V = 1874.0$ Å^3, and $Z = 4$) and has refined to $R = 0.053$ and $R_w = 0.055$ with 2004 observations and 223 parameters varied. $(\mu\text{-}SCS(CH_3)_2)Fe_2(CO)_6$ (**22**) crystallizes in $P\bar{1}$ ($a = 9.586$ (1) Å, $b = 10.276$ (1) Å, $c = 7.601$ (1) Å, $\alpha = 92.18$ (1)°, $\beta = 111.52$ (1)°, $\gamma = 86.94$ (1)°, $V = 695.3$ Å^3, and $Z = 2$) and has refined to $R = 0.029$ and $R_w = 0.039$ with 2395 observations and 196 parameters varied.

Introduction

Scheme I



In our studies of the preparation and reactivity of hexacarbonyldiiron complexes containing bridging organosulfur ligands,[1] we had occasion to prepare the methylenedithio-bridged complex 1 (Scheme I).[2] This compound is an inorganic analogue of an organic dithiane, **3**. The latter class of compounds has H_2CS_2 protons which are relatively acidic due to the electronic effects of the two adjacent sulfur atoms and hence such compounds are easily deprotonated by strong bases. This provides the basis for

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[1] (a) Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9. (b) Seyferth, D.; Kiwan, A. M. *J. Organomet. Chem.* **1985**, *286*, 219. (c) Seyferth, D.; Kiwan, A. M.; Sinn, E. *J. Organomet. Chem.* **1985**, *218*, 111. (d) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (e) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1984**, *3*, 1981. (f) Mak, T. C. W.; Book, L.; Chieh, C.; Gallagher, M. K.; Song, L.-C.; Seyferth, D. *Inorg. Chim. Acta* **1983**, *73*, 159. (g) Seyferth, D.; Hames, B. W. *Inorg. Chim. Acta* **1983**, *77*, L1. (h) Seyferth, D.; Womack, G. B.; Song, L.-C. *Organometallics* **1983**, *2*, 776. (i) Seyferth, D.; Womack, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6839. (j) Chieh, C.; Seyferth, D.; Song, L.-C. *Organometallics* **1982**, *1*, 473. (k) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (l) Seyferth, D.; Song, L.-C.; Henderson, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5103. (m) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218*, C34. (n) Seyferth, D.; Henderson, R. S.; Fackler, J. P., Jr.; Mazany, A. *J. Organomet. Chem.* **1981**, *213*, C21.

[2] $(\mu\text{-}SCH_2S)Fe_2(CO)_6$ has been prepared earlier by the reaction of $Fe_2(CO)_9$ with 1,3-dithia-5-cycloheptene, and its structure has been determined by X-ray diffraction: Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

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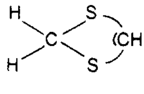
the utility of dithianes in the "acyl anion equivalent" approach to indirect nucleophilic acylation of organic electrophiles.[3] The methylene protons in **1** should be even more acidic than those in **3** since each sulfur atom in **1** donates an electron pair to an iron atom, thus generating a strong partial positive charge on the sulfur atoms. With these considerations in mind, we embarked on what was meant to be a brief study of the deprotonation of **1** and of the reactivity of the resulting organolithium reagent **4**. As the next section will show, the results were less straightforward and more interesting than we had anticipated.



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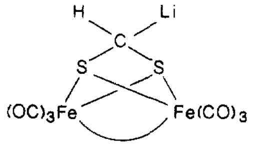
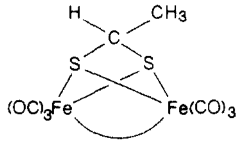


4

Results and Discussion

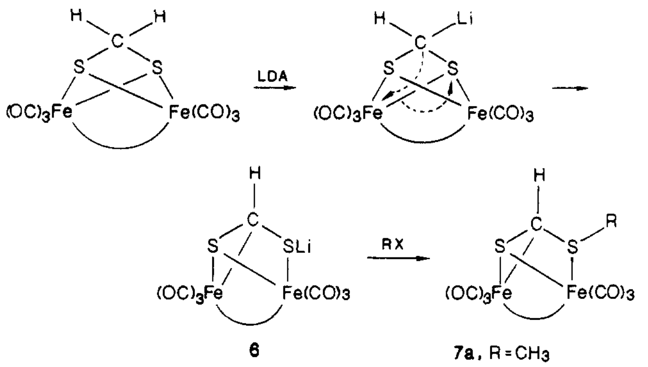
The addition of a slight excess of lithium diisopropylamide (LDA) to **1** in THF at −78 °C resulted in a color change from red to green. To this solution then was added iodomethane, and, as the mixture was allowed to warm to room temperature, it became red again. Removal of solvent, followed by filtration chromatography, gave a dark red oil in 78% yield. The expected product was **5**, and the combustion analysis and electron-impact mass spectrum of the red oil obtained in this reaction were in agreement with this formula. However, the proton NMR spectrum of the red oil showed no spin–spin coupling between the methine and the methyl group protons, as would be expected for **5**. Instead, the ^{1}H NMR spectrum consisted of two sharp singlets at δ 3.89 (1 H) and 2.33 (3 H). The proton-coupled ^{13}C NMR spectrum of the red oil confirmed the presence of the methyl and methine carbon atoms.



5

On the basis of this information, the product of the 1/LDA/CH_3I reaction could not be **5** but did appear to be an isomer of **5**. The observed green color of the deprotonated intermediate formed by the action of LDA on **1** suggested that a sulfur-centered anion might be involved rather than **4** since this is the characteristic color of THF solutions of sulfur-centered anions derived from (μ-S_2)-$Fe_2(CO)_6$.[1] Scheme II depicts a reaction course which involves such intermediates and provides an isomeric alternative to **5**. This proposed mechanism involves the expected deprotonation as the first step but is followed by an intramolecular anionic rearrangement which involves nucleophilic attack by the initially formed carbanion at one of the iron atoms. The result of the latter process is displacement of an electron pair onto a sulfur atom, i.e., formation of a sulfur-centered anion, **6**. Reaction of **6** with iodomethane would give **7a** in which the methyl group has been introduced at the sulfur atom. The ^{1}H NMR spectrum of **7a** would, of course, show no spin–spin coupling between the methine and methyl protons. Compound **7a** could be viewed as a complex between the $Fe_2(CO)_6$ unit and methyl dithioformate, HCS_2CH_3, acting as a six-electron donor ligand. Bonding to the Fe atoms would involve the π electrons and a sulfur lone pair of the C=S unit and a lone pair of the thiomethoxy group of the dithio ester. Such complexes of dithio esters of type RC(S)SR′ (**8**) had been prepared earlier by Patin and his co-workers[4] by reaction of the thio ester with $Fe_2(CO)_9$. Thus the conversions shown in Scheme II did not seem unreasonable.

Scheme II

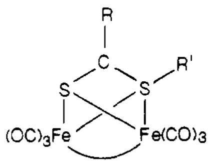


6

7a, R = CH_3
b, R = C_2H_5
c, R = CH_2=$CHCH_2$
d, R = $PhCH_2$

Since the product of the 1/LDA/CH_3I reaction was a red oil and hence not amenable to study by X-ray crystallography, other 1/LDA/RX reactions were carried out. The ethyl derivative also was a dark red oil, as was the allyl derivative. On the other hand, the benzyl and the acetylmethyl derivatives were red, crystalline solids. All of these complexes had proton NMR spectra which showed a singlet assignable to the methine proton, and thus they all had the same structural framework.

The acetylmethyl derivative was chosen for an X-ray structural study since the expected product from C-alkylation of the initially formed anion by $CH_3C(O)CH_2Br$ (**9**), mp 90–91 °C, had been prepared previously in these laboratories by the piperidine-induced reaction of (μ-$HS)_2Fe_2(CO)_6$ with HC≡CC(O)CH_3,[11] and its structure had been unambiguously determined in an X-ray diffraction study.[5] (The proton NMR spectrum of **9**, it may be noted, did display spin–spin coupling (J = 6.5 Hz) between the methine and methylene protons.)



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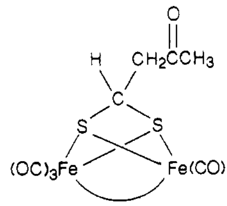

9

The product of the 1/LDA/bromoacetone reaction, mp 80–82 °C, obviously was not **9** but was shown by combustion analysis and mass spectroscopy to have the same elemental composition as **9**. The proton NMR spectrum of the product showed, in addition to the methine proton singlet, the methylene protons of the acetylmethyl group as an AX quartet. That the product is a dithioformate ester/$Fe_2(CO)_6$ complex, **10**, is suggested by the diaste-

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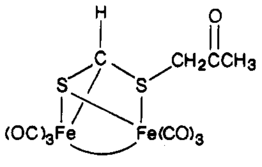
[3] Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1969**, *17*; **1977**, 357.

[4] Benoit, A.; La Marouille, J.-Y.; Mahe, C.; Patin, H. *J. Organomet. Chem.* 1981, *218*, C67.

[5] (a) Seyferth, D.; Womack, G. B.; Song, L.-C.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 928. (b) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 0000.

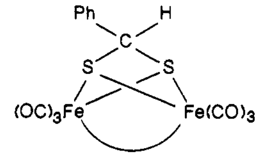


10

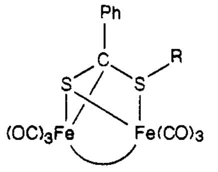
reotopic nature of the CH_2 protons which would be induced by the chiral formate carbon of **10**. This structure was confirmed by an X-ray diffraction study (Figure 1, see below). It would appear that anion **4** is not stable and undergoes the rearrangement postulated in Scheme II.

Once it had been established that the products of the $(\mu\text{-}SCH_2S)Fe_2(CO)_6/LDA/RX$ reactions were alkyl dithioformate ester/$Fe_2(CO)_6$ complexes of type **7**, a simple, alternate route to such compounds was devised (Scheme III).[1e] Prepared by this "one-pot" procedure were complexes **7a–c**. The spectroscopic properties of these complexes were in complete agreement with those of the methyl, ethyl, and allyl derivatives as obtained by the anionic rearrangement route.

The anion obtained by LDA deprotonation of complex **11** (prepared by reaction of α,α-toluenedithiol with $Fe_2(CO)_9$) underwent the same type of rearrangement, despite the fact that a more stabilized benzylic carbanion was involved. Alkylation of the intermediate anion with CH_3I and C_2H_5I gave products of type **12**. The proton NMR spectrum of **12** ($R = C_2H_5$) showed the SCH_2 proton signal as a complex multiplet resulting from the chirality of the molecule which renders them diastereotopic.



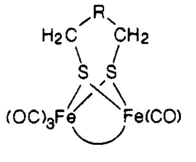
11



12

The ^{13}C NMR spectra of complexes of type **7** and **12** usually showed two signals in the C≡O ligand region, one sharp and the other broad. This is the result of two independent fluxional $Fe(CO)_3$ units between which there is no scrambling of CO ligands.[6] The two fluxional processes apparently occur at different rates, the slower one resulting in a broad signal at room temperature.

It was of interest to see if this deprotonation/rearrangement chemistry could be extended to other α,ω-dithioalkylene-bridged $Fe_2(CO)_6$ complexes **13**. In order to study this question, complexes **14**–**16** were prepared by reactions of the appropriate α,ω-dithiol with $Fe_3(CO)_{12}$, a route developed by Winter, Zsolnai, and Huttner.[7] In the case of these compounds the CH_2 groups are activated toward deprotonation by only one adjacent sulfur atom. However, $i\text{-}Pr_2NLi$ does deprotonate them, although not as effectively, in THF at −78 °C. In the case of complex **14**, β-elimination (Scheme IV) was faster than the anionic rearrangement observed with **1**, and the product, obtained in 70% yield after addition of CH_3I to the green reaction mixture, was the vinyl-substituted complex **17**. An authentic sample of **17** had been prepared earlier in these laboratories by reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ with $CH_2{=}CHMgBr$ followed by addition of CH_3I.[1a]



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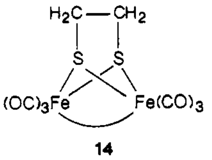

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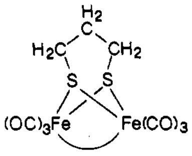

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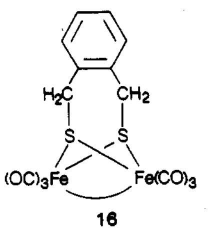

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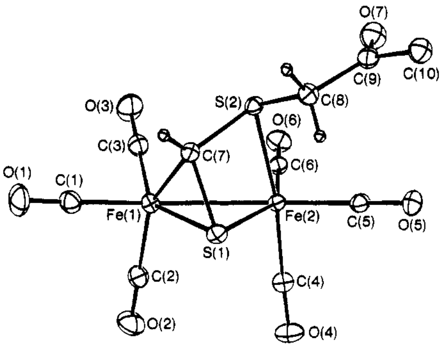
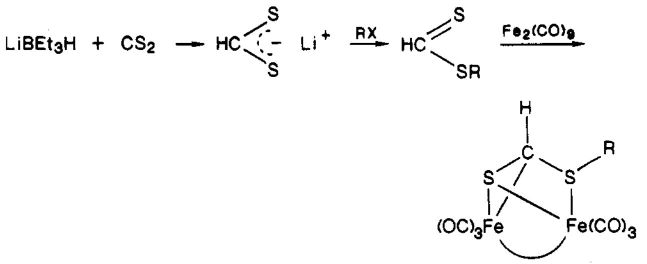


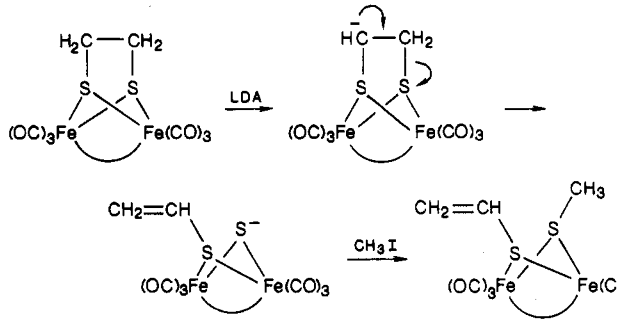
Figure 1. Perspective drawing of $(\mu\text{-}CH_3C(O)CH_2SCHS)Fe_2(CO)_6$ (**10**) showing the numbering scheme. Thermal ellipsoids (20%) are shown except for hydrogens that are artificially small.

