

Reactions of Dithio Esters and O-Alkyl Thio Esters with Diiron Nonacarbonyl. Unexpectedly Different Products Formed from RC(S)OR' and HC(S)OR'

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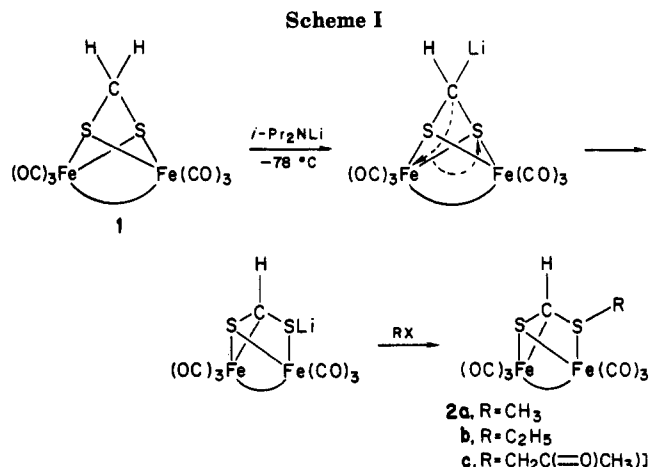
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Dithioformate esters, formed in situ by reaction of LiBEt_3H with CS_2 followed by addition of an alkyl halide, react with $\text{Fe}_2(\text{CO})_9$ to give 1:1 $\text{HCS}_2\text{R}'/\text{Fe}_2(\text{CO})_6$ complexes of type 2. Similar complexes in which the OR' group is coordinated to Fe, 5, are formed in reactions of $\text{RC}(\text{S})\text{OR}'$ with $\text{Fe}_2(\text{CO})_9$. However, reaction of $\text{HC}(\text{S})\text{OEt}$ with $\text{Fe}_2(\text{CO})_9$ gives a product of type $[\text{HCSOR}]_2\text{Fe}_2(\text{CO})_6$. This product, a red-brown solid, crystallizes in the space group $P\bar{1}$ with $a = 8.237(1) \text{ \AA}$, $b = 9.448(2) \text{ \AA}$, $c = 6.392(2) \text{ \AA}$, $\alpha = 107.31(2)^\circ$, $\beta = 104.59(2)^\circ$, $\gamma = 97.18(1)^\circ$, $V = 448.7 \text{ \AA}^3$, and $Z = 1$. On the basis of 1533 unique observations and 109 parameters varied, the structure was refined by full-matrix, least-squares techniques to $R = 0.029$ and $R_w = 0.039$. The two Fe centers are not bound directly to each other but are bridged by the two thio ester groups. Each group is π bonded through its C=S moiety to a different metal and is then coordinated to the other metal via a dative bond from sulfur. The oxygen atoms of these ligands are aimed away from the bridging positions. A rationale for the two different types of products obtained from the reactions of $\text{HC}(\text{S})\text{OEt}$ and $\text{RC}(\text{S})\text{OEt}$ with $\text{Fe}_2(\text{CO})_9$ is presented.

Introduction

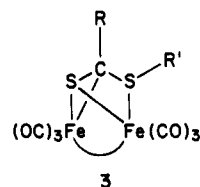
Several research groups have studied the interaction of various organic thiocarbonyl compounds with iron carbonyls. Among the thiocarbonyl compounds examined were thioketones,¹ thio esters,^{2,5b} dithio esters,³ thioketenes,⁴ thioamides,⁵ xanthates,⁶ trithiocarbonates,⁷ dithiochloroformates,^{8a} and *N,N*-dialkyl thiocarbamoyl chlorides.⁸ In many of these reactions cleavage of C-S bonds was accompanied by formation of diiron hexacarbonyl complexes with bridging chlorides.⁸

In a recent communication⁹ we reported the formation of dithioformate ester/ $\text{Fe}_2(\text{CO})_6$ complexes, 2, by deprotonation of 1 and alkylation of the resulting sulfur-centered anion (Scheme I). Such dithioformate complexes, we expected, also should be more directly accessible by the interaction of alkyl dithioformates with $\text{Fe}_2(\text{CO})_9$. We report here the results of our investigation of this possibility as well as of related work in which the reactions of O-alkyl monothio esters with $\text{Fe}_2(\text{CO})_9$ were studied.



Results and Discussion

Patin and his co-workers³ had shown previously that dithio esters, $\text{RC}(\text{S})\text{SR}'$ ($\text{R}, \text{R}' = \text{alkyl}$) react with $\text{Fe}_2(\text{CO})_9$ to give complexes of the type 3. However, simple alkyl



dithioformates are not readily available as starting materials for such reactions. When synthesized, they are isolated as trimers with the trithiane structure.^{10,11} We have found that alkyl dithioformates may be prepared very simply in solution by reaction of LiBEt_3H with CS_2 , followed by reaction of the dithioformate anion with an alkyl

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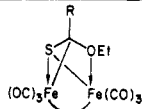
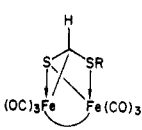
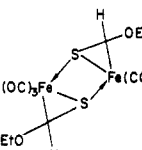
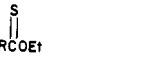
(8) (a) Dean, W. K. *J. Organomet. Chem.* 1977, 135, 195. (b) Dean, W. K.; Vanderveer, D. G. *J. Organomet. Chem.* 1978, 144, 65.

