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Michael-Type Addition Reactions of Bis(μ-mercapto)bis(tricarbonyliron): Proximity-Induced Formation of Bidentate Organosulfur Ligands

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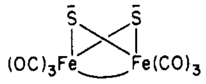
Bis(μ-mercapto)bis(tricarbonyliron), $(\mu\text{-HS})_2Fe_2(CO)_6$, reacts with α,β-unsaturated ketones, esters, and nitriles which contain terminal $CH_2{=}$ or $RCH{=}$ groups in the presence of piperidine to give 2:1 adducts in which each HS unit has added to a molecule of the activated olefin. In the case of disubstituted ketones of type $RR'C{=}CHC(O)CH_3$, $(\mu\text{-HS})_2Fe_2(CO)_6$ reacts with only one molecule of the substrate, one HS adding to the C=C bond and the other to the C=O bond, to give a product with a three-carbon bridge between the sulfur atoms. In reactions with α,β-unsaturated acetylenes, the two HS units add to the C≡C bond of one molecule of the substrate to give products with a one-carbon bridge between the sulfur atoms. An exception is dimethyl acetylenedicarboxylate, in which case a product with a two-carbon bridge is formed. The structure of one such adduct, $\mu\text{-}(CH_3C(O)CH_2CHS_2)Fe_2(CO)_6$, was determined by X-ray diffraction. This compound crystallizes in the space group $C2/c$ with a = 15.378 (2) Å, b = 9.6620 (9) Å, c = 21.768 (3) Å, β = 108.23 (1)°, V = 3072.0 Å^3, and Z = 8. On the basis of 1593 unique observed reflections and 190 variables, the structure was refined to R = 0.040 and R_w = 0.047.

Introduction

Protonation of the $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$ anion, **1**,[1] gives the



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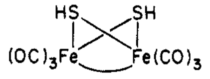
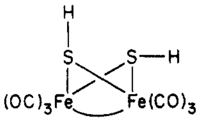
bis(μ-mercapto) complex **2** in nearly quantitative yield.[2]

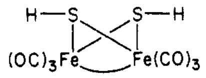


2

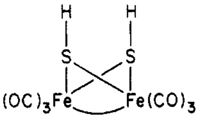
Proton NMR spectroscopy showed **2** to be a mixture of three isomers, **2a**, **2b**, and **2c** in 14:2:1 ratio.[2,3] This



2a, a,e isomer



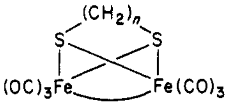
2b, e,e isomer



2c, a,a isomer

mixture of isomers was isolated in the form of an air-sensitive, red solid, mp 97–99 °C. In the development of its chemistry this mixture of isomers was used.

(μ-Dithio)bis(tricarbonyliron) is an inorganic mimic of organic disulfides,[1] and we expected $(\mu\text{-HS})_2Fe_2(CO)_6$ to be an inorganic mimic of mercaptans, RSH. We have noted the utility of **2** as a precursor in the slow, room-temperature, amine-induced release of dianion **1**, a procedure which was especially useful in the preparation of **3a** and **3b**.[4]



3a, n = 1
b, n = 2

A characteristic reaction of mercaptans is their base-induced addition to α,β-unsaturated systems.[5] If similar reactions were possible with $(\mu\text{-HS})_2Fe_2(CO)_6$, then a simple, general route for the preparation of diverse functionally substituted $(\mu\text{-RS})_2Fe_2(CO)_6$ would be in hand. With this idea in mind, we studied the organic base-induced reactions of $(\mu\text{-HS})_2Fe_2(CO)_6$ with activated olefins and acetylenes.

Results and Discussion

Our investigations showed that $(\mu\text{-HS})_2Fe_2(CO)_6$ does indeed have reactivity toward α,β-unsaturated ketones, esters, and nitriles similar to that of organic mercaptans. Complex **2** reacted with α,β-unsaturated systems containing a terminal $CH_2{=}$ function ($CH_2{=}CHCO_2CH_3$, $CH_2{=}CHC(O)CH_3$, $CH_2{=}CHCN$) in the presence of piperidine to give 2:1 adducts as a mixture of the a,e and e,e isomers, e.g., eq 1. The ester and ketone products were isolated as dark red, slightly air-sensitive oils. The product obtained in the reaction with acrylonitrile was a red solid. Although we used a stoichiometric amount of piperidine in many of the reactions carried out in this study, this is not necessary. A catalytic amount of piperidine is sufficient. The reaction with the highly reactive acrylonitrile proceeded readily in 93% yield in the absence of added piperidine.

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(1) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(2) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

(3) The isomer designation a = axial and e = equatorial is used: Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(4) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218*, C34.

(5) Ohno, A.; Oae, S. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977; Chapter 4.

(6) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

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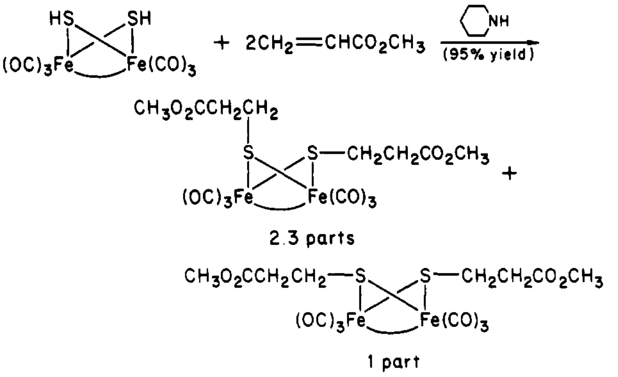
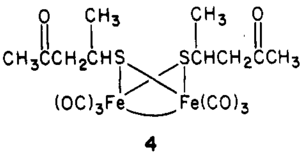


(1)

The formation of 2:1 adducts also was observed in the case of α,β-unsaturated substrates of type RCH=CHY. For instance, *trans*-3-pentenone and 2-cyclohexenone gave products **4** and **5** in yields of 62% and 70%, respectively. Methyl crotonate and diethyl maleate gave **6** and **7** in lower yields. In all cases, as determined by ^{1}H and/or ^{13}C NMR spectroscopy, a mixture of a,e and e,e isomers was present and none of these products was a crystalline solid.



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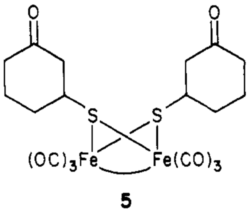

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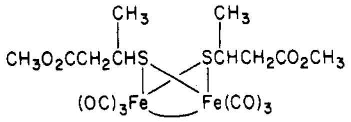

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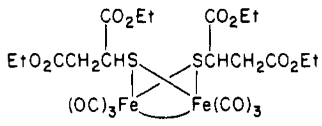

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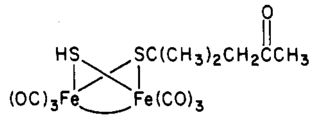
In the cases considered so far, the two HS functions of complex **2** reacted independently. However, in the "butterfly" structure of (μ-RS)$_2$Fe$_2$(CO)$_6$ complexes the two sulfur atoms are in close proximity. Thus the nonbonded S···S distance in the a,e isomer of (μ-C$_2$H$_5$S)$_2$Fe$_2$(CO)$_6$ is 2.93 Å.[7] As a result, when such 2:1 base-catalyzed HS addition to α,β-unsaturated ketones of type R$_2$C=CHC(O)R′ are attempted, steric hindrance dictates an alternate reaction course. For instance, in the case of mesityl oxide, the initially formed product no doubt is **8**. The presence of a tertiary carbon center at one sulfur ligand then makes difficult or even impossible the addition of the other SH function to a second molecule of mesityl oxide. Instead, the SH function adds to the C=O group of the alkanethio function already present to give **9** in 81% yield. Thus the product is an alcohol, or, if one follows the organic analogy, a hemithioketal analog. The product was isolated by chromatography as an orange powder with a pungent, very unpleasant odor, like that of thioacetone, so graphically described by Berzelius.[7] (Note that complex **9** has within its structure the elements of thioacetone and minor air oxidation could release this highly odiferous compound.) Complex **9** proved difficult to purify, but conversion to the trimethylsilyl ether **10** gave an easily purified, red, crystalline solid. Such organic bridge formation between the sulfur atoms of **2** appears to be a general and highly favored process. Only formation of **9** was observed even when a large excess of mesityl oxide was used. The ketones CH$_3$(C$_2$H$_5$)C=CHC(O)C$_2$H$_5$ and cyclohexylideneacetone reacted similarly with (μ-HS)$_2$Fe$_2$(CO)$_6$, giving three-carbon-bridged alcohol analogues of **9** as red oils. The trimethylsilyl ether **11** was isolated as a 1:1 mixture of diastereomers.