Scheme III



7a, $R = CH_3$
b, $R = C_2H_5$
c, $R = CH_2{=}CHCH_2$

Scheme IV



17

The anion obtained by deprotonation of **15** did undergo a rearrangement of the type shown in Scheme II. Again, a red-to-green color change was noted on treatment of **15** with LDA in THF at −78 °C. Addition of CH_3I gave an orange-red solid in 70% yield. Combustion analysis and the electron-impact mass spectrum were in agreement with the expected formula $C_{10}H_8O_6S_2Fe_2$. The decoupled and

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[6] Kruger, G. J.; Linford, L.; Raubenheimer, H. G.; Chalmers, A. A. *J. Organomet. Chem.* **1984**, *262*, 69.

[7] Winter, A.; Zsolnai, L.; Huttner, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1430.

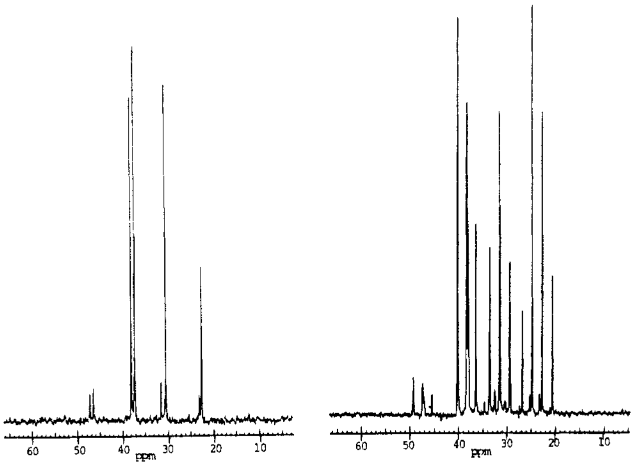
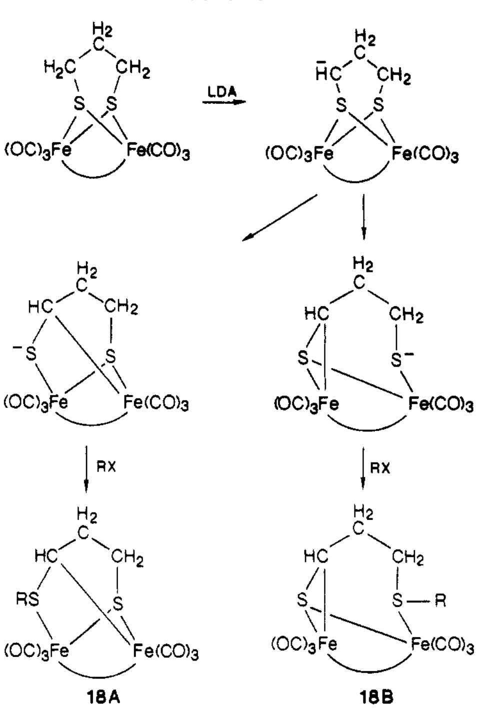


Figure 2. Carbon-13 NMR spectra of **18A**/**18B**. Only the alkyl region (5–65 ppm) is shown. The proton-decoupled spectrum is shown on the left and the normal spectrum on the right.

Scheme V



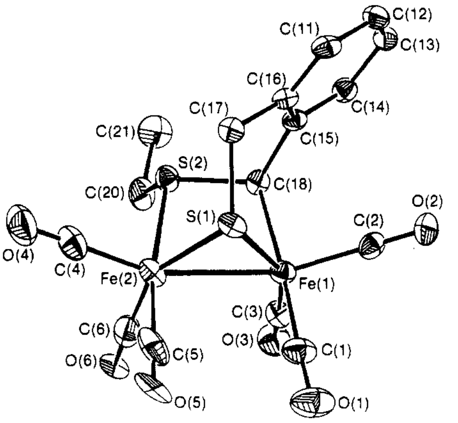
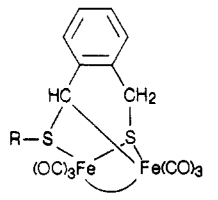


Figure 3. Perspective drawing of (μ-$SCH_2C_6H_4CHSC_2H_5$)$Fe_2(CO)_6$ (**19**). Thermal ellipsoids (50%) are shown.

the gated decoupled ^{13}C NMR spectra of the product supported its formulation as **18A** (Scheme V), the product of deprotonation/rearrangement/methylation. The observed spectrum showed four resonances in the alkyl carbon region with the methyl resonance at δ_C 22.85 and the two CH_2 resonances at δ_C 30.63 and 37.42, while the methine signal was at δ_C 38.22. Unexpectedly, however, another set of resonances was observed in this region, which must be due to the presence of another isomer. The isomer ratio was 10:1 by NMR integration (Figure 2), with the major isomer being the one whose ^{13}C NMR spectrum is described above. As Scheme V shows, the anionic rearrangement of the trimethylene-bridged complex **15** could lead to two different sulfur-centered anions, depending on which of the two Fe–S bonds is broken. Then methylation would give two different products, **18A** and **18B**. In the former the methine carbon atom would be at the bridgehead of a four- and a five-membered ring system and in the latter the methine carbon atom at the bridgehead of a three- and a six-membered ring system. The smaller ring size in **18B** should result in a downfield shift of the methine carbon resonance, as is observed for the less abundant isomer in the mixture ^{13}C NMR spectrum (δ_C 47.33 vs. δ_C 38.22). The two isomers cannot be separated by column chromatography or by fractional crystallization, so a conclusive structure determination has not been possible. Other homologues of **18A** were prepared by treatment of **15**/LDA reaction mixtures with iodoethane, allyl chloride, and benzyl chloride. In each case, the ^{13}C NMR spectrum of the product showed the presence of only one isomer, which, on the basis of the chemical shift of the methine carbon atom, δ_C 38.34, 38.06, and 38.87, respectively, must have a structure analogous to that of **18A**.

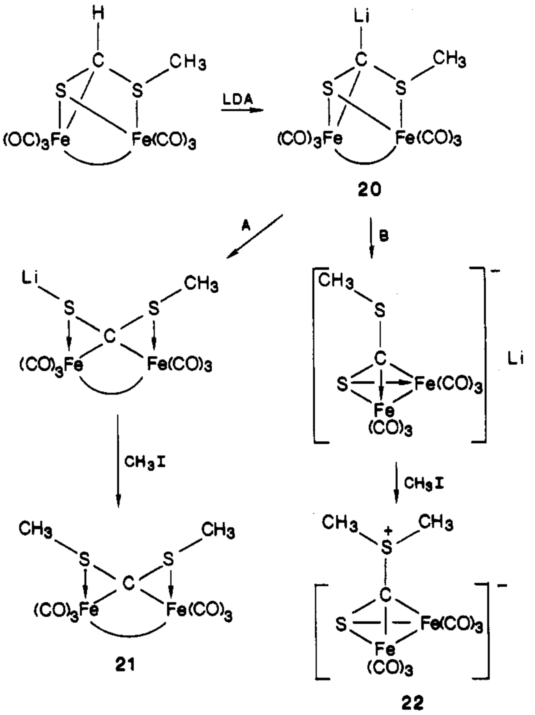
Deprotonation of (μ-*o*-xylylene-α,α'-dithiolato)bis(tricarbonyliron), **16**, with LDA proceeded with rearrangement, although the color of the reaction mixture only deepened to dark red-brown. Treatment with iodomethane gave a 50% yield of an orange-red solid. The corresponding ethyl, allyl, and benzyl derivatives also were prepared. NMR spectroscopic data, especially the methine carbon ^{13}C resonances, were in agreement with structure **19** for the alkylated products. Only a single isomer was present in each case. (In the other isomer the methine carbon atom would be at the bridgehead of three- and seven-membered rings.) Confirmation of this structural assignment was provided by an X-ray diffraction study of **19** (R = CH_3) (Figure 3).



19

The dithioformate ester/$Fe_2(CO)_6$ complexes **7** also contain a C–H bond that should be relatively acidic due to the electronic effects of the two adjacent sulfur atoms. When the procedure used to deprotonate **1** was applied to **7a**, the reaction mixture darkened to red-brown. Treatment with iodomethane introduced another CH_3 group, giving an orange solid in 77% yield whose combustion analysis and mass spectrum supported the molecular formula $(CH_3)_2CS_2Fe_2(CO)_6$. If one assumes that deprotonation to give **20** is followed by an anionic rearrangement, i.e., by attack of the carbanion at iron, then two different anions could be formed, depending on which Fe–S bond is lost in the process (Scheme VI). Path A would give a bridging dithiocarbene complex, **21**, in which the two thiomethoxy groups are coordinated to the two iron atoms, a structure for which there is no precedent.

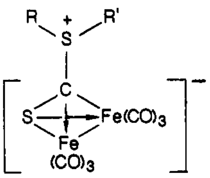
Scheme VI



Path B would give an equally unprecedented structure, 22, a dimethyl sulfide adduct of the $CS[Fe(CO)_3]_2$ cluster, which may be viewed as a novel sulfur ylide in which the negative charge is delocalized in the $CSFe_2$ cluster.

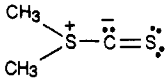
Both in 21 and in 22 the methyl groups are equivalent, and, as expected, the proton and ^{13}C NMR spectra of the product showed equivalent methyl groups. (In any case, the product was *not* that resulting from an unrearranged anion, the $Fe_2(CO)_6$ complex of methyl dithioacetate 8 ($R = R' = CH_3$.)

The electron-impact mass spectrum of the $(CH_3)_2SCSFe_2(CO)_6$ product showed, inter alia, fragment ions of type $[M^+ - nCO - Me_2S]$ ($n = 4, 5$), as well as $[Fe_2SC]^+$, which suggests, but does not require, that both methyl substituents are on the same sulfur atom. This speaks in favor of structure 22. When the intermediate anion was treated with allyl bromide, an orange crystalline product, $CH_3(CH_2{=}CHCH_2)CS_2Fe_2(CO)_6$, was obtained. Its proton NMR spectrum showed its allylic protons to be diastereotopic. This would be expected to be the case if a $CH_3(CH_2{=}CHCH_2)S$ ligand was bonded to a $CSFe_2$ tetrahedral cluster as in **23a**.



23a, $R = CH_3$, $R' = CH_2{=}CHCH_2$
b, $R = CH_3$, $R' = C_2H_5$
c, $R = C_2H_5$, $R' = C_2H_5$

Unambiguous proof that the products of these methyl dithioformate/$Fe_2(CO)_6$ complex/LDA/RX reactions are of structure 22 was provided by an X-ray diffraction study of complex 22 itself, which clearly showed the presence of a $(CH_3)_2S$ group attached to the carbon atom of a $CSFe_2$ cluster (see below). Thus, in these complexes we are dealing with an $Fe_2(CO)_6$ unit complexed by a μ,η^2-thiocarbonyl bridging ligand, 24. To achieve an 18-electron configuration for each iron atom, this thiocarbonyl ligand must function as a six-electron donor. As a sulfonium ylide with an available electron pair on the carbon atom, 24 can donate the required six electrons.



24

Other reactions were carried out in which the deprotonated ethyl dithioformate/$Fe_2(CO)_6$ complex was treated with iodomethane and iodoethane. Orange complexes of type 23 were obtained. In each case, the ^{13}C NMR spectrum of the product showed a resonance assignable to the bridging thiocarbonyl carbon atom at δ_C 102.1 (**23b**) and 99.9 (**23c**) (vs. δ_C 106.7 for 22).

In conclusion, the rearrangement reported here which occurs on deprotonation of a carbon atom α to a sulfur of $S(CH_2)_nS$ ($n = 1, 3$), $SCH_2(o\text{-}C_6H_4)CH_2S$ and $-SC(H)(R)S-$ bridging ligands appears to be a general process for which other examples may yet be found. This rearrangement is more general still, since it is applicable as well to $Fe_2(CO)_6$ complexes of the bridging phosphorus ligands which are analogous to these bridging sulfur ligands.[8]

Description of the Structures

The crystallographic analyses on compounds 10, 19, and 22 unambiguously confirm the unusual rearrangements that have occurred upon deprotonation of the dithiolato-bridged complexes followed by alkylation, as described in the previous section. A representation of compound 10, $(\mu\text{-}SCHSCH_2C(O)CH_3)Fe_2(CO)_6$, is presented in Figure 1, and bond lengths and angles for the compound appear in Tables V and VI. The structure of compound 10 is clearly no longer a simple sulfur-bonded butterfly species as was observed in the precursor 1[2] and related complexes;[5,9,10] instead one of the Fe–S interactions has been replaced by a bond between Fe(1) and C(7) of the original methylene group and a bond between S(2) and the propanone substituent, derived from bromoacetone. The resulting bridging $SC(H)SCH_2C(O)CH_3$ ligand functions as a six-electron donor to the two Fe nuclei giving each an 18-electron, pseudooctahedral geometry. The structure of compound 10 is very similar to that of $(\mu\text{-}CH_3SC(S)C_4H_3S)Fe_2(CO)_6$,[4] which was obtained directly by the reaction of the dithio ester with $Fe_2(CO)_9$, and also resembles the structure of $(\mu\text{-}SCOR)(\mu\text{-}SCH_3)Fe_2(CO)_6$[11] (R = 1-adamantanylmethanol), which was formed by the cleavage of an S–C bond in the *S*-alkyl xanthate precursor. In compound 10 three of the coordination sites of each metal are occupied by the carbonyl groups in a facial arrangement, one is occupied by the Fe–Fe bond and the remaining two are taken by the bridging dithio ester moiety as shown in Figure 1. The angles at both Fe nuclei involving the dithio ester group deviate considerably from the idealized octahedral values, primarily due to the strain imposed by the bridging group. This strain also results in a staggering[12] of the two $Fe(CO)_3$ moieties by approximately 14° as was observed in the previous dithio ester

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[8] Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1121 (note correction: *Organometallics* **1984**, *3*, 1933).

[9] Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

[10] Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1.

[11] Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J.-Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.

[12] When considering the staggering of the two $Fe(CO)_3$ units the torsion angle involving the carbonyls which lies almost opposite the Fe–Fe bond was not taken into account since this does not give an accurate indication of the twist.

Table I. Summary of Crystal Data and Details of Intensity Collection for Compounds 10, 19, and 22

	$(\mu\text{-}CH_3C(O)CH_2SCHS)Fe_2(CO)_6$ (10)	$(\mu\text{-}C_2H_5SCHC_6H_4CH_2S)Fe_2(CO)_6$ (19)	$(\mu\text{-}SCS(CH_3)_2)Fe_2(CO)_6$ (22)
fw	414.0	476.1	386.0
formula	$C_{10}H_6O_7S_2Fe_2$	$C_{16}H_{12}O_6S_2Fe_2$	$C_9H_6O_6S_2Fe_2$
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	2	4	2
cell param[a]			
a, Å	10.296 (2)	15.003 (2)	9.586 (1)
b, Å	11.306 (2)	7.530 (1)	10.276 (1)
c, Å	6.617 (1)	16.599 (2)	7.601 (1)
α, deg	100.45 (1)		92.18 (1)
β, deg	93.36 (2)	92.11 (1)	111.52 (1)
γ, deg	103.38 (1)		86.94 (1)
V, Å^3	732.9	1874.0	695.3
ρ(calcd), g/cm^3	1.88	1.69	1.84
radiatn	Mo Kα (λ = 0.71067 Å), graphite monochromated	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated
2θ limits, deg	2.0–50.0	3.0–55.0	2.0–46.0
diffractometer	Enraf-Nonius CAD-4F	Nicolet P3F	CAD-4F
μ, cm^{-1}	22.8	17.9	23.9
range in transmissn factors	b	0.514–0.666	0.681–0.769
unique data collected	2818 ($\pm h,\pm k,-l$)	4963 ($h,k,\pm l$)	2924 ($\pm h,\pm k,-l$)
no. of observn ($F_o^2 \geq 3\sigma(F_o^2)$)	2073	2004	2395
no. of param varied	194	223	196
R^b	0.042	0.053	0.029
R_w	0.055	0.055	0.039
error in observn unit weight	1.77	1.17	1.33

[a] Data collection was carried out at ambient temperature for all compounds. [b] No absorption correction was applied to compound 10. [c] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Temperature Factors for Compound 10

atom	x	y	z	B, Å^2
Fe(1)	3062.9 (6)	2107.7 (6)	642 (1)	2.96[a]
Fe(2)	1370.5 (6)	3424.8 (5)	1939 (1)	2.56
S(1)	2777 (1)	2722 (1)	−566 (2)	3.22
S(2)	3383 (1)	4501 (1)	3823 (2)	2.95
O(1)	5350 (4)	1318 (4)	−1111 (8)	6.72
O(2)	1022 (4)	45 (3)	−1923 (7)	5.82
O(3)	3251 (5)	1124 (4)	4409 (7)	5.86
O(4)	−978 (4)	1916 (4)	−863 (6)	5.14
O(5)	119 (4)	5529 (3)	2684 (7)	5.00
O(6)	553 (4)	2108 (3)	5282 (6)	4.30
O(7)	2630 (5)	6268 (4)	6899 (7)	6.18
C(1)	4456 (6)	1629 (5)	−448 (9)	4.23
C(2)	1801 (5)	831 (4)	−922 (9)	3.87
C(3)	3171 (5)	1510 (5)	2942 (9)	3.79
C(4)	−41 (5)	2491 (4)	196 (8)	3.46
C(5)	599 (5)	4707 (4)	2399 (8)	3.35
C(6)	866 (4)	2616 (4)	3976 (8)	3.08
C(7)	4013 (4)	3900 (4)	1519 (8)	3.06
C(8)	3648 (5)	6152 (4)	3764 (8)	3.53
C(9)	3077 (5)	6820 (5)	5574 (9)	4.10
C(10)	3104 (6)	8170 (5)	5599 (11)	5.29
H(7)[b]	4956 (44)	4226 (37)	1324 (72)	2.9 (9)
H(8a)[c]	4593	6522	3820	4.5
H(8b)	3226	6246	2492	4.5

[a] Thermal parameters for non-hydrogen atoms are equivalent isotropic B's. [b] Atom refined isotropically. [c] Hydrogen atoms H(8a) and H(8b) attached to C(8) were not refined.

complex,[4] where a twist of 19.7° was observed. In most bridged $Fe_2(CO)_6$ complexes the $Fe(CO)_3$ moieties are essentially eclipsed (see, for example, compound **22**).

Within the bridging dithio ester group the S(1)–C(7) and S(2)–C(7) bonds (1.771 (5) and 1.775 (5) Å) appear to display slight multiple-bond character, being much shorter than the S(2)–C(8) distance of 1.831 (4) Å, which represents a normal single bond.[13] The Fe–S bonds appear normal, although there is a significant variation in the values observed, presumably reflecting the strain within the complex (vide infra). A similar trend in Fe–S distances and comparable S–C distances was obtained in $(\mu\text{-}CH_3SC(S)C_4H_3S)Fe_2(CO)_6$.[4] The Fe(1)–C(7) distance of 1.998 (4) Å is normal and compares well with the values observed in analogous species.[1e,4,11,14] Similarly the Fe(1)–Fe(2) distance of 2.627 (1) Å is very close to the values observed in the above dithio ester and xanthate products[4,11] and is longer than such distances in the butterfly and related species;[2,5,9,10] this is probably a consequence of the two-atom-bridging connection in the former group of complexes, forcing the metals apart somewhat. The strain of this bridging group is also shown in the angles at S(1), S(2), and C(7) where several of these values are much smaller than the idealized tetrahedral value. Within the propanone fragment the parameters are normal. It should also be noted that C(7) is now a chiral center.

The structure of compound **19**, $(\mu\text{-}SCH_2C_6H_4CHSC_2H_5)Fe_2(CO)_6$, is shown in Figure 3, with relevant parameters given in Tables VII and VIII. As was the case in compound **10**, deprotonation of a methylene group and alkylation of one sulfur atom has resulted in replacement of an Fe–S bond by the Fe(1)–C(18) and S(2)–C(20) bonds, yielding a bridging group which is rather analogous to that in **10** and which again functions as a six-electron donor. Although compounds **10** and **19** are therefore structurally analogous, there are differences which result primarily due to replacement of the one-carbon bridge between the two sulfurs in **10** by four carbons in **19**. Consequently, the bridging group in **19** appears to be less strained than that in **10**, resulting in angles at S(2) and C(18) which more closely approach the idealized values than the analogous angles in compound **10**. Compound **19** is very closely related to the phosphido-bridged species $(\mu\text{-}C_6H_5PCH_2C_6H_4CHP(CH_3)C_6H_5)Fe_2(CO)_6$,[8] which was prepared in an analogous manner, and many of the structural parameters within the two complexes are

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(13) MacGillavry, C. H., Rieck, G. D., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. III, Table 4.2.6.

(14) Wormsbächer, D.; Edelmann, F.; Behrens, U. *Chem. Ber.* **1981**, *114*, 153.

Table III. Atomic Coordinates (×10^4) and Temperature Factors for Compound 19

atom	x	y	z	B, Å^2
Fe(1)	1779 (1)	5240 (1)	5125 (1)	3.08[a]
Fe(2)	2261 (1)	7682 (2)	4105 (1)	3.95
S(1)	1011 (1)	7729 (3)	4832 (1)	3.47
S(2)	3010 (1)	8461 (3)	5279 (1)	3.40
O(1)	737 (4)	3091 (10)	3947 (4)	7.34
C(1)	1133 (5)	3986 (12)	4393 (5)	4.90
O(2)	928 (4)	3551 (8)	6497 (4)	5.13
C(2)	1249 (5)	4193 (10)	5974 (5)	3.63
C(3)	2739 (5)	3891 (10)	5030 (4)	3.63
O(3)	3368 (4)	3063 (8)	4971 (3)	5.21
C(4)	2363 (6)	9859 (13)	3671 (5)	5.45
O(4)	2423 (5)	11224 (9)	3387 (4)	7.97
C(5)	1514 (6)	6912 (15)	3246 (5)	6.55
O(5)	1078 (5)	6513 (15)	2750 (4)	5.61
C(6)	3246 (6)	6467 (12)	3691 (5)	5.45
O(6)	3789 (5)	5716 (11)	3445 (4)	3.71
C(11)	755 (3)	9041 (6)	7117 (3)	3.63
C(12)	947 (3)	8349 (6)	7883 (3)	4.11
C(13)	1679 (3)	7227 (6)	8011 (3)	3.71
C(14)	2218 (3)	6797 (6)	7372 (3)	3.24
C(15)	2025 (3)	7490 (6)	6606 (3)	2.76
C(16)	1294 (3)	8612 (6)	6478 (3)	2.92
C(17)	1080 (5)	9379 (9)	5659 (4)	3.24
C(18)	2556 (4)	6784 (9)	5914 (4)	2.84
C(20)	4183 (4)	7868 (12)	5292 (5)	4.34
C(21)	4653 (5)	8333 (12)	6092 (5)	5.53
H(11)	252	9812	7030	3.4[b]
H(12)	577	8645	8324	3.4
H(13)	1812	6751	8539	3.4
H(14)	2722	6025	7461	3.4
H(17a)	516	9976	5676	3.3 (10)[c]
H(17b)	1537	10222	5539	3.3 (10)
H(18)	3024	6132	6191	2.1 (13)
H(20a)	4465	8499	4868	4.7 (12)
H(20b)	4234	6614	5202	4.7 (12)
H(21a)	5270	7995	6078	6.3 (12)
H(21b)	4375	7709	6520	6.3 (12)
H(21c)	4612	9589	6184	6.3 (12)

[a] Thermal parameters for non-hydrogen atoms are equivalent isotropic B's. [b] Hydrogen atoms H(11), H(12), H(13), and H(14) were not refined. [c] Hydrogen atoms H(17a)–H(21c) had their isotropic thermal parameters refined.

Table IV. Atomic Coordinates (×10^4) and Temperature Factors for Compound 22

atom	x	y	z	B, Å^2
Fe(1)	−3040.4 (4)	2911.8 (3)	2939.6 (5)	2.85[a]
Fe(2)	−2426.8 (4)	1891.0 (3)	194.9 (5)	2.67
S(1)	582.8 (7)	1795.7 (6)	4288.5 (9)	3.09
S(2)	−1608.2 (7)	3805.3 (6)	1579.6 (9)	3.08
O(1)	−6119 (3)	3859 (3)	783 (4)	6.50
O(2)	−2431 (4)	4500 (3)	6384 (4)	6.94
O(3)	−3800 (3)	542 (2)	4291 (4)	6.03
O(4)	−5139 (3)	2715 (3)	−2975 (3)	5.99
O(5)	−3210 (3)	−750 (2)	629 (4)	5.80
O(6)	−498 (3)	−1168 (2)	−1919 (3)	5.00
C(1)	−4934 (4)	3512 (3)	1622 (4)	4.14
C(2)	−2668 (4)	3879 (3)	5039 (5)	4.30
C(3)	−3519 (3)	1483 (3)	3760 (4)	3.83
C(4)	−4091 (3)	2370 (3)	−1756 (4)	3.84
C(5)	−2921 (3)	293 (3)	446 (4)	3.65
C(6)	−1241 (3)	1465 (3)	−1082 (4)	3.35
C(7)	−1165 (3)	2334 (2)	2740 (3)	2.65
C(8)	1153 (4)	3060 (4)	6063 (5)	4.20
C(9)	1840 (4)	2014 (4)	3081 (5)	4.12
H(8a)[b]	1247	2720	7248	5.2
H(8b)	2090	3358	6128	5.2
H(8c)	419	3755	5738	5.2
H(9a)	2828	1759	3870	5.1
H(9b)	1540	1502	1947	5.1
H(9c)	1802	2912	2778	5.1

[a] Thermal parameters for non-hydrogen atoms are equivalent isotropic B's. [b] Hydrogen atoms were not refined. These are numbered according to their attached carbon atom.