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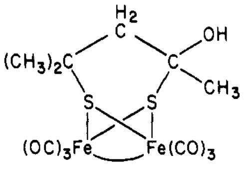

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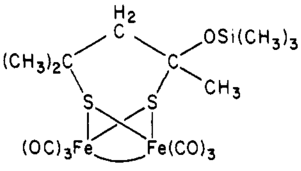

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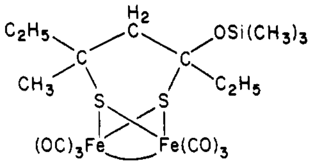
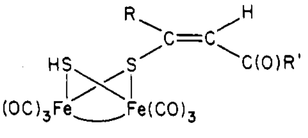


11

This bridging reaction appears to be restricted to ketones of the R$_2$C=CHC(O)R′ type. Attempts to obtain such a bridged product with CH$_2$=CHC(O)CH$_3$ were unsuccessful, the use of a deficiency of the ketone in a reaction with (μ-HS)$_2$Fe$_2$(CO)$_6$ giving only the 2:1 adduct in correspondingly diminished yield. A cyclic ketone of this general type, 3-methyl-2-cyclohexenone, failed to give an isolable product on reaction with **2** in the presence of piperidine. This was the case also with an ester, (CH$_3$)$_2$C=CHCO$_2$CH$_3$, whose C=O function apparently is not sufficiently reactive. The C=O addition of the SH function in intermediate **8** appears to be proximity induced. No products were obtained when (μ-HS)$_2$Fe$_2$(CO)$_6$ was treated with an excess of acetone in the presence of piperidine.

Acetylenes containing carbonyl groups conjugated to the C≡C bond were found to react with (μ-HS)$_2$Fe$_2$(CO)$_6$ to yield 1:1 adducts resulting from two consecutive Michael additions. In these reactions the first intermediate is **12** (in a reaction of RC≡CC(O)R′) in which the activated vinyl group is in close proximity to the remaining SH function. The thiolate anion generated by the action of piperidine on **12** would be expected to attack at the vinylic carbon atom which is bonded to sulfur since in this way the negative charge accumulating on the adjacent atom would be stabilized by delocalization onto the oxygen atom. Thus a final product with a one-carbon bridge between the sulfur atoms would be expected. This is what was observed (eq 2). In the reaction of (μ-HS)$_2$Fe$_2$(CO)$_6$ with dimethyl acetylenedicarboxylate, the intermediate **14** has a carbo-



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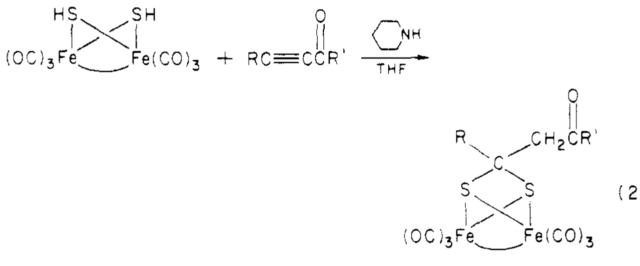
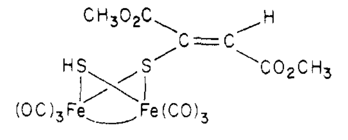
(7) *Chem. Ind.* (*London*) **1964**, 1621.



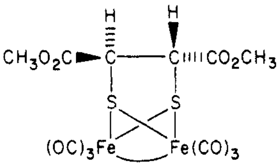
(2)

13a, R = H; R' = OCH$_3$
b, R = H; R' = CH$_3$
c, R = CH$_3$, R' = CH$_3$



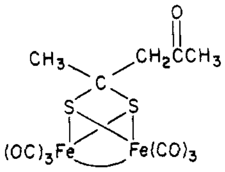
14

methoxy substituent on each olefinic carbon atom. Thus stabilization of the negatively charged intermediate in the second Michael addition would be obtained whichever way thiolate anion addition to the C=C bond occurred. This being the case, steric factors are decisive and the less strained product with a two-carbon bridge between the sulfur atoms, **15**, is formed exclusively.

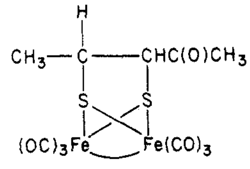


15

In these acetylene/$(\mu\text{-HS})_2Fe_2(CO)_6$ adducts the structure assignments are based mainly on proton and ^{13}C NMR data. The case of the $CH_3C{\equiv}CC(O)CH_3/(\mu\text{-HS})_2Fe_2(CO)_6$ reaction product is straightforward. The two possible structures for this product are **16a** and **16b**. The ^1H NMR

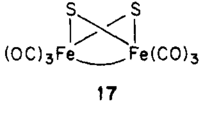


16a



16b

spectrum of the product in $CDCl_3$ showed only three singlets at δ 1.89 (3 H), 2.13 (3 H), and 3.21 (2 H), in agreement with structure **16a** but not with **16b**. It seemed reasonable to assume that the addition products resulting from $HC{\equiv}CC(O)R$ (R = CH_3, OCH_3) also have a methylene bridge structure. Table I shows the similarity of the chemical shifts for the bridging alkylene group protons and carbon atoms of these two products to those of the simple methylene-bridged species (entries 1 and 6) as opposed to the ethylene-bridged complexes (entries 2 and 3). Also, if the $HC{\equiv}CC(O)R$ compounds had given ethylene-bridged products **17**, then the presence of a chiral carbon atom should give rise to diastereotopic methylene groups and hence to more complicated proton NMR spectra than were observed.



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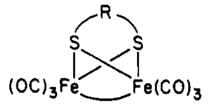
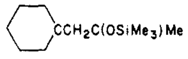
Identification of complex **15** as the two-carbon bridge product was confirmed by the equivalence of the carboxylate methyl groups in the ^1H and ^{13}C NMR spectra (Table I). These data indicate whether the CO_2CH_3 substituents were in a cis or trans configuration. With regard to this question, Shaver et al.[8] had shown that unsymmetrical groups bridging the $S_2Fe_2(CO)_6$ framework could make the $Fe(CO)_3$ groups inequivalent in the ^{13}C NMR spectra, a discovery which indicated the $Fe(CO)_3$ groups of such compounds to be independently fluxional. In the case of **15**, if the CO_2CH_3 groups were cis to one another, the $Fe(CO)_3$ units would be inequivalent. However, since the ^{13}C NMR spectrum of **15** showed a singlet at δ_C 206.9 for the CO ligand carbon atoms, the $Fe(CO)_3$ very likely are equivalent and the trans isomer is present as indicated.

Table I. ^1H and ^{13}C NMR Data for Alkylene-Bridged Derivatives of $(\mu\text{-HS})_2Fe_2(CO)_6$



		δ		
no.	bridge (R)	bridge protons	bridge carbons	iron carbonyls
1	CH_2	4.64	63.35[a]	209.3
2	CH_2CH_2[b]	2.45	36.29	208.23
3	$MeO_2CHCHCO_2Me$	3.71	54.9	206.9
4	$CHCH_2CO_2Me$	5.07	72.6	208.0, 208.4
5	$CHCH_2C(O)Me$	5.02	72.3	208.0, 208.2
6	$MeCCH_2C(O)Me$		82.3	208.1, 208.2
7	$Me_2CCH_2C(OSiMe_3)Me$		77.9, 57.0, 37.7	207.9, 208.2
8	 CCH$_2$C(OSiMe$_3$)Me		77.7, 54.9, 41.4	208.0, 208.3

[a] Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313. [b] Gallagher, M. K. Ph.D. dissertation, MIT, Cambridge, MA, 1981, p 141.

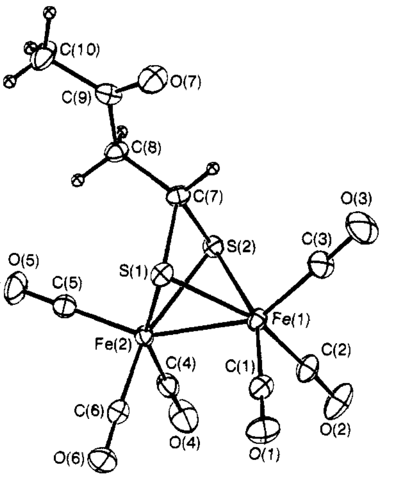


Figure 1. Perspective drawing of $(\mu\text{-}CH_3C(O)CH_2CHS_2)Fe_2(CO)_6$ (**13b**). Thermal ellipsoids are drawn at the 20% probability level except for hydrogens which are drawn artifically small.