Table V. Bond Lengths (Å) for Compound 10

Fe(1)–Fe(2)	2.627 (1)	S(2)–C(7)	1.775 (5)
Fe(1)–S(1)	2.193 (1)	S(2)–C(8)	1.831 (4)
Fe(1)–C(1)	1.791 (6)	C(7)–H(7)	0.98 (4)
Fe(1)–C(2)	1.810 (5)	C(8)–C(9)	1.520 (7)
Fe(1)–C(3)	1.781 (6)	C(9)–C(10)	1.517 (7)
Fe(1)–C(7)	1.998 (4)	C(9)–O(7)	1.217 (7)
Fe(2)–S(1)	2.284 (1)	C(1)–O(1)	1.143 (7)
Fe(2)–S(2)	2.304 (1)	C(2)–O(2)	1.126 (6)
Fe(2)–C(4)	1.791 (5)	C(3)–O(3)	1.141 (6)
Fe(2)–C(5)	1.796 (5)	C(4)–O(4)	1.144 (6)
Fe(2)–C(6)	1.798 (5)	C(5)–O(5)	1.141 (6)
S(1)–C(7)	1.771 (5)	C(6)–O(6)	1.144 (6)

Table VI. Angles (deg) for Compound 10

(a) Bond Angles			
Fe(2)–Fe(1)–S(1)	55.69 (4)	S(2)–Fe(2)–C(5)	94.8 (2)
Fe(2)–Fe(1)–C(1)	163.1 (2)	S(2)–Fe(2)–C(6)	91.9 (1)
Fe(2)–Fe(1)–C(2)	95.3 (2)	C(4)–Fe(2)–C(5)	91.8 (2)
Fe(2)–Fe(1)–C(3)	94.4 (2)	C(4)–Fe(2)–C(6)	92.2 (2)
Fe(2)–Fe(1)–C(7)	69.6 (1)	C(5)–Fe(2)–C(6)	103.0 (2)
S(1)–Fe(1)–C(1)	108.7 (2)	Fe(1)–S(1)–Fe(2)	71.84 (4)
S(1)–Fe(1)–C(2)	103.4 (2)	Fe(1)–S(1)–C(7)	59.4 (1)
S(1)–Fe(1)–C(3)	143.6 (2)	Fe(2)–S(1)–C(7)	82.0 (2)
S(1)–Fe(1)–C(7)	49.7 (1)	Fe(2)–S(2)–C(7)	81.4 (1)
C(1)–Fe(1)–C(2)	94.9 (2)	Fe(2)–S(2)–C(8)	109.2 (2)
C(1)–Fe(1)–C(3)	97.1 (2)	C(7)–S(2)–C(8)	103.0 (2)
C(1)–Fe(1)–C(7)	95.6 (2)	Fe(1)–C(7)–S(1)	70.9 (2)
C(2)–Fe(1)–C(3)	99.2 (2)	Fe(1)–C(7)–S(2)	107.8 (2)
C(2)–Fe(1)–C(7)	153.1 (2)	S(1)–C(7)–S(2)	107.8 (2)
C(3)–Fe(1)–C(7)	103.9 (2)	S(2)–C(8)–C(9)	110.8 (4)
Fe(1)–Fe(2)–S(1)	52.46 (4)	C(8)–C(9)–C(10)	116.3 (5)
Fe(1)–Fe(2)–S(2)	76.10 (4)	C(8)–C(9)–O(7)	119.9 (5)
Fe(1)–Fe(2)–C(4)	95.8 (2)	O(7)–C(9)–C(10)	123.7 (5)
Fe(1)–Fe(2)–C(5)	159.7 (2)	Fe(1)–C(1)–O(1)	178.8 (5)
Fe(1)–Fe(2)–C(6)	95.5 (1)	Fe(1)–C(2)–O(2)	178.8 (5)
S(1)–Fe(2)–S(2)	77.26 (5)	Fe(1)–C(3)–O(3)	179.4 (5)
S(1)–Fe(2)–C(4)	95.2 (2)	Fe(2)–C(4)–O(4)	177.0 (5)
S(1)–Fe(2)–C(5)	108.1 (2)	Fe(2)–C(5)–O(5)	179.3 (5)
S(1)–Fe(2)–C(6)	147.6 (1)	Fe(2)–C(6)–O(6)	179.5 (4)
S(2)–Fe(2)–C(4)	171.2 (2)		
(b) Torsion Angles			
C(1)–Fe(1)–Fe(2)–C(5)	5.3 (8)		
C(2)–Fe(1)–Fe(2)–C(4)	−10.5 (2)		
C(3)–Fe(1)–Fe(2)–C(6)	−17.4 (2)		

Table VII. Bond Lengths (Å) for Compound 19

Fe(1)–Fe(2)	2.620 (2)	Fe(1)–S(1)	2.244 (2)
Fe(1)–C(1)	1.795 (9)	Fe(1)–C(2)	1.822 (8)
Fe(1)–C(3)	1.775 (7)	Fe(1)–C(18)	2.077 (7)
Fe(2)–S(1)	2.268 (2)	Fe(2)–S(2)	2.290 (2)
Fe(2)–C(4)	1.800 (9)	Fe(2)–C(5)	1.873 (9)
Fe(2)–C(6)	1.889 (9)	S(1)–C(17)	1.851 (7)
S(2)–C(18)	1.796 (7)	S(2)–C(20)	1.814 (7)
O(1)–C(1)	1.150 (11)	O(2)–C(2)	1.118 (10)
C(3)–O(3)	1.138 (9)	C(4)–O(4)	1.136 (12)
C(5)–O(5)	1.075 (11)	C(6)–O(6)	1.085 (12)
C(11)–C(12)	1.395	C(11)–C(16)	1.395
C(12)–C(13)	1.395	C(13)–C(14)	1.395
C(14)–C(15)	1.395	C(15)–C(16)	1.395
C(15)–C(18)	1.517 (8)	C(16)–C(17)	1.502 (8)
C(20)–C(21)	1.522 (11)		

rather similar. In addition, both of these species resemble the xanthate adduct[11] since cleavage of the S–C bond of the xanthate group relieved much of the strain in the molecule allowing a very similar alignment within the molecule. The slight relief in strain results in the two $Fe(CO)_3$ moieties being staggered[12] by only about 9°, somewhat less than that observed in **10**. The S–C distances involving the metalated carbon (C(18)) in compound **19** are larger than those in **10**, and all are close to the single-bonded extreme. Other parameters within the bridging group appear normal. As was the case in compound **10**, the metalated carbon center is chiral.

Table VIII. Bond Angles (deg) for Compound 19

Fe(2)–Fe(1)–S(1)	54.9 (1)	Fe(2)–Fe(1)–C(1)	94.9 (3)
S(1)–Fe(1)–C(1)	91.9 (3)	Fe(2)–Fe(1)–C(2)	160.4 (2)
S(1)–Fe(1)–C(2)	107.1 (2)	C(1)–Fe(1)–C(2)	93.3 (4)
Fe(2)–Fe(1)–C(3)	95.7 (2)	S(1)–Fe(1)–C(3)	150.5 (3)
C(1)–Fe(1)–C(3)	93.3 (4)	C(2)–Fe(1)–C(3)	101.5 (3)
Fe(2)–Fe(1)–C(18)	81.5 (2)	S(1)–Fe(1)–C(18)	86.6 (2)
C(1)–Fe(1)–C(18)	176.4 (3)	C(2)–Fe(1)–C(18)	90.3 (3)
C(3)–Fe(1)–C(18)	86.4 (3)	Fe(1)–Fe(2)–S(1)	54.1 (1)
Fe(1)–Fe(2)–S(2)	76.6 (1)	S(1)–Fe(2)–S(2)	86.2 (1)
Fe(1)–Fe(2)–C(4)	158.1 (3)	S(1)–Fe(2)–C(4)	106.5 (3)
S(2)–Fe(2)–C(4)	93.5 (3)	Fe(1)–Fe(2)–C(5)	95.9 (3)
S(1)–Fe(2)–C(5)	85.8 (3)	S(2)–Fe(2)–C(5)	171.3 (3)
C(4)–Fe(2)–C(5)	92.0 (4)	Fe(1)–Fe(2)–C(6)	97.7 (3)
S(1)–Fe(2)–C(6)	151.0 (3)	S(2)–Fe(2)–C(6)	93.9 (3)
C(4)–Fe(2)–C(6)	102.5 (4)	C(5)–Fe(2)–C(6)	91.5 (4)
Fe(1)–S(1)–Fe(2)	71.0 (1)	Fe(1)–S(1)–C(17)	112.7 (2)
Fe(2)–S(1)–C(17)	112.3 (2)	Fe(2)–S(2)–C(18)	97.7 (2)
Fe(2)–S(2)–C(20)	113.1 (3)	C(18)–S(2)–C(20)	102.1 (3)
Fe(1)–C(1)–O(1)	175.8 (8)	Fe(1)–C(2)–O(2)	179.6 (8)
Fe(1)–C(3)–O(3)	178.3 (7)	Fe(2)–C(4)–O(4)	179.1 (7)
Fe(2)–C(5)–O(5)	178.2 (11)	Fe(2)–C(6)–O(6)	177.2 (8)
C(12)–C(11)–C(16)	120.0	C(11)–C(12)–C(13)	120.0
C(12)–C(13)–C(14)	120.0	C(13)–C(14)–C(15)	120.0
C(14)–C(15)–C(16)	120.0	C(14)–C(15)–C(18)	117.6 (3)
C(16)–C(15)–C(18)	121.9 (3)	C(11)–C(16)–C(15)	120.0
C(11)–C(16)–C(17)	119.3 (3)	C(15)–C(16)–C(17)	120.7 (3)
S(1)–C(17)–C(16)	114.7 (4)	Fe(1)–C(18)–S(2)	103.9 (3)
Fe(1)–C(18)–C(15)	112.0 (4)	S(2)–C(18)–C(15)	114.8 (4)
S(2)–C(20)–C(21)	111.8 (5)		

Table IX. Bond Lengths (Å) for Compound 22

Fe(1)–Fe(2)	2.5429 (6)	S(1)–C(7)	1.732 (2)
Fe(1)–S(2)	2.2458 (8)	S(1)–C(8)	1.790 (3)
Fe(1)–C(1)	1.809 (3)	S(1)–C(9)	1.789 (3)
Fe(1)–C(2)	1.778 (3)	S(2)–C(7)	1.733 (2)
Fe(1)–C(3)	1.762 (3)	C(1)–O(1)	1.126 (4)
Fe(1)–C(7)	1.920 (2)	C(2)–O(2)	1.140 (4)
Fe(2)–S(2)	2.2348 (8)	C(3)–O(3)	1.144 (4)
Fe(2)–C(4)	1.795 (3)	C(4)–O(4)	1.139 (3)
Fe(2)–C(5)	1.770 (3)	C(5)–O(5)	1.147 (4)
Fe(2)–C(6)	1.775 (3)	C(6)–O(6)	1.140 (3)
Fe(2)–C(7)	1.921 (2)		

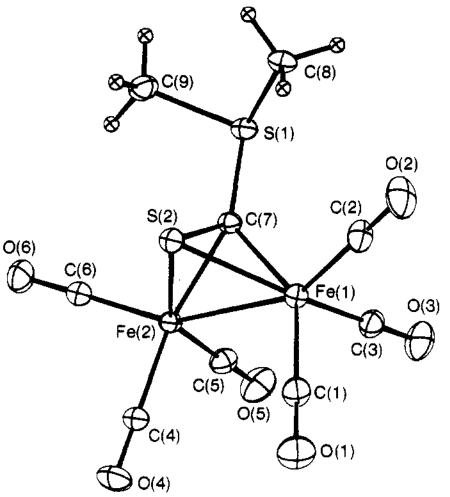

Figure 4. Perspective drawing of (μ-η^2-SCS(CH$_3$)$_2$)Fe$_2$(CO) (**22**). Thermal ellipsoids (20%) are shown.