Unambiguous proof of the structure of complex **13b**, the $HC{\equiv}CC(O)CH_3$-derived product, was provided by an X-ray diffraction study. Figure 1 shows a perspective view of this species, while relevant bond lengths and angles are presented in Tables IV and V, respectively. The complex contains a $Fe_2(CO)_6$ moiety, bridged by a $S_2CHCH_2C(O)CH_3$ ligand which is coordinated to the metals through the two sulfur atoms, functioning as a six-electron donor. The Fe_2S_2 core of the molecule has a butterfly-type structure in which the angle between the S–S and Fe–Fe

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

Table II. Summary of Crystal Data and Details of Intensity Collection

compd	$(\mu\text{-}CH_3C(O)CH_2CHS_2)Fe_2(CO)_6$
fw	413.98
formula	$Fe_2S_2O_7C_{10}H_6$
space group	$C2/c$
Z	8
cell parameters	
a, Å	15.378 (2)
b, Å	9.6621 (9)
c, Å	21.768 (3)
β, deg	108.23 (1)
V, Å^3	3072.0
ρ(calcd), g/cm^3	1.790
temp, °C	22 °C
radiatn	Mo Kα (λ = 0.71069 Å), graphite monochromated
receiving aperture, mm	2.00 + 0.50 tan θ wide × 4.00 high, 173 from crystal
take off angle, deg	2.55
scan speed, deg/min	variable between 1.12 and 10.06
scan width, deg	0.60 + 0.350 tan θ in ω
2θ limits, deg	0.10–50.00
μ, cm^{-1}	21.734
range in transmissn factors	0.717–0.807
cryst shape	monoclinic prism with faces of the form $\{0,0,1\}$, $\{1,1,\bar{1}\}$, and $\{\bar{2},1,1\}$
cryst dimens, mm	0.158 × 0.066 × 0.249
unique data collected	2781, ($\pm h,k,l$)
unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	1593
final no. of parameters refined	190
error in observn of unit weight	1.306
R	0.040
R_w	0.047

vectors is 89.38 (5)°. Each Fe atom has a distorted octahedral geometry with its six-coordination sites occupied by three carbonyl groups, in a facial arrangement, the two sulfur atoms of the bridging group, and the "bent" Fe–Fe bond. Both $Fe(CO)_3$ fragments are essentially eclipsed with (OC)Fe–Fe(CO) torsion angles of between 3.1 (3)° and 3.4 (7)°. All carbonyl groups are normal and structurally very similar. The Fe–Fe distance (2.485 (1) Å) compares well with other Fe–Fe single bonds[3,6,9–12] in related molecules and is identical with that observed in the closely related species $(\mu\text{-}CH_2S)Fe_2(CO)_6$.[3] This Fe–Fe bond results in acute Fe–S–Fe angles of ca. 66.5°. All Fe–S distances are normal and are again comparable to analogous distances in related species.

The nominally nonbonded S–S separation of 2.662 (3) Å is very close to that observed in $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$ (2.673 (2) Å), in which the sulfur atoms are also connected by a single carbon atom bridge. This separation falls between that observed in $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ (2.93 (1) Å),[6] in which the sulfur atoms are not bound together, and that observed in $(\mu\text{-}S_2)Fe_2(CO)_6$ (2.007 (5) Å),[9] in which there is a direct S–S bond. The resulting compression of the two sulfur atoms by the bridging alkylene moiety gives rise to S–Fe–S angles (average 71.96 (6)°) that, like those in $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$, are distorted significantly from idealized octahedral values and are intermediate between those in the above $(C_2H_5S)_2$- and S_2-bridged species (81.0 (3)° and 53.5 (1)°, respectively). The dihedral angle between the two Fe_2S planes in the present structure is 89.27 (7)°.

The S(1)–C(7)–S(2) angle at the bridging alkylene group is rather acute (92.9 (3)°) and again compares closely with that of the methylene-bridged analogue (94.5 (3)°). Although these angles are by themselves not extraordinary,[13] we feel that under the circumstances they are unusual. Clearly the bridging alkylene groups require that the sulfur atoms be closer together than in the unbridged case. However, the small S(1)–C(7)–S(2) angle in the present compound (and the analogous angle in the CH_2S_2 complex) does not seem to be required by any obvious strain within the molecule. By moving the sulfur atoms apart slightly, toward the positions observed in the unbridged case, a more favorable angle at C(7) could be attained. It is possible that the acute angle at C(7) results from the rather short nonbonded contacts between C(7) and the iron atoms (2.867 (6) and 2.917 (6) Å); these contacts are shorter than the van der Waals distances and might prevent the angle at C(7) from opening up, since this would move C(7) closer to the metals. However, we suggest instead that the compressed angle results from mutual attraction of the two sulfur atoms. It may be that moving the two sulfur atoms together to a distance required by the bridging alkylene unit results in mutual overlap of sulfur orbitals, which results in a slight bonding interaction between these atoms, pulling them closer together and compressing the S(1)–C(7)–S(2) angle. This latter idea is supported by calculations on the related diphosphido-bridged complexes $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]$,[14,15] in which bonding interactions between the two phosphorus atoms were postulated based on significant positive P···P overlap populations at P–P separations close to the S–S separations observed in our compound. Apart from the unusual angle at C(7) all other parameters within the alkylene moiety are normal.

A plane bisecting the Fe–Fe bond and directed through S(2), C(7), and S(2) clearly shows that the two $Fe(CO)_3$ units are inequivalent and hence distinguishable by ^{13}C NMR spectroscopy (cf. Table I). This table also presents the chemical shifts of the iron–carbonyl carbons and bridge carbons for other bridged $S_2Fe_2(CO)_6$ derivatives. Those compounds with symmetrical bridging groups (entries 1–3) have a single peak for the iron carbonyls, indicating the equivalence and fluxional behavior of the two $Fe(CO)_3$ groups. However, for bridges which result in inequivalent $Fe(CO)_3$ groups (entries 4 through 8) the ^{13}C NMR spectra reveal this inequivalence by showing two iron–carbonyl signals. This supports the suggestion of Shaver[13] that the two $Fe(CO)_3$ groups in alkyl derivatives of $(\mu\text{-}HS)_2Fe_2(CO)_6$ are independently fluxional.

The most interesting feature of this study was the observation of intramolecular Michael additions of an SH group to the C=C bond of an SCR=CHX grouping on the other wing of the butterfly structure (as in intermediates 12 and 14). This $Fe_2(CO)_6$ template construction of bidentate organosulfur ligands of type –S–(R)–S– is of potential interest in organosulfur syntheses, since, as has been demonstrated,[16] the organosulfur ligands in simple $(\mu\text{-}RS)_2Fe_2(CO)_6$ systems can be released either oxidatively (to give sulfides or disulfides) or reductively (to give mercaptans). We have elaborated this concept of intramolecular addition in further studies which will be described in a following paper.

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Table III. Positional (×10^4) and Equivalent Isotropic Thermal Parameters for the Refined Atoms

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	4187.9 (6)	996.5 (9)	6085.2 (4)	3.30	Fe(2)	5118.8 (6)	2812.6 (9)	5778.4 (4)	3.06
S(1)	5432 (1)	1966 (2)	6800.3 (7)	3.55	S(2)	5418 (1)	530 (2)	5753.8 (7)	3.27
O(1)	2907 (4)	2601 (6)	6556 (3)	6.36	O(2)	2792 (4)	604 (7)	4831 (3)	7.21
O(3)	4079 (5)	−1696 (6)	6684 (4)	8.65	O(4)	4163 (5)	2986 (5)	4388 (3)	7.11
O(5)	6839 (4)	4034 (6)	5722 (3)	6.73	O(6)	4179 (4)	5271 (6)	6048 (3)	7.10
O(7)	7394 (3)	−402 (6)	7712 (2)	6.15	C(1)	3398 (5)	1970 (7)	6373 (3)	4.35
C(2)	3338 (5)	733 (7)	5313 (4)	4.55	C(3)	4109 (5)	−635 (8)	6458 (4)	5.11
C(4)	4538 (5)	2925 (6)	4926 (3)	4.42	C(5)	6184 (5)	3578 (7)	5760 (3)	4.06
C(6)	4546 (5)	4328 (7)	5936 (4)	4.64	C(7)	6128 (4)	593 (6)	6606 (3)	3.69
C(8)	7135 (4)	906 (6)	6752 (3)	3.71	C(9)	7699 (4)	392 (7)	7405 (3)	4.02
C(10)	8651 (5)	882 (9)	7655 (4)	6.44					