Table X. Angles (deg) for Compound 22

(a) Bond Angles

Fe(2)–Fe(1)–S(2)	55.22 (2)	C(4)–Fe(2)–C(5)	98.2 (1)
Fe(2)–Fe(1)–C(1)	98.35 (9)	C(4)–Fe(2)–C(6)	98.7 (1)
Fe(2)–Fe(1)–C(2)	154.5 (1)	C(4)–Fe(2)–C(7)	144.4 (1)
Fe(2)–Fe(1)–C(3)	98.06 (9)	C(5)–Fe(2)–C(6)	97.3 (1)
Fe(2)–Fe(1)–C(7)	48.54 (7)	C(5)–Fe(2)–C(7)	101.9 (1)
S(2)–Fe(1)–C(1)	105.1 (1)	C(6)–Fe(2)–C(7)	107.6 (1)
S(2)–Fe(1)–C(2)	102.2 (1)	C(7)–S(1)–C(8)	104.7 (2)
S(2)–Fe(1)–C(3)	147.0 (1)	C(7)–S(1)–C(9)	105.2 (1)
S(2)–Fe(1)–C(7)	48.37 (7)	C(8)–S(1)–C(9)	100.4 (2)
C(1)–Fe(1)–C(2)	99.4 (1)	Fe(1)–S(2)–Fe(2)	69.16 (2)
C(1)–Fe(1)–C(3)	97.1 (1)	Fe(1)–S(2)–C(7)	55.95 (8)
C(1)–Fe(1)–C(7)	144.3 (1)	Fe(2)–S(2)–C(7)	56.20 (8)
C(2)–Fe(1)–C(3)	97.8 (1)	Fe(1)–C(7)–Fe(2)	82.92 (9)
C(2)–Fe(1)–C(7)	108.8 (1)	Fe(1)–C(7)–S(1)	136.1 (1)
C(3)–Fe(1)–C(7)	100.3 (1)	Fe(1)–C(7)–S(2)	75.68 (9)
Fe(1)–Fe(2)–S(2)	55.63 (2)	Fe(2)–C(7)–S(1)	135.3 (1)
Fe(1)–Fe(2)–C(4)	100.37 (9)	Fe(2)–C(7)–S(2)	75.24 (9)
Fe(1)–Fe(2)–C(5)	96.31 (9)	S(1)–C(7)–S(2)	126.8 (1)
Fe(1)–Fe(2)–C(6)	154.72 (8)	Fe(1)–C(1)–O(1)	178.4 (3)
Fe(1)–Fe(2)–C(7)	48.54 (7)	Fe(1)–C(2)–O(2)	179.9 (3)
S(2)–Fe(2)–C(4)	102.3 (1)	Fe(1)–C(3)–O(3)	178.4 (3)
S(2)–Fe(2)–C(5)	147.64 (9)	Fe(2)–C(4)–O(4)	177.8 (3)
S(2)–Fe(2)–C(6)	103.98 (9)	Fe(2)–C(5)–O(5)	178.6 (3)
S(2)–Fe(2)–C(7)	48.56 (7)	Fe(2)–C(6)–O(6)	178.4 (3)

(b) Torsion Angles

C(1)–Fe(1)–Fe(2)–C(4)	4.7 (1)
C(2)–Fe(1)–Fe(2)–C(6)	9.3 (3)
C(3)–Fe(1)–Fe(2)–C(5)	3.6 (1)

Interestingly, the Fe–S distances (2.244 (2)–2.290 (2) Å) span a much narrower range than in **10**, and this may be an additional consequence of the relaxing of the strain within compound **19**. The Fe(1)–C(18) bond (2.077 (7) Å) in **19** appears normal. Although it is longer than those in other Fe$_2$S$_2$C complexes, it is still shorter than that observed (2.139 (3) Å) in (μ-C$_6$H$_5$PCH$_2$C$_6$H$_4$CHP(CH$_3$)C$_6$H$_5$)Fe$_2$(CO)$_6$.[8]

A diagram showing the structure of compound **22** is presented in Figure 4 with relevant parameters given in Tables IX and X. As this figure clearly shows, alkylation has occurred at the sulfur atom already having the methyl substituent, yielding a Me$_2$SCS bridging group. This group binds side-on to both metals in a symmetrical manner through the "free", non-alkylated C–S end of the ligand, such that this moiety lies perpendicular to the Fe–Fe bond (the angle between the Fe(1)–Fe(2) and S(2)–C(7) vectors is 90.28 (9)°). A very similar structure has been reported for the thioketene complex (C$_{10}$H$_{18}$CS)Fe$_2$(CO)$_6$.[15] As has been noted, the bridging group functions as a six-electron donor, even though it binds through only the two atoms. This bridging group is symmetrically bonded giving the molecule almost idealized C_s symmetry. Both Fe–C(7) distances (1.920 (2) and 1.921 (2) Å) and both Fe–S(2) distances (2.2458 (8) and 2.2348 (8) Å) clearly reflect the pseudosymmetry in the molecule, and these values compare well with those of previous determinations, being particularly close to those of the thioketene complex.[15] The Fe(CO)$_3$ fragments are almost eclipsed with an average torsion angle[12] of about 4.2° between the carbonyl groups; this is less than observed in compounds **10** and **19** where, as noted, the additional strain caused some staggering of the iron carbonyl groups. The Fe(1)–Fe(2) distance (2.5429 (6) Å) is also significantly shorter than in **10** and **19**, which is again a function of the binding mode; the additional atom bridging the metals in these latter compounds causes lengthening of their Fe–Fe bonds. In **22** the Fe–Fe bond is similar to those observed in the butterfly structures[2,9,10] where the bridging groups have similar orientations.

Both the S(1)–C(7) and S(2)–C(7) distances (1.732 (2) and 1.733 (2) Å) are short, displaying some multiple-bond character. By comparison, the S(1)–C(8) and S(1)–C(9) distances (1.790 (3) and 1.789 (3) Å) are close to the single-bonded limit.

Within the pseudotetrahedral Fe$_2$SC core of the molecule, the angles are understandably acute while within the rest of the complex the remaining angles are normal,

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(15) Umland, H.; Edelmann, F.; Wormsbächer, D.; Behrens, U. *Angew. Chem., Int. Ed. Engl.* **1983**, 153.

considering the distortions imposed by the binding of the bridging ligand. Similarly, all carbonyl parameters are normal.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone ketyl. Carbon disulfide was distilled from phosphorus pentoxide. Reagent grade pentane and dichloromethane were deoxygenated by bubbling nitrogen through them for 15 min prior to use. The gem-dithiols[16] were prepared following literature procedures, as were $Fe_2(CO)_9$,[1] $Fe_3(CO)_{12}$,[18] $(\mu\text{-}S_2)Fe_2(CO)_6$,[19] and $(\mu\text{-}HS)_2Fe_2(CO)_6$.[5b]

Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. Column chromatography was performed with a 350 × 25 mm column using silicic acid. All chromatography was done without exclusion of atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at −20 °C.

Infrared spectra were obtained by using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL FX-90Q or a Bruker 250 NMR spectrometer operating at 90 and 250 MHz, respectively. ^{13}C NMR spectra were obtained using a JEOL FX-90Q or Bruker 270 NMR instrument operating at 22.5 and 67.9 MHz, respectively. Mass spectra were obtained with a Varian MAT-44 or a Finnigan-3200 spectrometer operating at 70 eV. Field desorption mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Melting points of analytically pure samples were obtained on a Büchi melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Reaction between Triiron Dodecacarbonyl and α,ω-Dithiols. 1. Methanedithiol. A 250-mL, three-necked, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 4.53 g (9.0 mmol) of $Fe_3(CO)_{12}$ and flushed with nitrogen. THF (50 mL) and 0.71 g (8.86 mmol) of $H_2C(SH)_2$ were added by syringe, and the mixture was refluxed gently for 1 h. The solvent was removed, and the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 2.71 g (7.57 mmol, 85% yield based on $H_2C(SH)_2$) of $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$ as an air-stable, red solid, mp 74–76 °C (lit.[1k] mp 73–75 °C) after crystallization from pentane. It was identified by comparison of its ^1H NMR and IR spectra to those reported in the literature.[1k,2]

IR (pentane): terminal carbonyl region, 2081 (s), 2041 (vs), 2010 (vs), 2001 (vs), 1990 (m), 1960 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 4.61.

Caution! Methanedithiol, $CH_2(SH)_2$, is a volatile, very vile-smelling, and toxic compound. A well-ventilated hood is mandatory when it is prepared and used.

2. α,α-Toluenedithiol. The same procedure using 4.53 g (9.0 mmol) of $Fe_3(CO)_{12}$ and 1.38 g (8.8 mmol) of α,α-toluenedithiol in 50 mL of THF (1-h gentle reflux) gave 0.83 g (22%) of complex **11**: a red solid; mp 93–94 °C (from pentane).

IR ($CHCl_3$): 3065 (w), 1603 (w), 1496 (m), 1448 (m), 1230 (br), 1110 (w), 1033 (w), 1004 (w), 847 (m), 700 (s), 620 (s), 565 (s), 488 (m) cm^{-1}; terminal carbonyl region (pentane), 2084 (s), 2043 (vs), 2007 (vs), 1988 (m), 1958 (w) cm^{-1}. ^1H NMR (acetone-d_6 90 MHz): δ 6.37 (s, 1 H, CH), 7.4 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 79.1 (d, J = 166 Hz, CH), 125.0 (d, J = 160 Hz, Ph), 128.3 (d, J = 162 Hz, Ph), 142.8 (s, ipso Ph), 208.0 and 208.4 (both s, CO). Mass spectrum: m/z (relative intensity) 434 (M^+, 7), 406 (M^+ − CO, 7), 378 (M^+ − 2CO, 9), 350 (M^+ − 3CO, 15), 322 (M^+ − 4CO, 8), 294 (M^+ − 5CO, 16), 266 (M^+ − 6CO, 100), 188 (Fe_2S_2C, 29), 176 (Fe_2S_2, 11), 144 (Fe_2S, 44), 122 (Fe_2, 5), 88 (FeS, 5), 56 (Fe, 14). Anal. Calcd for $C_{13}H_6Fe_2O_6S_2$: C, 35.98; H, 1.39. Found: C, 36.11; H, 1.47.

3. 1,2-Ethanedithiol. This preparation has been reported by Winter, Zsolnai, and Huttner.[7] A reaction of 2.98 mmol each of $Fe_3(CO)_{12}$ and 1,2-ethanedithiol in toluene at 70 °C gave 2.7 mmol of $(\mu\text{-}SCH_2CH_2S)Fe_2(CO)_6$ (**14**): a red solid; mp 74–76 °C (lit.[7] mp 77–78 °C).

^1H NMR ($CDCl_3$): δ 2.38 (s, CH_2). ^{13}C NMR ($CDCl_3$): δ_C 36.29 (s, CH_2), 208.23 (s, C≡O).

4. 1,3-Propanedithiol. A similar preparation using 14.9 mmol of $Fe_3(CO)_{12}$ and 15.3 mmol of 1,3-propanedithiol gave 11.9 mmol of $(\mu\text{-}S(CH_2)_3S)Fe_2(CO)_6$ (**15**): a dark red solid; mp 86–88 °C (from petroleum ether at −30 °C) (lit.[7] mp 78 °C).

NMR ($CDCl_3$): δ 1.93 (m, 2 H, $-CH_2-$), 2.16 (t, J = 4.5 Hz, 4 H, SCH_2).

5. α,α′-Dimercapto-*o*-xylene.[20] A similar reaction of 14.9 mmol of $Fe_3(CO)_{12}$ and 14.7 mmol of the dithiol in 150 mL of benzene at reflux for 6 h gave 12.5 mmol of $(\mu\text{-}SCH_2\text{-}o\text{-}C_6H_4CH_2S)Fe_2(CO)_6$: a dark red solid; mp 160–162 °C (from CH_2Cl_2/pentane) (lit.[1k] mp 160–162 °C).

NMR ($CDCl_3$): δ 3.49 (A_2B_2, 4 H, $-CH_AH_B-$), 6.95–7.25 (m, 4 H, C_6H_4).

Reactions between (μ-Methanedithiolato)bis(tricarbonyliron) and Lithium Diisopropylamide. 1. Preparation of the Methyl Derivative. A 250-mL, round-bottomed, three-necked flask equipped with a magnetic stir bar and serum caps was charged with 0.837 g (2.34 mmol) of $(\mu\text{-}SCH_2S)Fe_2(CO)_6$ and flushed with nitrogen. THF (50 mL) was added and the red solution cooled to −78 °C. Lithium diisopropylamide (2.50 mmol) in 10 mL of THF was added, causing a color change to green. The reaction mixture was stirred for 15 min; and then 1.0 mL (16.1 mmol) of iodomethane was added. The solution was removed from the cold bath and stirred for 1 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in 4:1 pentane/CH_2Cl_2. This solution was filtered through a pad of silicic acid. After removal of the solvent, the residue was subjected to column chromatography (silicic acid/pentane). Pentane eluted a minor yellow band of starting material and pentane/CH_2Cl_2 (4:1, v/v), a red band which yielded 0.678 g (1.82 mmol, 78% yield) of $(\mu\text{-}HCS_2CH_3)Fe_2(CO)_6$ as a slightly air-sensitive, red oil. Analytical and spectroscopic data (IR and ^1H and ^{13}C NMR) have been given in ref 1e.

Mass spectrum: m/z (relative intensity) 372 (M^+, 3), 344 (M^+ − CO, 2), 316 (M^+ − 2CO, 5), 288 (M^+ − 3CO, 5), 260 (M^+ − 4CO, 8), 232 (M^+ − 5CO, 27), 204 (M^+ − 6CO, 42), 189 (Fe_2S_2CH, 21), 176 (Fe_2S_2, 52) 144 (Fe_2S, 58), 112 (Fe_2, 31), 88 (FeS, 19), 56 (Fe, 100).

2. Preparation of the Acetylmethyl Derivative. A similar procedure was used in the reaction of 1.95 mmol of **1** with 2.10 mmol of *i*-Pr_2NLi in THF at −78 °C, with subsequent addition of 5.96 mmol of 1-bromo-2-propanone. Column chromatography (Florisil, 4:1 pentane/CH_2Cl_2) eluted a red band from which complex **10** was isolated as a red solid: mp 80–82 °C (from pentane/CH_2Cl_2); 0.447 g (55% yield).

IR ($CHCl_3$): 1715 (s) cm^{-1} (C=O); terminal carbonyl region, 2070 (s), 2015 (vs), 2003 (vs), 1994 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 2.23 (s, 3 H, CH_3), 3.50, 3.69 (AXq, J = 15.9 Hz, 2 H, SCH_2), 3.94 (s, 1 H, S_2CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 29.4 (q, J = 128 Hz, CH_3), 53.4 (d, J = 190 Hz, S_2CH), 62.0 (t, J = 140 Hz, CH_2), 199.4 (s, ketone CO), 208.3 (br, CO), 210.9 (s, CO). Anal. Calcd for $C_{10}H_6Fe_2O_7S_2$: C, 29.01; H, 1.46. Found: C, 28.96; H, 1.61.

3. Other Derivatives. a. Ethyl derivative 7b, an air-sensitive, red oil, was obtained in 68% yield (column chromatography, silicic acid, 4:1 pentane/CH_2Cl_2). Analytical and spectroscopic data (IR and ^1H and ^{13}C NMR) and the electron-impact mass spectrum have been given in ref 1e.

b. Benzyl derivative 7d, a red solid, mp 116–118 °C (from pentane/CH_2Cl_2), was obtained in 56% yield.

IR (pentane): terminal carbonyl region, 2070 (s), 2024 (vs), 2002 (vs), 1992 (s), 1979 (m), 1974 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 270

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MHz): δ 3.82 (s, 1 H, S_2CH), 3.79 (ABq, J_{AB} = 13.1 Hz, 2 H, SCH_2), 3.79 and 7.28 (both m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 52.4 (d, *J* = 192 Hz, S_2CH), 57.8 (t, *J* = 140 Hz, SCH_2), 128.5 (d, *J* = 162 Hz, Ph), 129.1 (d, *J* = 162 Hz, Ph), 133.6 (s, ipso Ph), 208.6 (br, CO), 211.1 (s, CO). Mass spectrum: *m/z* (relative intensity) 448 (M^+, 1), 364 (M^+ - 3CO, 3), 357 (M^+ - $PhCH_2$, 59), 336 (M^+ - 4CO, 5), 329 (M^+ - $PhCH_2$ - CO, 10), 308 (M^+ - 5CO, 9), 301 (M^+ - $PhCH_2$ - 2CO, 7), 280 (M^+ - 6CO, 100), 273 (M^+ - $PhCH_2$ - 3CO, 2), 217 (M^+ - $PhCH_2$ - 5CO, 7), 189 (Fe_2S_2CH, 53), 188 (Fe_2S_2C, 24), 176 (Fe_2S_2, 83), 144 (Fe_2S, 73), 112 (Fe_2, 15), 91 ($PhCH_2$, 47), 88 (FeS, 5), 56 (Fe, 21). Anal. Calcd for $C_{14}H_8Fe_2O_6S_2$: C, 37.53; H, 1.80. Found: C, 37.36; H, 1.92.

c. Allyl derivative 7c, a slightly air-sensitive, red oil, was obtained in 70% yield (column chromatography, silicic acid, 9:1 pentane/CH_2Cl_2). Analytical and spectroscopic data (IR and ^1H and ^{13}C NMR) and the electron-impact mass spectrum have been given in ref 1e.

Reaction between (μ-SCH(Ph)S)$Fe_2(CO)_6$ and Lithium Diisopropylamide. 1. Methyl Derivative 12 (R = CH_3). Lithium diisopropylamide (0.90 mmol) was added to 0.36 g (0.83 mmol) of (μ-$PhHCS_2$)$Fe_2(CO)_6$ in 50 mL of THF at -78 °C, producing a green reaction mixture. After it had been stirred for 25 min at -78 °C, 0.5 mL (8.0 mmol) of iodomethane was added. The solution was removed from the cold bath and stirred for 1.5 h during which time it became red. Subsequently, the solvent was removed and the remaining red oil taken up in pentane and applied to filtration chromatography (silicic acid). Pentane eluted a yellow band which yielded 0.06 g (0.14 mmol, 17% yield) of recovered starting material. Pentane/CH_2Cl_2 (9:1) eluted a red band which gave 0.29 g (0.65 mmol, 78% yield) of (μ-$SCPhSCH_3$)$Fe_2(CO)_6$ (**12**, R = CH_3), as an air-stable, red solid, mp 101-102 °C after recrystallization from pentane/CH_2Cl_2.

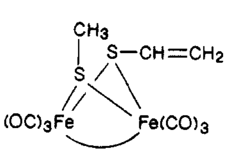
IR (pentane): terminal carbonyl region, 2070 (s), 2028 (vs), 2004 (vs), 1994 (s), 1982 (m), 1973 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 2.13 (s, 3 H, CH_3), 7.2 (m, 5 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz): δ_C 32.7 (CH_3), 73.7 (S_2C), 123.3, 127.4, 129.1 (Ph), 147.4 (ipso, Ph), 211.6 (br, CO). Mass spectrum: *m/z* (relative intensity) 448 (M^+, 8), 420 (M^+ - CO, 19), 392 (M^+ - 2CO, 43), 364 (M^+ - 3CO, 43), 336 (M^+ - 4CO, 36), 308 (M^+ - 5CO, 33), 280 (M^+ - 6CO, 100), 265 (Fe_2S_2CPh, 23), 176 (Fe_2S_2, 97), 144 (Fe_2S, 33), 121 (PhCS, 16), 112 (Fe_2, 5), 56 (Fe, 10). Anal. Calcd for $C_{14}H_8Fe_2O_6S_2$: C, 37.53; H, 1.80. Found: C, 37.53; H, 1.85.

2. Ethyl derivative 12 (R = C_2H_5), a red oil, was obtained in 61% yield, in addition to a 25% recovery of starting material.

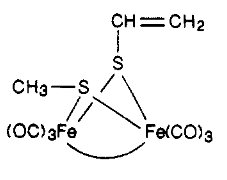
IR (pentane): terminal carbonyl region, 2076 (s), 2032 (vs), 2008 (vs), 1994 (s), 1983 (m), 1974 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 1.04 (t, *J* = 7.3 Hz, 3 H, CH_3), 2.52 (m, 2 H, SCH_2), 7.23 (s, 5 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22.5 MHz): δ_C 11.7 (CH_3), 44.0 (SCH_2), 72.4 (S_2C), 123.4, 127.5, 129.1, 148.4 (Ph), 209.7 (br, CO), 211.6 (CO). Anal. Calcd for $C_{15}H_{10}Fe_2O_6S_2$: C, 38.99; H, 2.18. Found: C, 39.04; H, 2.35.

Reaction between (μ-1,2-Ethanedithiolato)bis(tricarbonyliron) and Lithium Diisopropylamide. Iodomethane Quench. A 250-mL Schlenk flask equipped with a magnetic stir bar and a serum stopper was charged with 0.836 g (2.25 mmol) of (μ-SCH_2CH_2S)$Fe_2(CO)_6$ and then flushed with nitrogen. THF (100 mL) was added by syringe, and an orange-red solution was obtained. The solution was cooled to -78 °C, and 3.45 mmol of freshly prepared lithium diisopropylamide in 25 mL of THF was added dropwise through a 20 gauge cannula. At the start of the addition the solution deepened to a dark red, but after the addition was complete the solution had turned a dark, olive green. After it had been stirred for 30 min, 1.0 mL (16.1 mmol) of iodomethane was added by syringe. The reaction mixture was allowed to warm slowly and was stirred at room temperature for 1 h. Filtration through a pad of silicic acid was followed by evaporation of the filtrate at reduced pressure. The orange-red residue which remained was purified by column chromatography (silicic acid). Pentane eluted an orange-red band from which 0.597 g (1.55 mmol) of an air-stable, red-orange solid was isolated in 70% yield. This product was identified as (μ-CH_3S)(μ-$H_2C{=}CHS$)$Fe_2(CO)_6$.

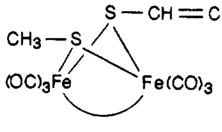
The product was shown by its NMR spectrum to be a mixture of three isomers:



A(a, e)



B(e, a)



C(e, e)

^1H NMR ($CDCl_3$, 90 MHz): δ 1.63 (s, 3 H, CH_3S); isomer A, δ 2.09 (s, 3 H, CH_3S) 2.12 (s, 3 H, CH_3S); isomers B and C, 5.55-6.19 (m, 3 H, CH_2CHS) [lit.[1a] ^1H NMR ($CDCl_3$, 60 MHz): δ 1.66 (s, 3 H, CH_3S); isomer A, 5.53-6.28 (m, 3 H, $CH_2{=}CH$); isomers B and C, 2.10 (s, 3 H, CH_3S) 2.12 (s, 3 H, CH_3S), 5.55-6.25 (m, 3 H, $CH_2{=}CH-$)].

Reaction between (μ-1,3-Propanedithiolato)bis(tricarbonyliron) and Lithium Diisopropylamide. 1. Methyl Derivative 18. The usual apparatus was charged with 0.772 g (2.0 mmol) of (μ-$SCH_2CH_2CH_2S$)$Fe_2(CO)_6$ (**15**) and THF (100 mL). The resulting orange-red solution was cooled to -78 °C, and 3.0 mmol of lithium diisopropylamide in 20 mL of THF was added dropwise. At the start of the addition the solution deepened to a dark red, but after the addition was complete, the solution had turned to a dark, olive-green. After it had been stirred for 30 min, 0.50 mL (8.0 mmol) of iodomethane was added. The reaction mixture was stirred for 30 min at -78 °C and then allowed to warm slowly to room temperature. The color of the solution turned dark red-brown around 0 °C, and the solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure. The red-brown residue was purified by column chromatography (silicic acid). Petroleum ether eluted some starting material (6% recovery). Subsequent elution with 96:4 petroleum ether/dichloromethane gave an orange-red band from which 0.5909 g (1.47 mmol) of an air-stable, orange-red solid, **18**, was isolated in 70% yield. After recrystallization from pentane, mp 104-106 °C, a mixture of two isomers (R = CH_3), **18A** (major) and **18B** (minor), was present.

^1H NMR ($CDCl_3$, 90 MHz): δ 1.68 (s, 3 H, CH_3S), 2.20-2.43 (m, 3 H, CH_2CH_2), 2.84-2.89 (m, 1 H, CH_2), 3.17-3.31 (m, 1 H, CH). ^{13}C NMR (C_6D_6, 67.9 MHz): major isomer (**18A**, R = CH_3), δ 22.85 (q, *J* = 139 Hz, CH_3), 30.63 (t, *J* = 137 Hz, CH_2), 37.42 (t, *J* = 128 Hz, CH_2), 38.22 (d, *J* = 152 Hz, CH), 208.71, 211.03, 214.17 (all s, CO); minor isomer (**18B**, R = CH_3), δ 23.39 (q, *J* = 135 Hz, CH_3) 31.62 (t, *J* = 138 Hz, CH_2), 46.52 (t, *J* = 128 Hz, CH_2) 47.33 (d, *J* = 150 Hz, CH). IR (*n*-pentane): terminal carbonyl region, 2062 (s), 2020 (vs), 1998 (sh), 1995 (s), 1978 (s), 1963 (m) cm^{-1}. Mass spectrum: *m/z* (relative intensity) 400 (2.2, M^+), 372 (13.2, M^+ - CO), 344 (20.9, M^+ - 2CO), 316 (13.6, M^+ - 3CO), 288 (13.4, M^+ - 4CO), 260 (15.7, M^+ - 5CO), 232 (46.4, M^+ - 6CO), 217 (14.1, $(CH_2)_3S_2Fe_2^+$), 176 (100.0, $S_2Fe_2^+$), 144 (44.7, SFe_2^+), 56 (23.8, Fe^+). Anal. Calcd for $C_{10}H_8Fe_2O_6S_2$: C, 30.03; H, 2.02. Found: C, 30.24; H, 2.15.

b. Ethyl derivative 18A (R = C_2H_5), orange-red crystals, mp 77-79 °C, was obtained in 51% yield, in addition to a 24% recovery of starting material.