Table IV. Selected Bond Lengths (Å) for Compound 13b

Fe(1)–Fe(2)	2.485 (1)	S(2)–C(7)	1.836 (6)
Fe(1)–S(1)	2.258 (2)	C(7)–C(8)	1.512 (9)
Fe(1)–S(2)	2.270 (2)	C(8)–C(9)	1.499 (8)
Fe(2)–S(1)	2.276 (2)	C(9)–C(10)	1.472 (10)
Fe(2)–S(2)	2.257 (2)	C(9)–O(7)	1.206 (7)
Fe(1)–C(1)	1.797 (7)	C(1)–O(1)	1.136 (8)
Fe(1)–C(2)	1.796 (8)	C(2)–O(2)	1.127 (8)
Fe(1)–C(3)	1.795 (7)	C(3)–O(3)	1.144 (8)
Fe(2)–C(4)	1.794 (7)	C(4)–O(4)	1.133 (8)
Fe(2)–C(5)	1.809 (7)	C(5)–O(5)	1.126 (8)
Fe(2)–C(6)	1.796 (8)	C(6)–O(6)	1.137 (8)
S(1)–C(7)	1.835 (6)		

Table V. Selected Angles (deg) for Compound 13b

(a) Bond Angles			
Fe(2)–Fe(1)–C(1)	103.5 (2)	S(2)–Fe(2)–C(5)	101.9 (2)
Fe(2)–Fe(1)–C(2)	99.2 (2)	S(2)–Fe(2)–C(6)	156.4 (2)
Fe(2)–Fe(1)–C(3)	150.2 (2)	C(4)–Fe(2)–C(5)	96.6 (3)
Fe(2)–Fe(1)–S(1)	57.12 (5)	C(4)–Fe(2)–C(6)	91.9 (3)
Fe(2)–Fe(1)–S(2)	56.46 (5)	C(5)–Fe(2)–C(6)	100.0 (3)
S(1)–Fe(1)–C(1)	93.5 (2)	Fe(1)–S(1)–Fe(2)	66.47 (5)
S(1)–Fe(1)–C(2)	156.3 (2)	Fe(1)–S(1)–C(7)	88.3 (2)
S(1)–Fe(1)–C(3)	102.4 (3)	Fe(1)–S(2)–Fe(2)	66.57 (5)
S(1)–Fe(1)–S(2)	72.01 (6)	Fe(1)–S(2)–C(7)	87.9 (2)
S(2)–Fe(1)–C(1)	159.4 (2)	Fe(2)–S(1)–C(7)	89.7 (2)
S(2)–Fe(1)–C(2)	96.3 (2)	Fe(2)–S(2)–C(7)	90.3 (2)
S(2)–Fe(1)–C(3)	98.6 (2)	S(1)–C(7)–S(2)	92.9 (3)
C(1)–Fe(1)–C(2)	91.5 (3)	S(1)–C(7)–C(8)	116.1 (4)
C(1)–Fe(1)–C(3)	98.9 (3)	S(2)–C(7)–C(8)	117.7 (4)
C(2)–Fe(1)–C(3)	99.6 (3)	C(7)–C(8)–C(9)	112.5 (5)
Fe(1)–Fe(2)–C(4)	100.3 (2)	C(8)–C(9)–C(10)	117.2 (6)
Fe(1)–Fe(2)–C(5)	153.7 (2)	C(8)–C(9)–O(7)	121.9 (6)
Fe(1)–Fe(2)–C(6)	99.5 (2)	C(10)–C(9)–O(7)	120.9 (6)
Fe(1)–Fe(2)–S(1)	56.41 (5)	Fe(1)–C(1)–O(1)	179.0 (6)
Fe(1)–Fe(2)–S(2)	56.97 (5)	Fe(1)–C(2)–O(2)	177.9 (7)
S(1)–Fe(2)–C(4)	156.6 (2)	Fe(1)–C(3)–O(3)	177.5 (7)
S(1)–Fe(2)–C(5)	104.6 (2)	Fe(2)–C(4)–O(4)	179.2 (6)
S(1)–Fe(2)–C(6)	94.1 (2)	Fe(2)–C(5)–O(5)	177.0 (6)
S(1)–Fe(2)–S(2)	71.91 (6)	Fe(2)–C(6)–O(6)	178.4 (7)
S(2)–Fe(2)–C(4)	94.2 (2)		
(b) Torsion and Related Angles			
C(1)–Fe(1)–Fe(2)–C(6)	−3.2 (3)[a]	Fe(1)–S(1)–Fe(2)/ Fe(1)–S(2)–Fe(2)	89.27 (7)[b]
C(2)–Fe(1)–Fe(2)–C(4)	−3.1 (3)	S(1)–C(7)–S(2)/ Fe(1)–Fe(2)	2.6 (3)[c]
C(3)–Fe(1)–Fe(2)–C(5)	−3.4 (7)	Fe(1)–Fe(2)/ S(1)–S(2)	89.38 (5)[d]

[a] Torsion angle. [b] Angle between two planes. [c] Angle between plane normal and vector. [d] Angle between two vectors.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Diethyl ether was distilled from lithium aluminum hydride. Reagent grade pentane and dichloromethane were deoxygenated by bubbling nitrogen through them for 15 min prior to use. 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. The eluting solvent then was passed through with suction filtration. Column chromatography was performed with a 350 × 25 mm column using either silicic acid or Florisil (Fisher, 100–200 mesh). All chromatography was done under atmospheric conditions; all solid products were recrystallized from deoxygenated solvents at −20 °C.

Infrared spectra were obtained in $CHCl_3$ solution using a Perkin-Elmer Model 457A or Model 283 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60, JEOL FX-900, or Bruker 250 NMR spectrometer operating at 60, 90, and 250 MHz, respectively. ^{13}C NMR spectra were obtained by using a JEOL FX-90Q or Bruker 270 instrument operating at 22.5 and 67.9 MHz, respectively. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Melting points were determined on analytically pure samples using a Büchi capillary melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Isomer ratios of the $(\mu\text{-RS})_2Fe_2(CO)_6$ type complexes were determined by the integration of the appropriate signals in the ^1H NMR spectra. (μ-Dithio)bis(tricarbonyliron) was synthesized by using a literature procedure.[1]

Preparation and Characterization of $(\mu\text{-HS})_2Fe_2(CO)_6$. The standard dianion solution was prepared by the addition of 6.0 mL (6 mmol, 2×) of a 1 M solution of $LiEt_3BH$ to a solution of 1.00 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 75 mL of THF at −78 °C.[1] To the reagent solution was added 1.0 mL (11.40 mmol, 3.9×) of CF_3COOH (Aldrich) which caused an immediate color change from green to red. The reaction solution was warmed to room temperature. Volatiles were removed in vacuo leaving a dark red solid which was extracted with 4 × 25 mL of hexane. The combined extracts were filtered under nitrogen through a medium-porosity fritted funnel. Removal of the solvent in vacuo gave 1.00 g (2.90 mmol, 99% yield) of $(\mu\text{-HS})_2Fe_2(CO)_6$ as a red, air-sensitive solid. After recrystallization from hexane, mp 97–99 °C, it was identified on the following basis. IR: 1220 (m), 616 (m), 570 (m) cm^{-1}; terminal carbonyl region, 2084 (m), 2046 (s), 2006 (s) cm^{-1}. NMR ($CDCl_3$): δ −2.21, 0.22 (s, 14 H, −SH anti isomer **2a**), −0.40 (s, 2 H, −SH syn equatorial isomer **2b**), and −2.43 (s, 1 H, −SH syn axial isomer **2c**). Mass spectrum: molecular ion at *m/e* 346 with fragment ions corresponding to $M - (CO)_x$ for $x = 1\text{–}6$, S_2Fe_2, SFe_2, Fe_2, SFe, and Fe. Anal. Calcd for $C_6H_2Fe_2O_6S_2$: C, 20.83; H, 0.58. Found: C, 21.00; H, 0.76.