^1H NMR ($CDCl_3$, 250 MHz): δ 1.08 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2S), 1.54-1.71 (m, 2 H, CH_3CH_2S), 2.20-2.38 (m, 4 H, CH_2CH_2CH), 3.18-3.32 (m, 1 H, SCH). ^{13}C NMR (C_6D_6, 67.9 MHz): δ 12.63 (q, *J* = 128 Hz, CH_3), 31.06 (t, *J* = 142 Hz, CH_2), 34.13 (t, *J* = 141 Hz, CH_2), 36.36 (d, *J* = 152 Hz, CH), 37.45 (t, *J* = 127 Hz, CH_2), 206.82, 208.61, 211.12 (all s, CO). IR (pentane): terminal carbonyl region, 2060 (s), 2018 (s), 1996 (sh), 1993 (s), 1976 (s), 1962 (m) cm^{-1}. Mass spectrum: *m/z* (relative intensity) 414 (2.4, M^+), 386 (11.6, M^+ - CO), 358 (15.2, M^+ - 2CO), 330 (8.6, M^+ - 3CO), 302 (12.5, M^+ - 4CO), 274 (14.3, M^+ - 5CO), 246 (24.0, M^+ - 6CO), 218 (48.3, M^+ - 6CO - Et - 1), 176 (100.0, $S_2Fe_2^+$), 144 (37.1, SFe_2^+), 56 (33.1, Fe^+). Anal. Calcd for $C_{11}H_{10}Fe_2O_8S_2$: C, 31.91; H, 2.43. Found: C, 32.30; H, 2.61.

c. Allyl derivative 18A (R = $CH_2{=}CHCH_2$), a dark red, air-sensitive oil, was obtained in 39% yield (in addition to a 34%

recovery of starting material) and was purified by short-path distillation at 135–140 °C at 0.05 mmHg.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.64–1.75 (m, 2 H, CH_2), 1.68 (s, 1 H, CH), 1.71 (dd, J_c = 7.32 Hz, J_{ax} = 13.5 Hz, 1 H, $CH_aH_xCH_c{=}CH_2$), 2.43 (dd, J_c = 7.32 Hz, J_{ax} = 13.5 Hz, 1 H, $CH_aH_xCH_c{=}CH_2$), 2.52–2.64 (m, 2 H, CH_2), 4.70 (d, J_{ac} = 17 Hz, 1 H, 4.83 (d, J_{bc} = 9.8 Hz, 1 H), 5.00–5.13 (m, 1 H, $CH_c{=}CH_2$). ^{13}C NMR (C_6D_6, 67.9 MHz): δ_C 30.78 (t, *J* = 142 Hz, CH_2), 38.06 (t, *J* = 130 Hz, CH_2), 38.06 (d, *J* = 154 Hz, *C*H), 44.07 (t, *J* = 142 Hz, CH_2), 120.25 (t, *J* = 158 Hz, $CH_2{=}CH$), 130.75 (d, *J* = 158 Hz, $CH{=}CH_2$), 208.71, 210.94, 213.85 (all s, CO). IR (*n*-pentane): terminal carbonyl region, 2071 (s), 2048 (s), 2028 (m), 2006 (sh), 1995 (vs), 1961 (m), 1951 (m) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 384 (6.6, $M^+ - S$), 356 (21.9, $M^+ - S - CO$), 328 (21.5, $M^+ - S- 2CO$), 300 (23.2, $M^+ - S - 360$), 272 (24.7, $M^+ - S - 4CO$), 244 (39.2, $M^+ - S - 5CO$), 216 (39.2, $M^+ - S - 6CO$), 176 (100, $S_2Fe_2^+$), 144 (62.6, SFe_2^+), 88 (9.0, SFe^+), 56 (45.5, Fe^+). Anal. Calcd for $C_{12}H_{10}Fe_2O_6S_2$: C, 33.83; H, 2.37. Found: C, 34.86; H, 2.71.

d. Benzyl derivative 18A (R = $PhCH_2$), an orange-red solid, mp 103–104 °C (from pentane/CH_2Cl_2), was obtained in 68% yield, in addition to a 15% recovery of starting material.

^{1}H NMR (CD_2Cl_2, 250 MHz): δ 2.13–2.52 (m, 3 H, CH_2CH_2CH), 2.82 (d, J_{ax} = 13.4 Hz, 1 H, CH_aH_x), 2.93 (m, 1 H, CH_2CH_2CH), 3.25 (t, *J* = 12 Hz, 1 H, C*H*), 3.52 (d, J_{ax} = 13.4 Hz, 1 H, CH_aH_x), 7.13–7.30 (m, 5 H, C_6H_5). ^{13}C NMR (CD_2Cl_2, 67.9 MHz): δ_C 31.34 (t, *J* = 134 Hz, CH_2), 38.87 (t, *J* = 130 Hz, CH_2), 38.87 (d, *J* = 154 Hz, *C*H), 46.77 (t, *J* = 141 Hz, CH_2); phenyl region, δ_C 128.28 (d, *J* = 162 Hz), 129.34 (d, *J* = 160 Hz), 135.25 (s), 208.80, 210.84, 213.98 (all s, CO). IR (*n*-pentane): terminal carbonyl region, 2068 (s), 2032 (vs), 1998 (vs), 1995 (sh), 1978 (s) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 476 (0.1, M^+), 448 (0.1, $M^+ - CO$), 420 (4.4, $M^+ - 2CO$), 392 (21.0, $M^+ - 3CO$), 385 (50.1, $M^+ - PhCH_2$), 364 (2.8, $M^+ - 4CO$), 357 (8.1, $M^+ - PhCH_2 - CO$), 336 (18.5, $M^+ - 5CO$), 329 (11.9, $M^+ - PhCH_2 - 2CO$), 308 (100.0, $M^+ - 6CO$), 301 (8.1, $M^+ - PhCH_2 - 3CO$), 273 (9.4, $M^+ - PhCH_2 - 4CO$), 245 (4.6, $M^+ - PhCH_2 - 5CO$), 217 (13.7, $M^+ - PhCH_2 - 6CO$), 176 (59.2, $S_2Fe_2^+$), 144 (20.2, SFe_2^+), 91 (40.9, $PhCH_2^+$), 56 (2.4, Fe^+). Anal. Calcd for $C_{16}H_{12}Fe_2O_6S_2$: C, 40.37; H, 2.54. Found: C, 40.36; H, 2.60.

Reaction between (μ-*o*-Xylylene-α,α'-dithiolato)bis(tricarbonyliron) and Lithium Diisopropylamide. 1. Methyl Derivative 19 (R = CH_3). A 200-mL Schlenk flask equipped with a magnetic stir bar and a serum stopper was charged with 0.448 g (1.0 mmol) of **16** and then flushed with nitrogen. THF (75 mL) was added by syringe, and an orange-red solution was obtained. The solution was cooled to −78 °C, and 2.14 mmol of freshly prepared lithium diisopropylamide in 20 mL of THF was added dropwise through a 20 gauge cannula. At the start of the addition the solution deepened to a dark red. However, when the addition was complete, no further color change was observed. After it had been stirred for 30 min at −78 °C, 1.0 mL (16.1 mmol) of iodomethane was added by syringe. The reaction mixture was stirred for 30 min at −78 °C and then allowed to warm slowly to room temperature. The color of the solution lightened slightly around 0 °C, and the solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure. The red-brown residue was purified by column chromatography (silicic acid). Petroleum ether eluted some starting material (35% recovery). Subsequent elution with 9:1 petroleum ether/dichloromethane gave an orange-red band from which 0.230 g (0.50 mmol) of an air-stable, orange-red solid was isolated in 50% yield. After crystallization from 4:1 pentane/dichloromethane, mp 111–113 °C, it was identified as complex **19** (R = CH_3).

^{1}H NMR ($CDCl_3$, 90 MHz): δ 2.14 (s, 3 H, CH_3), 3.12 (s, 1 H, *H*C), 3.33 (d, J_{ax} = 15.1 Hz, CH_2), 4.63 (d, J_{ax} = 15.1 Hz, CH_2), 6.70–7.20 (m, 4 H, C_6H_4). ^{13}C NMR (CD_2Cl_2, 67.9 MHz): δ 26.35 (t, *J* = 142 Hz, CH_3), 35.37 (t, *J* = 141 Hz, CH_2), 37.75 (d, *J* = 147 Hz, CH); phenyl region, δ_C 124.55 (d, *J* = 171 Hz), 126.83 (d, *J* = 160 Hz), 126.94 (d, *J* = 162 Hz), 129.95 (d, *J* = 157 Hz), 139.69 (s), 148.17 (b), 207.25, 207.44, 217.04 (all s, CO). IR (pentane): terminal carbonyl region, 2060 (s), 2020 (vs), 1993 (s), 1978 (vs) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 434 (1.0, $M^+ - CO$), 406 (1.8, $M^+ - 2CO$), 378 (3.8, $M^+ - 3CO$), 350 (2.0, $M^+ - 4CO$), 322 (3.3, $M^+ - 5CO$), 294 (13.2, $M^+ - 6CO$), 176 (100.0, $S_2Fe_2^+$), 144 (16.0, SFe_2^+), 56 (11.4, Fe^+). Anal. Calcd for $C_{15}H_{10}Fe_2O_6S_2$: C, 38.99; H, 2.18. Found: C, 39.25; H, 2.46.

2. Ethyl derivative 19 (R = C_2H_5), an orange-red solid, mp 114–116 °C, was obtained in 28% yield (elution with 4:1 petroleum ether/CH_2Cl_2).

^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.22 (t, *J* = 7.3 Hz, 3 H, CH_3CH_2), 2.51–2.98 (m, 2 H, CH_3CH_2S), 3.15 (s, 1 H, *H*C), 3.32 (d, *J* = 15.1 Hz, 1 H, CH_aH_x), 4.60 (d, *J* = 15.1 Hz, 1 H, CH_aH_x), 6.85–7.20 (m, 4 H, C_6H_4). ^{13}C NMR (CD_2Cl_2, 67.9 MHz): δ 13.34 (q, *J* = 128 Hz, CH_3CH_2), 35.09 (d, *J* = 150 Hz, *C*H), 35.09 (t, *J* = 142 Hz, CH_2), 37.32 (t, *J* = 142 Hz, CH_2); phenyl region, δ_C 123.73 (d, *J* = 150 Hz), 125.87 (d, *J* = 152 Hz), 126.86 (d, *J* = 162 Hz), 129.86 (d, *J* = 158 Hz), 139.65 (s), 148.70 (b), 207.06, 207.37, 217.07 (all s, CO). IR (*n*-pentane) terminal carbonyl region, 2058 (s), 2020 (s), 1996 (sh), 1991 (s), 1975 (s) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 476 (5.2, M^+), 448 (2.4, $M^+ - CO$), 420 (19.0, $M^+ - 2CO$), 392 (27.5, $M^+ - 3CO$), 364 (12.3, $M^+ - 4CO$), 336 (29.4, $M^+ - 5CO$), 308 (58.9, $M^+ - 6CO$), 280 (100.0, (μ-$SCH_2C_6H_4CH_2S)Fe_2^+$), 176 (31.5, $S_2Fe_2^+$), 144 (15.3, SFe_2^+), 56 (1.4, Fe^+). Anal. Calcd for $C_{16}H_{12}Fe_2O_6S_2$: C, 40.37; H, 2.54. Found: C, 40.44; H, 2.64.

3. Allyl derivative 19 (R = $CH_2{=}CHCH_2$), mp 107–109 °C (from 4:1 pentane/CH_2Cl_2), was obtained in 28% yield, in addition to a 34% recovery of starting material.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.16 (s, 1 H, C*H*), 3.22 (d, J_{zx} = 15 Hz, 1 H, CH_aH_x), 3.31–3.50 (m, 2 H, $CH_2CH{=}CH_2$), 4.52 (d, J_{ax} = 15 Hz, 1 H, CH_aH_x), 5.08–5.27 (m, 2 H, $CH_2{=}CH$), 5.42–5.59 (m, 1 H, $CH_2{=}CHCH_2$), 6.72–7.79 (m, 4 H, C_6H_4). ^{13}C NMR (CD_2Cl_2, 67.9 MHz): δ_C 34.16 (d, *J* = 143 Hz, CH), 33.15 (t, *J* = 142 Hz, CH_2), 45.74 (t, *J* = 143 Hz, CH_2), 122.21 (t, *J* = 162 Hz, $CH_2{=}CH$), 124.19 (d, *J* = 160 Hz, $CH_2{=}CH$): phenyl region, δ_C 125.87 (d, *J* = 162 Hz), 126.79 (d, *J* = 162 Hz), 129.83 (d, *J* = 160 Hz), 130.54 (d, *J* = 158 Hz), 139.65 (s), 207.04, 207.34, 217.04 (all s, CO). IR (pentane): terminal carbonyl region, 2058 (s), 2020 (s), 1996 (sh), 1976 (s) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 488 (2.4, M^+), 460 (3.3, $M^+ - CO$), 447 (4.2, $M^+ - CH_2{=}CHCH_2$), 432 (5.4, $M^+ - 2CO$), 404 (18.4, $M^+ - 3CO$), 376 (17.4, $M^+ - 4CO$), 348 (11.6, $M^+ - 5CO$), 320 (100, $M^+ - 6CO$), 279 (44.4, $M^+ - 6CO - CH_2{=}CH{-}CH_2$), 176 (62.1, $S_2Fe_2^+$), 144 (94.3, SFe_2^+), 103 (48.4, $C_6H_4(CH_2)(CH)^+$), 56 (43.9, Fe^+), 39 (41.3, $CH_2{=}CH{-}CH^+$). Anal. Calcd for $C_{17}H_{12}Fe_2O_6S_2$: C, 41.83; H, 2.48. Found: C, 41.89; H, 2.55.