In Situ Preparation of Bis(μ-mercapto)bis(tricarbonyliron). A dry, three-necked, 300-mL round-bottomed flask equipped with a stir bar and serum caps was charged with 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ and flushed with nitrogen. THF (50 mL) was added by syringe and the solution cooled to −78 °C. To this solution was added 6.0 mL (6.0 mmol) of 1 M $LiBEt_3H$ in THF (Aldrich), resulting in a red to green color change. After the solution was stirred for 15 min, 0.46 mL (6.0 mmol) of CF_3COOH (Baker) was added by syringe, which caused a color change to red. This solution was stirred for 10 min before further reactants were added.

Reaction of $(\mu\text{-HS})_2Fe_2(CO)_6$ with Acrylonitrile. The standard in situ preparation of $(\mu\text{-HS})_2Fe_2(CO)_6$ from 1.00 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$, 6.0 mL (6 mmol, 2×) of a 1 M solution of $LiEt_3BH$ in THF (Aldrich), 0.46 mL (6 mmol) of CF_3COOH (Aldrich), and 75 mL of THF was utilized. By syringe, 0.66 mL (10 mmol) of $H_2C{=}CHCN$ (Aldrich) was added. The resulting solution was stirred for 20 h at room temperature under nitrogen. Solvent was removed on a rotary evaporator, leaving a red solid which was chromatographed (silicic acid–CH_2Cl_2). Elution with

20% Et_2O/CH_2Cl yielded a red band which, upon removal of solvent, gave 1.22 g (2.70 mmol, 93% yield) of $(\mu\text{-}NCCH_2CH_2S)_2Fe_2(CO)_6$ as an air-stable, red solid, mp 90–92 °C, after recrystallization from CH_2Cl_2/hexane. IR: $\nu(C{\equiv}N)$ 2250; terminal CO, 2080 (s), 2044 (vs), 2010 (vs), 2001 (vs) cm^{-1}. NMR ($CDCl_3$): δ 2.35, 2.37 (t, J = 4 Hz, 2 H, $-SCH_2CH_2CN$), 2.65, 2.69 (t, J = 4 Hz, 2 H, $-SCH_2CH_2CN$). Isomer ratio could not be determined. Mass spectrum: m/z (relative intensity) 396 ($M^+ - 2CO$, 1), 368 ($M^+ - 3CO$, 4), 340 ($M^+ - 4CO$, 5), 312 ($M^+ - 5CO$, 4), 284 ($M^+ - 6CO$, 5), 230 ($NCCH_2CH_2S_2Fe_2$, 15), 176 (S_2Fe_2, 42), 144 (SFe_2, 54), 112 (Fe_2, 16), 88 (SFe, 32), 56 (Fe, 100%). Anal. Calcd for $C_{12}H_8Fe_2N_2O_6S_2$: C, 31.89; H, 1.78. Found: C, 31.96; H, 1.88.

General Procedure for Piperidine-Catalyzed Additions of $(\mu\text{-}HS)_2Fe_2(CO)_6$ to α,β-Unsaturated Substrates. The standard in situ preparation of $(\mu\text{-}HS)_2Fe_2(CO)_6$ was carried out, generally on a 1.0-g (2.91-mmol) scale at −78 °C under nitrogen as described above. The α,β-unsaturated substrate, generally an excess, and 0.5 mL (5.05 mmol) of piperidine were added successively by syringe. The reaction mixture was stirred for 30 min at −78 °C and then usually was stirred and allowed to warm to room temperature overnight. Subsequently, the reaction mixture was evaporated at reduced pressure. Usually a brown oil remained as residue.

Product Isolation and Characterization. 1. Products from Olefins. (a) Methyl Acrylate. Reaction of 2.91 mmol of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with 1.35 mL (15 mmol) of $CH_2{=}CHCO_2CH_3$ and 0.5 mL (5.05 mmol) of piperidine in 75 mL of THF at −78 °C gave a dark red oil which was purified by filtration chromatography. Dichloromethane eluted a small orange band which gave a trace amount of a red solid which was not identified. Elution with 20% Et_2O/CH_2Cl_2 yielded a red band which, upon removal of solvent, gave 1.435 g (2.77 mmol, 95% yield) of $(\mu\text{-}CH_3O_2CCH_2CH_2S)_2Fe_2(CO)_6$ as a slightly air-sensitive, deep red oil. It was rechromatographed two more times to obtain a sample that was analytically pure (short-path distillation at 185 °C (0.6 mm) gave samples that were unsuitable for analysis). IR: $\nu(C{=}O)$ 1740; terminal CO, 2075 (s), 2039 (vs), 2000 (vs), 1992 (vs) cm^{-1}. NMR ($CDCl_3$): δ 2.34 (anti up), 2.64 (syn), 2.67 (anti out) (all s, $H_3COOCCH_2CH_2S-$, 4 H) and 3.67, 3.70, 3.74 (all s, $H_3COOCCH_2CH_2S-$, 3 H); anti/syn = 2.27. Mass spectrum: m/z (relative intensity) 434 ($M^+ - 3CO$, 0.2), 406 ($M^+ - 4CO$, 0.1), 378 ($M^+ - 5CO$, 0.2), 350 ($M^+ - 6CO$, 1.2), 263 ($C_4H_2O_2S_2Fe_2$, 7), 176 (S_2Fe_2, 27), 144 (SFe_2, 13), 112 (Fe_2, 5), 88 (SFe, 36), 56 (Fe, 100). Anal. Calcd for $C_{14}H_{14}Fe_2O_{10}S_2$: C, 32.46; H, 2.72. Found: C, 32.25; H, 2.82.

(b) Methyl Vinyl Ketone. The $(\mu\text{-}HS)_2Fe_2(CO)_6$ (2.91 mmol) reacted with 1.22 mL (15 mmol) of $CH_2{=}CHC(O)CH_3$ in the presence of 0.5 mL of piperidine at −78 °C (0.5 h) and then at room temperature (18 h). Removal of solvent left a dark red oil which was chromatographed (silicic acid/CH_2Cl_2). Dichloromethane eluted a small orange band which gave a trace amount of a red solid which was not identified. Elution with 20% Et_2O/CH_2Cl_2 yielded a red band which, upon removal of solvent, gave 1.371 g (2.82 mmol, 97% yield) of $(\mu\text{-}MeC(O)CH_2CH_2S)_2Fe_2(CO)_6$ as a slightly air-sensitive, deep red oil. It was short-path distilled at 185 °C (0.6 mm) but gave a sample that was not suitable for analysis. It was rechromatographed two more times to obtain a sample that was analytically pure. IR (CCl_4): $\nu(C{=}O)$ 1723; terminal CO, 2074 (s), 2038 (vs), 2000 (vs), 1993 (vs) cm^{-1}. NMR ($CDCl_3$): δ 2.10, 2.14, 2.17 (all s, $CH_3C(O)CH_2CH_2S-$, 3 H), 2.25–2.82 (complex m, $CH_3C(O)CH_2CH_2S-$, 4 H); anti/syn ratio could not be determined. Mass spectrum: m/z (relative intensity): 402 ($M^+ - 3CO$, 0.7), 374 ($M^+ - 4CO$, 0.5), 346 ($M^+ - 5CO$, 0.7), 318 ($M^+ - 6CO$, 3.6), 247 ($C_4H_7OS_2Fe_2$, 9), 176 (S_2Fe_2, 46), 144 (SFe_2, 30), 112 (Fe_2, 15), 88 (SFe, 18), 56 (Fe, 70). Anal. Calcd for $C_{14}H_{14}Fe_2O_8S_2$: C, 34.59; H, 2.90. Found: C, 34.05; H, 2.88.

(c) *trans*-3-Penten-2-one: a reaction of 2.91 mmol of $(\mu\text{-}HS)_2Fe_2(CO)_6$, 1.46 mL (15 mmol) of *trans*-3-penten-2-one, and 0.5 mL of piperidine. The brown oil which remained was subjected to filtration chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded a red oil (1.27 g) that was further purified by column chromatography (silicic acid/CH_2Cl_2). Dichloromethane/pentane (3/1, v/v) eluted a yellow band (trace of brown solid, not identified), an orange band (0.118 g of red oil, mixture (by NMR) of product and organic impurities), and a red band which yielded 0.928 g (1.81 mmol, 62% yield) of $[\mu\text{-}CH_3C(O)CH_2C(CH_3)HS]_2Fe_2(CO)_6$ as a slightly air-sensitive, red oil, identified as a mixture of two isomers of **4** in 2.3/1 e,a/e,e ratio. IR: $\nu(C{=}O)$ 1715; terminal CO, 2071 (s), 2035 (vs), 1990 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.10, 2.13 (both s, a,e isomer, $C(O)CH_3$), 2.15 (s, e,e isomer, $C(O)CH_3$), 3.0–2.46 (m), 1.39–1.31 (m), 1.13 (d, J = 6.4 Hz) $[HC(CH_3)CH_2]$. Mass spectrum: m/z (relative intensity) 430 ($M^+ - 3CO$, 56), 402 ($M^+ - 4CO$, 14), 374 ($M^+ - 5CO$, 14), 346 ($M^+ - 6CO$, 100), 261 ($Fe_2S_2OC_5H_9$, 42), 176 (Fe_2S_2, 70), 144 (Fe_2S, 14), 112 (Fe_2, 14), 88 (SFe, 84), 56 (Fe, 56). Anal. Calcd for $C_{16}H_{18}Fe_2O_8S_2$: C, 37.38; H, 3.53. Found: C, 37.46; H, 3.68.

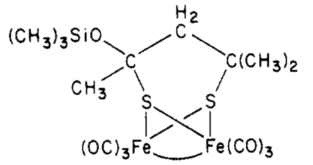
(d) 2-Cyclohexenone: a reaction of 2.91 mmol of **2**, 1.5 mL (15 mmol) of 2-cyclohexenone, and 0.5 mL of piperidine. The brown oil obtained was subjected to filtration chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded a red oil. Column chromatography (silicic acid/CH_2Cl_2) of this oil gave a minor orange band (not identified) and a red band which yielded 1.09 g (2.02 mmol, 70% yield) of an air-stable, red glassy solid, mp 102 °C dec, identified as **5**. IR: $\nu(C{=}O)$ 1710; terminal CO, 2078 (s), 2044 (vs), 1995 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.5–1.4 (m). $^{13}C\{^1H\}$ (C_6D_6, 67.9 MHz): δ_C 23.5, 33.7, 35.4, 39.5, 48.6, 49.3 (ring carbons), 204.3, 204.8, 205.1 (organic CO, e,e and e,a isomers), 208.6 (s, CO). Mass spectrum: m/z (relative intensity) 454 ($M^+ - 3CO$, 3), 426 ($M^+ - 4CO$, 3), 398 ($M^+ - 5CO$, 3), 370 ($M^+ - 6CO$, 20), 273 ($Fe_2S_2C_6H_9O$, 20), 176 (Fe_2S_2, 24), 112 (FeS, 10), 97 (C_6H_9O, 48), 56 (Fe, 100). Anal. Calcd for $C_{18}H_{18}Fe_2O_8S_2$: C, 40.17; H, 3.37. Found: C, 40.02; H, 3.61.

(e) Methyl crotonate: a reaction of 2.91 mmol of **2**, 1.6 mL (15 mmol) of the ester, and 0.5 mL of piperidine. The residual brown oil was subjected to filtration chromatography (silicic acid/CH_2Cl_2). Diethyl ether/CH_2Cl_2 (1/4, v/v) eluted a red-brown band which yielded a brown oil. Column chromatography (silicic acid/CH_2Cl_2) of this oil gave a red band which yielded 0.439 g (0.80 mmol, 28% yield) of $(\mu\text{-}CH_3OC(O)CH_2C(CH_3)HS)_2Fe_2(CO)_6$ as a slightly air-sensitive, viscous red oil. It was identified as a mixture of two isomers of **6** in 3.8/1 e,a/e,e ratio. IR: $\nu(C{=}O)$ 1727; terminal CO, 2060 (s), 2041 (vs), 1998 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 1.05–1.60 and 2.10–2.80 (both m, $HC(CH_3)CH_2$), 3.57 and 3.65 (both s, OCH_3). Mass spectrum: m/z (relative intensity) 462 ($M^+ - 3CO$, 6), 434 ($M^+ - 4CO$, 18), 406 ($M^+ - 5CO$, 30), 378 ($M^+ - 6CO$, 100), 277 ($Fe_2S_2C_5H_9O_2$, 36), 112 (Fe_2, 30), 88 (FeS, 18), 56 (Fe, 24). Anal. Calcd for $C_{16}H_{18}Fe_2O_{10}S_2$: C, 35.19; H, 3.32. Found: C, 34.66; H, 3.42.

(f) Diethyl maleate: a reaction of 2.91 mmol of **2** with 2.42 mL (15 mmol) of the diester and 0.5 mL of piperidine. The brown oil which remained was subjected to filtration chromatography (silicic acid/CH_2Cl_2). Dichloromethane/hexane (1/1, v/v) eluted a minor red-brown band which gave a brown oily residue (not identified); CH_2Cl_2 eluted a minor red band which gave 0.24 g of a red oil (not identified), and CH_2Cl_2/Et_2O (4/1, v/v) moved a red band which yielded a red oil (2.69 g). The diethyl maleate was removed from this oil by short-path distillation at reduced pressure (0.1 mmHg) using an oil bath not exceeding 75 °C. The remaining red oil was purified by column chromatography (silicic acid/CH_2Cl_2). Dichloromethane moved a red band which yielded 0.846 g (1.23 mmol, 42% yield) of a slightly air-sensitive, red oily solid identified as **7**. IR: $\nu(C{=}O)$ 1730; terminal CO, 2084 (s), 2050 (vs), 2010 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.42–1.21 (m, 12 H, CH_3), 4.34–4.07 (m, 8 H, OCH_2), 3.4–2.3 (m, 12 H, $CH_2{-}CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz): δ_C 13.7, 33.0, 38.9, 39.3, 47.3, 60.9, 61.1, 61.7, 62.2 (organic carbons), 169.6 (m, ester CO), 207.5 (s, CO). Mass spectrum (FD): M^+, 690; calcd, 690.26. Anal. Calcd for $C_{22}H_{26}Fe_2O_{14}S_2$: C, 38.28; H, 3.80. Found: C, 38.79; H, 4.01.

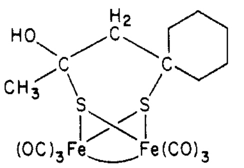
(g) Mesityl oxide: a reaction of 2.91 mmol of **2**, 1.7 mL (15 mmol) of the ketone, and 0.7 mL (5.03 mmol) of triethylamine. The residual brown oil was subjected to filtration chromatography (silicic acid/Et_2O). Diethyl ether eluted an orange band which gave 1.04 g (2.35 mmol, 81% yield) of **9** as a slightly air-sensitive, orange-brown solid with a pungent, unpleasant odor (resembling that described for thioacetone). IR: $\nu(OH)$ 3585 (s), 3360 (m, br); terminal CO, 2084 (s), 2043 (vs), 2000 (vs) cm^{-1}. A ketone carbonyl absorption was not observed.

Since an analytically pure sample of the alcohol could not be obtained, the trimethylsilyl ether was prepared for characterization. A 100-mL, three-necked, round-bottomed flask equipped with a stir bar, serum caps, and a 50-mL pressure-equalizing addition funnel was charged with 0.60 g (1.35 mmol) of the above alcohol and flushed with nitrogen. THF (30 mL) and three drops of trimethylchlorosilane were added. Hexamethyldisilazane (Petrarch) (6.74 mL, 32.3 mmol) and 5 mL of THF were added to the addition funnel. This solution was added dropwise to the alcohol solution. The resulting mixture then was stirred for 20 h. The solvent was removed leaving a black solid which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted an orange band which yielded 0.572 g (1.10 mmol, 82% yield) of an air-stable, red solid, mp 90–91 °C, after crystallization from pentane, identified as



IR: 1255 (Me_3Si); terminal CO, 2083 (s), 2045 (vs), 2012 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.21 (s, 9 H, $SiCH_3$), 1.63, 1.38, 1.24 (all s, 9 H, CH_3), 1.82 and 1.30 (AX quartet, J = 15.2 Hz, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 2.4 (q, J = 119 Hz, $SiCH_3$), 31.7 (q, J = 128 Hz, CH_3), 35.6 (q, J = 128 Hz, CH_3), 35.9 (q, J = 130 Hz, CH_3), 37.7 (s, CMe_2), 57.0 (t, J = 127 Hz, CH_2), 77.9 (s, $C(OSiMe_3)(Me)$), 207.9 and 208.2 (both s, CO). Mass spectrum: m/z (relative intensity) 516 (M^+, 1), 460 ($M^+ - 2CO$, 3), 432 ($M^+ - 3CO$, 8), 376 ($M^+ - 5CO$, 23), 348 ($M^+ - 6CO$, 81), 258 ($Fe_2S_2C_6H_{10}$, 20), 176 (Fe_2S_2, 44), 172 ($C_{12}H_{20}OSi$, 47), 144 (Fe_2S, 10), 112 (Fe_2, 24), 73 ($SiMe_3$, 100), 56 (Fe, 100). Anal. Calcd for $C_{15}H_{20}Fe_2O_7S_2Si$: C, 34.90; H, 3.91. Found: C, 34.89; H, 3.97.