4. Benzyl derivative 19 (R = $PhCH_2$), mp 128–130 °C (from 4:1 pentane/CH_2Cl_2), was obtained in 17% yield, along with a 32% recovery of starting material.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 3.20 (d, J_{ax} = 14.9 Hz, 1 H, CH_aH_x), 3.23 (s, 1 H, C *H*), 3.74 (d, J_{ax} = 12.4 Hz, 1 H, CH_aH_x), 3.90 (d, J_{ax} = 12.4 Hz, 1 H, CH_aH_x), 4.50 (d, J_{ax} = 14.9 Hz, 1 H, CH_aH_x), 6.44–7.17 (m, 9 H). ^{13}C NMR (CD_2Cl_2, 67.9 MHz): δ_C 33.63 (d, *J* = 147 Hz, CH), 35.25 (t, *J* = 141 Hz, CH_2), 47.14 (t, *J* = 143 Hz, CH_2); phenyl region, δ_C 124.29 (d, *J* = 168 Hz), 125.89 (d, *J* = 162 Hz), 126.74 (d, *J* = 161 Hz), 128.93 (d, *J* = 162 Hz), 129.27 (d, *J* = 164 Hz), 129.71, (d, *J* = 159 Hz), 129.80 (d, *J* = 158 Hz), 134.46 (s), 135.59 (s), 148.08 (s), 207.07, 207.38, 217.13 (all s, CO). IR (pentane): terminal carbonyl region, 2058 (s), 2032 (m), 2019 (vs), 1996 (sh), 1991 (s), 1975 (s) cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 538 (1.9, M^+), 510 (0.8, $M^+ - CO$), 482 (10.2, $M^+ - 2CO$), 454 (18.7, $M^+ - 3CO$), 447 (5.5, $M^+ - PhCH_2$), 426 (6.6, $M^+ - 4CO$), 398 (9.6, $M^+ - 5CO$), 370 (100, $M^+ - 6CO$), 279 (19.4, $M^+ - 6CO - PhCH_2$), 278 (23.4, $M^+ - 6CO - PhCH_2{-}H$), 176 (29.0, $S_2Fe_2^+$), 144 (32.4, SFe_2^+), 103 (19.7, $CH_2C_6H_4CH^+$), 91 (45.2, $PhCH_2^+$), 56 (20.1, Fe^+). Anal. Calcd for $C_{21}H_{14}Fe_2O_6S_2$: C, 46.87; H, 2.62. Found: C, 47.07; H, 2.91.

Reaction between (μ-$HCS_2CH_3)Fe_2(CO)_6$ and Lithium Diisopropylamide. 1. Iodomethane Quench. A 250-mL round-bottomed flask containing 0.624 g (1.68 mmol) of (μ-$HCS_2CH_3)Fe_2(CO)_6$ was equipped with a stir bar and a serum cap and flushed with nitrogen. THF (50 mL) was added and the red solution cooled to −78 °C. Lithium diisopropylamide (1.90 mmol) in 15 mL of THF then was cannulated into the solution which became red-brown. The reaction mixture was stirred for 45 min; then 1.0 mL (16.1 mmol) of iodomethane was added. The reaction vessel was removed from the cold bath, and the solution was stirred for 22 h. The solvent was removed and the residue taken up in CH_2Cl_2 and filtered through a pad of silicic acid. The solvent was again removed leaving an orange solid which was subjected to column chromatography (silicic acid/pentane). Pentane/

CH_2Cl_2 (4:1) eluted a minor orange band which yielded 0.11 g (0.30 mmol, 11% yield) of (μ-HCS_2CH_3)$Fe(CO)_6$, identified by comparison of its ^1H NMR spectrum to that of an authentic sample. Further elution with pentane/CH_2Cl_2 (1:1) moved an orange band which yielded 0.50 g (1.30 mmol, 77% yield) of [μ-$SCS(CH_3)_2$]-$Fe_2(CO)_6$ as an air-stable, orange solid. It was recrystallized from pentane/CH_2Cl_2; mp 130 °C dec.

IR (CH_2Cl_2): terminal carbonyl region, 2047 (s), 2003 (vs), 1975 (vs), 1954 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 2.80 (s, CH_3). ^{13}C NMR (acetone-d_6, 67.9 MHz): δ_C 33.2 (q, J = 144 Hz, CH_3), 106.7 (s, S_2C), 214.0 (s, CO). Mass spectrum: m/z (relative intensity) 386 (M^+, 1), 358 (M^+ - CO, <1), 274 (M^+ - 4CO, 1), 246 (M^+ - 5CO, 2), 212 (M^+ - 4CO - Me_2S, 1), 184 (M^+ - 5CO - Me_2S, 1), 176 (Fe_2S_2, 3), 156 (Fe_2SC, 3), 144 (Fe_2S, 1), 112 (Fe_2S, 5), 100 (FeSC, 3), 76 (CS_2, 3), 62 (Me_2S, 75), 47 (SMe, 100). Anal. Calcd for $C_9H_6Fe_2O_6S_2$: C, 28.01; H, 1.57. Found: C, 28.02; H, 1.67.

2. Allyl Bromide Quench. An air-stable, orange solid, **23a**, was obtained in 39% yield; mp 81–83 °C.

IR (CH_2Cl_2): terminal carbonyl region, 2050 (s), 2005 (s), 1974 (s), 1953 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.73 (s, 3 H, SCH_3), 3.55 (dd, J = 12.8, J = 10.7 Hz, 1 H, allylic proton), 3.90 (dd, J = 12.8 Hz, J = 9.6 Hz, 1 H, allylic proton), 5.60 (d, J = 17.3 Hz, 1 H, vinyl), 5.65 (d, J = 9.9 Hz, 1 H, vinyl), 5.84 (m, 1 H, CH_2CH=). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 29.7 (q, J = 144 Hz, CH_3), 53.7 (t, J = 146 Hz, SCH_2), 101.5 (s, SCS), 124.3 (d, J = 166 Hz, CH=), 126.9 (t, J = 162 Hz, =CH_2), 212.9 (s, CO). Mass spectrum: m/z (relative intensity) 412 (M^+, 14), 384 (M^+ - CO, 3), 371 (M^+ - C_3H_5,), 356 (M^+ - 2CO, 5), 343 (M^+ - CO - C_3H_5, 1), 328 (M^+ - 3CO, 11), 315, (M^+ - 2CO - C_3H_5, 4), 300 (M^+ - 4CO, 9), 287 (M^+ - 3CO - C_3H_5, 4), 272 (M^+ - 5CO, 23), 259 (M^+ - 4CO - C_3H_5, 7), 244 (M^+ - 6CO, 31), 240 (M^+ - 3CO - SMe(C_3H_5), 6), 231 (M^+ - 5CO - C_3H_5, 7), 212 (M^+ - 4CO - SMe(C_3H_5), 10), 203 (M^+ - 6CO - C_3H_5, 14), 188 (Fe_2SC, 26), 184 (M^+ - 5CO - SMe(C_3H_5), 15), 176 (Fe_2S_2, 100), 156 (Fe_2SC, 21), 144 (Fe_2S, 47), 112 (Fe_2, 29), 100 (FeSC, 14), 88 (FeS, 8), 56 (Fe, 41). Anal. Calcd for $C_{11}H_8Fe_2O_6S_2$: C, 32.07; H, 1.96. Found: C, 32.12; H, 2.02.

Reaction between (μ-$HCS_2C_2H_5$)$Fe_2(CO)_6$ and Lithium Diisopropylamide. 1. Iodomethane Quench. An air-stable, orange solid, **23b**, mp 73–75 °C (from pentane/CH_2Cl_2), was obtained in 85% yield.

IR (CH_2Cl_2): terminal carbonyl region, 2048 (s), 2005 (vs), 1973 (vs), 1954 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.49 (t, J = 7.8 Hz, 3 H, CH_3), 1.73 (s, 3 H, SCH_3), 3.07 (q, J = 7.8 Hz, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ_C 9.2 (q, J = 130 Hz, CH_3), 29.8 (q, J = 144 Hz, SCH_3), 44.7 (t, J = 143 Hz, CH_2), 102.1 (s, S_2C), 212.8 (s, CO). Mass spectrum: m/z (relative intensity) 400 (M^+, 34), 372 (M^+ - CO, 19), 344 (M^+ - 2CO, 16), 316 (M^+ - 3CO, 16), 288 (M^+ - 4CO, 32), 260 (M^+ - 5CO, 75), 240 (M^+ - 3CO - SMe(Et), 19), 232 (M^+ - 6CO, 24), 212 (M^+ - 4CO - SMe(Et), 23), 204 ($Fe_2S_2C_2H_4$, 14), 184 (M^+ - 5CO - SMe(Et), 28), 176 (Fe_2S_2, 100), 156 (Fe_2SC, 51), 144 (Fe_2S, 54), 112 (Fe_2, 51), 100 (FeSC, 27), 88 (FeS, 10), 76 (SMe(Et), 54), 61 (SEt, 74), 56 (Fe, 56), 47 (SMe, 39). Anal. Calcd for $C_{10}H_8Fe_2O_6S_2$: C, 30.03; H, 2.02. Found: C, 30.11; H, 2.03.

2. Iodoethane Quench. An air-stable, orange solid, **23c**, mp 75–77 °C (from pentane/CH_2Cl_2), was obtained in 45% yield.

IR (CH_2Cl_2): terminal carbonyl region, 2057 (s), 2009 (vs), 1973 (vs), 1954 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.51 (t, J = 7.5 Hz, CH_3), 3.07 (m, 2 H, SCH_2). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 9.6 (q, J = 130 Hz, CH_3), 42.2 (t, J = 144 Hz, SCH_2), 99.9 (s, CS_2), 212.9 (s, CO). Anal. Calcd for $C_{11}H_{10}Fe_2O_6S_2$: C, 31.91; H, 2.43. Found: C, 32.11; H, 2.45.

X-ray Data Collection. Suitable crystals of compounds **10**, **19**, and **22** were obtained as already outlined. All data were collected at ambient temperature by utilizing the conditions noted in Table I. For compounds **10** and **22** the $\bar{1}$ diffraction symmetry and the lack of systematic absences were consistent with the space groups $P1$ and $P\bar{1}$, the latter of which was ultimately established for both compounds as the more probable one based on the successful refinement of the structures. Cell reductions failed to show the presence of higher symmetry cells for both compounds. For compound **19** the space group was unambiguously established as $P2_1/n$, a nonstandard setting of $P2_1/c$. Absorption corrections were applied to the data for compounds **19** and **22** by using empirical techniques and Gaussian integration, respectively. The intensities for compound **19** were linearized between standards although there was no significant drop in the standards over the duration of data collection. For compounds **10** and **22** no significant variation in the standards was observed, so no correction was applied.

Structure Solution and Refinement. The heavy atom cores (Fe and S atoms) of the three compounds were located by using Patterson (**10**) or direct method techniques (SOLV for **19** and MULTAN for **22**).[21] All additional non-hydrogen atoms were located in subsequent difference Fourier syntheses. All hydrogen atoms were located apart from the methyl hydrogens in compound **10**. In compound **10** the methine hydrogen was refined isotropically, but the methylene hydrogens were input as fixed contributions in their idealized positions at 0.95 Å from their attached carbon atom; these atoms were given thermal parameters of 1.0 Å^2 greater than that of their attached carbon. In compound **19** all hydrogens were placed in idealized positions as above; those on the phenyl group were not refined; however, the others had their isotropic thermal parameters refined. For compound **22** all hydrogens were idealized and not refined. All non-hydrogen atoms in the three structures were refined anisotropically. The carbon atoms of the phenyl group in compound **19** were refined as a rigid group.

All structures were refined by full-matrix, least-squares techniques using the atomic scattering factors[22,23] and anomalous dispersion terms[24] from the usual sources. The final positional and thermal parameters of the atoms are given in Tables II–IV. Tables of anisotropic thermal parameters and listings of structure factor amplitudes are available.[25]

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Registry No. **1**, 69878-86-0; **7a**, 85534-04-9; **7b**, 85534-05-0; **7c**, 91993-58-7; **7d**, 105472-02-4; **10**, 85534-06-1; **11**, 105472-01-3; **12** (R = CH_3), 80137-02-6; **12** (R = C_2H_5), 105472-13-7; **14**, 15492-14-5; **15**, 70789-83-2; **16**, 80084-50-0; (a,e)-**17**, 102844-54-2; (e,a)-**17**, 105561-13-5; (e,e)-**17**, 102918-11-6; **18A** (R = CH_3), 105472-03-5; **18A** (R = C_2H_5), 105472-05-7; **18A** (R = $PhCH_2$), 105472-07-9; **18B** (R = CH_3), 105472-04-6; **18B** (R = C_2H_5), 105472-06-8; **19** (R = CH_3), 105472-08-0; **19** (R = C_2H_5), 105472-09-1; **19** (R = CH_2=$CHCH_2$), 105472-10-4; **19** (R = $PhCH_2$), 105472-11-5; **22**, 87183-21-9; **23a**, 87183-23-1; **23b**, 87183-22-0; **23c**, 105472-12-6; $Fe_3(CO)_{12}$, 17685-52-8; methanedithiol, 6725-64-0; α,α-toluenedithiol, 78872-76-1; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8; α,α'-dimercapto-*o*-xylene, 41383-84-0; 1-bromo-2-propanone, 598-31-2; allyl bromide, 106-95-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for compounds 10, 19, and 22 (3 pages); listings of observed and calculated structure factors for 10, 19, and 22 (39 pages). Ordering information is given on any current masthead page.

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(21) All computing for compound **19** was carried out by using the NICOLET Structure Solution Package while the calculations on compounds **10** and **22** were performed on an AMDAHL V-8 computer using the programs described in: Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1984**, *3*, 1891.

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(25) Supplementary material.