(h) Cyclohexylideneacetone: a reaction of 2.91 mmol of 2, 3.0 g (16 mmol) of cyclohexylideneacetone[17] (as a mixture of α,β and β,γ isomers, 74% α,β by ^1H NMR), and 0.5 mL of piperidine. The brown oil obtained was subjected to filtration chromatography (silicic acid/pentane). Pentane/CH_2Cl_2 (1/1, v/v) eluted a minor brown band (not collected), and CH_2Cl_2 eluted a red band which gave 1.48 g of a red oil. This was applied to column chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded 1.04 g (2.15 mmol, 74% yield) of a red tar identified as



IR: ν(OH) 3579 (s), 3350 (s, br); terminal CO, 2085 (s), 2055 (s), 2015 (s) cm^{-1}.

To facilitate the characterization of this alcohol, the trimethylsilyl ether was prepared.

To 1.0 g (2.06 mmol) of the above alcohol in 40 mL of THF were added four drops of Me_3SiCl and 8.51 mL (40.8 mmol) of hexamethyldisilazane (Petrarch). The reaction mixture was stirred for 20 h. Removal of the solvent left a brown tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.50 g (0.90 mmol, 44% yield) of an air-stable, red solid identified as the Me_3Si ether of the above alcohol, mp 85–86 °C, after crystallization from pentane. Further elution with Et_2O/CH_2Cl_2 (1/4, v/v) moved a red band which gave 0.274 g (0.57 mmol, 28% yield) of the starting alcohol. Identification of the silylated product was based on the following data. IR: 1253 (Me_3Si); terminal CO, 2075 (s), 2037 (vs), 2000 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.20 (s, 9 H, $SiCH_3$), 2.06, 1.15 (AXq, J = 15.0 Hz, 2 H, CH_2), 1.24–1.63 (m, 13 H, ring protons and CH_3). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 2.29 (q, J = 119 Hz, $SiCH_3$), 21.8 (t, J = 127 Hz, CH_2), 22.2 (t, J = 127 Hz, CH_2), 25.7 (t, J = 130 Hz, CH_2), 35.6 (q, J = 128 Hz, CH_3), 39.9 (t, J = 126 Hz, CH_2), 41.4 (s, $\overline{CCH_2CH_2CH_2CH_2}$), 43.3 (t, J = 113 Hz, CH_2), 54.9 (t, J = 127 Hz, CH_2), 77.7 (s, $CMe(OSiMe_3)$), 208.0 and 208.3 (both s, CO). Mass spectrum: m/z (relative intensity) 500 ($M^+ - 2CO$, 1), 472 ($M^+ - 3CO$, 8), 444 ($M^+ - 4$ CO, 1), 416 ($M^+ - 5CO$, 32), 388 ($M^+ - 6CO$, 87), 298 ($Fe_2S_2C_9H_{14}$, 31), 212 ($C_{12}H_{24}OSi$, 100), 176 (Fe_2S_2, 1), 144 (Fe_2S, 7), 112 (Fe_2, 8), 73 ($SiMe_3$, 8), 56 (Fe, 3). Anal. Calcd for $C_{12}H_{24}Fe_2O_7S_2Si$: C, 38.86; H, 4.35. Found: C, 39.01; H, 4.41.

(i) 5-Methyl-4-hepten-3-one: a reaction of 2.91 mmol of 2, 30 mmol of 5-methyl-4-hepten-3-one[18] (6.10 g of a mixture of α,β and β,γ isomers, 62% α,β by ^1H NMR), and 0.5 mL of piperidine.

The red oil which was obtained was subjected to filtration chromatography (silicic acid/CH_2Cl_2) twice which gave a red oil, containing product, extremely contaminated with the starting ketone.

Since we were unable to purify the alcohol product, the trimethylsilyl ether was prepared. To the above red oil in 40 mL of THF was added four drops of Me_3SiCl, and 8.5 mL (40.8 mmol) of hexamethyldisilazane. The reaction mixture was stirred for 45 h. Removal of the solvent left a brown oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted an orange band which gave 0.49 g (0.90 mmol, 31% yield based on $S_2Fe_2(CO)_6$) of an air-stable, red solid, mp 58–61 °C, after crystallization from pentane. It was identified as a 1:1 mixture of diastereomers of **10**. IR: 1254 (Me_3Si); terminal CO, 2067 (s), 2030 (vs), 1999 (s), 1992 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.21, 0.22 (both s, 9 H, $SiCH_3$), 8.7–2.0 (m, 15 H, all other protons). Mass spectrum: m/z (relative intensity) 404 ($M^+ - 5CO$, 5), 376 ($M^+ - 6CO$, 32), 286 ($Fe_2S_2C_8H_{14}$, 32), 176 (Fe_2S_2, 15), 144 (Fe_2S, 15), 112 (Fe_2, 3), 88 (FeS, 2), 73 ($SiMe_3$, 100), 56 (Fe, 16). Anal. Calcd for $C_{17}H_{24}Fe_2O_7S_2Si$: C, 37.51; H, 4.44. Found: C, 37.60; H, 4.40.

2. Products from Acetylenes. (a) Dimethyl acetylenedicarboxylate: a reaction of 2.91 mmol of 2, 1.84 mL (15 mmol) of the acetylene diester, and 0.7 mL of triethylamine. The brown tar which remained after removal of volatiles was subjected to filtration chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded 0.96 g (1.97 mmol, 68% yield) of an air-stable, red solid, mp 119–120 °C, after crystallization from CH_2Cl_2/pentane, identified as **15**. IR: ν(C=O) 1735; terminal CO, 2093 (s), 2055 (vs), 2020 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.77 (s, 6 H, OCH_3), 3.71 (s, 2 H, CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 53.1 (q, J = 148 Hz, CH_3), 54.9 (d, J = 147 Hz, CH), 169 (s, ester carbonyl), 206.9 (s, CO). Mass spectrum: m/z (relative intensity) 432 ($M^+ - 2CO$, 1), 404 ($M^+ - 3CO$, 1), 376 ($M^+ - 4CO$, 4), 348 ($M^+ - 5CO$, 6), 320 ($M^+ - 6CO$, 41), 176 (Fe_2S_2, 100), 144 (Fe_2S, 8), 112 (Fe_2, 4), 88 (FeS, 4), 56 (Fe, 14). Anal. Calcd for $C_{12}H_8Fe_2O_{10}S_2$: C, 29.53; H, 1.65. Found: C, 29.68; H, 1.70.

(b) Methyl propiolate: a reaction of 2.91 mmol of 2, 1.3 mL (15 mmol) of methyl propiolate, and 0.5 mL of piperidine. The brown oil obtained was filtered through a pad of silica gel (Fisher, 200 mesh). Removal of the solvent from the red filtrate left a red oil which was subjected to column chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded 0.589 g (1.37 mmol, 47% yield) of **13a** as a slightly air-sensitive, red oil. IR: ν(C=O) 1734; terminal CO, 2065 (s), 2024 (vs), 1996 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 3.00 (d, J = 7.2 Hz, 2 H, CH_2), 3.63 (s, 3 H, OCH_3), 5.07 (t, J = 7.2 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 47.4 (t, J = 131 Hz, CH_2), 52.0 (q, J = 147 Hz, OCH_3), 72.6 (d, J = 161 Hz, S_2CH), 168.4 (s, ester CO), 208.2 and 208.4 (both s, CO). Mass spectrum: m/z (relative intensity) 402 ($M^+ - CO$, 1), 374 ($M^+ - 2CO$, 19), 346 ($M^+ - 3CO$, 18), 318 ($M^+ - 4CO$, 17), 290 ($M^+ - 5CO$, 25), 262 ($M^+ - 6CO$, 100), 176 (Fe_2S_2, 74), 144 (Fe_2S, 22), 112 (Fe_2, 2), 56 (Fe, 7). Anal. Calcd for $C_{10}H_6Fe_2O_8S_2$: C, 27.93; H, 1.41. Found: C, 28.32; H, 1.59.

(c) 3-Butyn-2-one: a reaction of 2.91 mmol of 2, 1.17 mL (15 mmol) of the ketone, and 0.5 mL of piperidine. The brown oil which remained was taken up in CH_2Cl_2 and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to column chromatography (silicic acid/CH_2Cl_2). Dichloromethane eluted a red band which yielded 0.533 g (1.29 mmol, 44% yield) of the **13b** as an air-stable, red solid, mp 90–91 °C, after crystallization from pentane/CH_2Cl_2. IR: ν(C=O) 1716; terminal CO, 2079 (s), 2039 (vs), 1996 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 2.10 (s, 3 H, CH_3), 3.08 (d, J = 6.5 Hz, 2 H, CH_2), 5.02 (t, J = 6.5 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 30.0 (q, J = 128 Hz, CH_3), 56.3 (t, J = 128 Hz, CH_2), 72.3 (d, J = 160 Hz, CH), 201.9 (s, ketonic CO), 208.0 and 208.4 (both s, CO). Mass spectrum: *m/z* (relative intensity) 358 ($M^+ - 2CO$, 10), 330 ($M^+ - 3CO$, 10), 302 ($M^+ - 4CO$, 5), 274 ($M^+ - 5CO$, 10), 246 ($M^+ - 6CO$, 25), 176 (Fe_2S_2, 45), 144 (Fe_2S, 15), 112 (Fe_2, 5), 88 (FeS, 10), 56 (Fe, 100). Anal. Calcd for $C_{10}H_6Fe_2O_7S_2$: C, 29.01; H, 1.46. Found: C, 29.12; H, 1.57.

(d) 3-Pentyn-2-one: a reaction of 2.91 mmol of **2**, 1.23 mL (15 mmol) of 3-pentyn-2-one,[17] and 0.5 mL of piperidine. The brown oil which was obtained was taken up in CH_2Cl_2 and filtered through a pad of silicic acid. Removal of the solvent left a red oil which was subjected to column chromatography (silicic acid/CH_2Cl_2). Pentane/CH_2Cl_2 (2/1, v/v) eluted a minor brown band which was not collected, followed by a red band. The silicic acid was removed from the column, and the red band was extracted from it with CH_2Cl_2. Removal of the solvent yielded 0.508 g (1.21 mmol, 42% yield) of **13c** as a slightly air-sensitive red oil. IR: ν(C=O) 1710; terminal CO, 2080 (s), 2040 (vs), 2011 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.89 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 3.21 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 30.7 (q, J = 128 Hz, CH_3), 38.1 (q, J = 132 Hz, CH_3), 62.7 (t, J = 128 Hz, CH_2), 82.3 (s, S–C–S), 202.2 (s, ketonic CO), 208.1 and 208.2 (both s, CO). Mass spectrum: *m/z* (relative intensity) 372 ($M^+ - 2CO$, 8), 344 ($M^+ - 3CO$, 12), 316 ($M^+ - 4CO$, 12), 288 ($M^+ - 5CO$, 12), 260 ($M^+ - 6CO$, 72), 176 (S_2Fe_2, 100), 144 (SFe_2, 28), 112 (Fe_2, 16), 88 (SFe, 4), 56 (Fe, 100). Anal. Calcd for $C_{11}H_8Fe_2O_7S_2$: C, 30.87; H, 1.88. Found: C, 30.80; H, 2.01.

X-ray Data Collection. Red crystals of (μ-$CH_3C(O)CH_2CHS_2$)$Fe_2(CO)_6$, suitable for an X-ray crystal study, were obtained from pentane/CH_2Cl_2. The systematic absences and the $2/m$ diffraction symmetry were consistent with the space groups Cc and $C2/c$; the centrosymmetric one was chosen and later confirmed by the successful refinement of the structure. Accurate cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections, in the range 14.0° $\leq 2\theta \leq$ 36.5°, which were accurately centered on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation. See Table II for pertinent crystal data and intensity collection details.

Intensity data were collected on the CAD-4 instrument in the bisecting mode by employing the ω-2θ scan technique. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess crystal decomposition or movement. No significant variation was noted in these standards so no correction was applied. The 2781 unique reflections were processed in the usual way[20] using a value of 0.04 for p, giving rise to 1593 observations ($F_o^2 \geq 3\sigma(F_o^2)$), which were used in subsequent calculations. An absorption correction was applied to the data by using Gaussian integration.[21]

Structure Solution and Refinement. The Fe and S positions were obtained by using MULTAN-80,[22] and all other atoms were obtained by subsequent least-squares and difference Fourier calculations. Atomic scattering factors for hydrogen,[23] and the other atoms[24] were taken from the usual tabulations; anomalous dispersion terms[25] for Fe and S were included in the calculation of F_c. All hydrogen atoms were located and were input to the least-squares cycles as fixed contributions in their idealized positions using C–H distances of 0.95 Å. The hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than the equivalent isotropic B of their attached carbon atom. All other atoms were refined anisotropically.

Refinement by full-matrix techniques converged at R = 0.040 and R_w = 0.047. On the final difference Fourier map the highest peak was 0.22 e Å^{-3}, and the top ten residuals were located at various points over the molecule, mainly in the vicinities of the Fe and S atoms; by comparison, carbon atoms on earlier maps had intensities between 1.8 and 2.5 e Å^{-3}. The final positional and isotropic thermal parameters of the refined atoms are given in Table III. Tables of anisotropic thermal parameters and idealized hydrogen positions and a listing of observed and calculated structure amplitudes used in the refinements are available.[26]

Acknowledgment. We are grateful to the National Science Foundation for support of the work carried out at MIT and to the University of Alberta and the Natural Sciences and Engineering Research Council of Canada for support of the structural study, also to the MIT Mass Spectrometry Facility (supported by NIH Division of Research Resources, Grant No. RR00317; K. Biemann, principal investigator) for mass spectra, and to Dr. R. G. Ball of the University of Alberta Structure Determination Laboratory for collection of the X-ray data.

Registry No. 1, 69480-73-5; **2a**, 102517-77-1; **2b**, 102517-78-2; **2c**, 102517-79-3; *anti*-**4**, 83649-94-9; *syn*-**4**, 83708-79-6; **5**, 102517-84-0; *anti*-**6**, 102436-41-9; *syn*-**6**, 102517-85-1; **7**, 102436-42-0; **9**, 83649-95-0; **10**, 102436-43-1; **11** (isomer 1), 102518-91-2; **11** (isomer 2), 102436-44-2; **13a**, 83649-99-4; **13b**, 83650-00-4; **13c**, 83650-01-5; **15**, 102517-86-2; (μ-S_2)$Fe_2(CO)_6$, 97093-65-7; *anti*-(μ-$NCCH_2CH_2S$)$_2Fe_2(CO)_6$, 102517-80-6; *syn*-(μ-$NCCH_2CH_2S$)$_2Fe_2(CO)_6$, 102517-81-7; *anti*-(μ-$CH_3O_2CCH_2CH_2S$)$_2Fe_2(CO)_6$, 80125-18-4; *syn*-(μ-$CH_3O_2CCH_2CH_2S$)$_2Fe_2(CO)_6$, 80080-63-3; *anti*-(μ-MeC(O)CH_2CH_2S)$_2Fe(CO)_6$, 102517-82-8; *syn*-(μ-MeC(O)CH_2CH_2S)$_2Fe_2(CO)_6$, 102517-83-9; (μ-SC(CH_3)(OH)$\mathrm{CH_2\overline{CCH_2CH_2CH_2CH_2C}H_2S}$)$Fe_2(CO)_6$, 83649-97-2; ($\mu$-SC($CH_3$)($OSiMe_3$)$\mathrm{CH_2\overline{CCH_2CH_2CH_2CH_2C}H_2S}$)$Fe_2(CO)_6$, 102492-32-0; $CH_2{=}CHCO_2CH_3$, 96-33-3; $CH_2{=}CHC(O)CH_3$, 78-94-4; H_2S, 7783-06-4; *trans*-3-penten-2-one, 3102-33-8; 2-cyclohexenone, 930-68-7; methyl crotonate, 18707-60-3; diethyl maleate, 141-05-9; mesityl oxide, 141-79-7; cyclohexylideneacetone, 874-68-0; 5-methyl-4-hepten-3-one, 1447-26-3; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; 3-butyn-2-one, 1423-60-5; 3-pentyn-2-one, 7299-55-0; acrylonitrile, 107-13-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen parameters, and observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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