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Table I. NMR Data^a

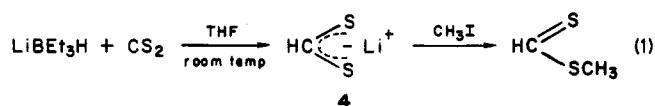
compd type	R	$\delta_{\text{C}}(\text{C}=\text{S})$	$\delta_{\text{C}}(\text{C}=\text{O})$	$\delta_{\text{H}}(\text{HC}(\text{s}))$
	CH ₃	122.7	212.1 (br)	
	C ₂ H ₅	128.8	212.1 (br)	
	CH ₃	55.4 (d, J = 188 Hz)	211.2 (br)	3.89
	C ₂ H ₅	52.2 (d, J = 188 Hz)	211.3 (br)	3.97
		114.3 (d, J = 187 Hz)	210.1 (br)	7.18
			207.9 (br)	
	CH ₃	218.8		
	C ₂ H ₅	224.4		
	H	206.3 (d, J = 202 Hz)		9.76

^a Measured in CDCl₃ solution. In parts per million from from internal tetramethylsilane. ^b Data from ref 9.

Table II. Summary of Crystal Data and Details of Intensity Collection for [HC(S)OEt]₂Fe₂(CO)₆

compd	[HC(S)OEt] ₂ Fe ₂ (CO) ₆
fw	460.0
space group	P $\bar{1}$ (No. 2)
a, Å	8.237 (1)
b, Å	9.448 (2)
c, Å	6.392 (2)
α , deg	107.31 (2)
β , deg	104.59 (2)
γ , deg	97.18 (1)
V, Å ³	448.7
ρ_{calcd} , g/cm ³	1.702
radiatn	Mo K α , $\lambda = 0.71069$ Å ⁻¹
detector aperture, mm	4 × (2.00 + 1.00 tan θ)
2 θ limits, deg	0.1 ≤ 2 θ ≤ 55.0
scan type	$\omega/2\theta$
scan width, deg	(0.65 + 0.347 tan θ) in ω
bkgd	25% on low- and high-angle sides
reflectns obsd	1533 ($\pm h, \pm k, l$)
abs coeff μ , cm ⁻¹	18.723
cryst dims, mm	0.10 × 0.09 × 0.25
range in trans factors	0.813-0.867
final no. of parameters varied	109
error in abs of unit weight	1.266
R	0.029
R _w	0.039

iodide (eq 1).¹² When the light orange solution of anion

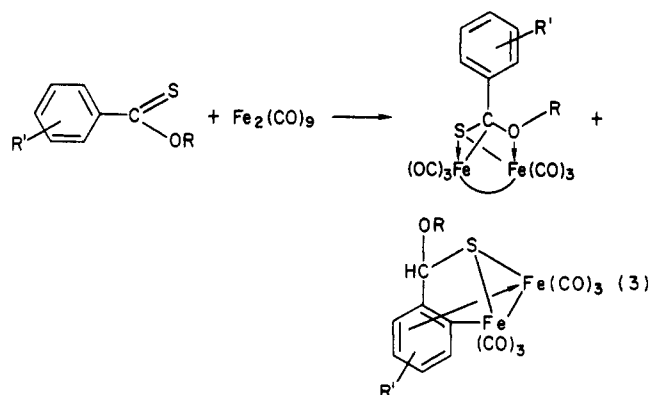


4 thus formed was treated with (η^5 -C₅H₅)Fe(CO)₂I, the η^1 -thioformate derivative (η^5 -C₅H₅)Fe(CO)₂SC(S)H was produced in 77% yield. Addition of methyl iodide to such a HCS₂Li solution, followed by cannulation into a THF

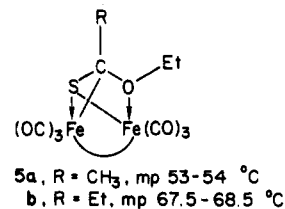
solution of Fe₂(CO)₉ gave complex 2a in 30% yield. The ethyl derivative 2b and the allyl derivative 2 (R = CH₂CH=CH₂) were made by the same procedure. Another example of coordinated alkyl dithioformates was reported recently by Schenk and Schwietzke,¹³ who used a preparative route somewhat similar to ours (eq 2).



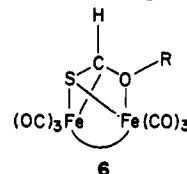
In an extension of the chemistry reported above, we have examined the reactions of *O*-alkyl thioformates, HC(S)OR, with Fe₂(CO)₉ and have obtained unexpected results. Alper and Foo² have investigated reactions of various *O*-methyl thiobenzoates with Fe₂(CO)₉ in benzene at room temperature. As shown in eq 3, two types of products were obtained.



We have found that the reactions of *O*-ethyl alkyl thioesters with Fe₂(CO)₉ (in toluene at 70 °C) gives complexes of type 5 as black-red, slightly air-sensitive solids in which the ethoxy group is coordinated to one of the iron atoms. In support of structure 5, the field desorption mass spectra of both complexes showed the molecular ion peaks for this constitution. Combustion analyses also agreed with this composition. The IR spectra (in pentane) of 5 showed seven bands in the terminal CO region, in harmony with the spectra observed previously for complexes of type 5 (R = Ph).² The ¹³C NMR spectra also suggested that structure 5 was correct. The CO ligand carbon atoms produced two poorly resolved signals very similar to those in the ¹³C NMR spectra of the alkyl dithioformate complexes 1 (Table I).



Patin et al.^{6b} have reported that the reactions of *O*-alkyl monothioformates, HC(S)OR (R = cholestanyl, cholesteryl), with Fe₂(CO)₉ give complexes of structure 6, but structural information was not given.



(12) The dithioformate anion was generated by earlier workers by the reaction of HCCl₃ with K₂S¹¹ and by the action of NaBH₄ on CS₂ in the presence of amines: Binder, H.; Diamantikos, W. Z. Naturforsch., B: Anorg. Chem., Org. Chem. 1983, 38B, 203.

(13) Schenk, W. A.; Schwietzke, T. Organometallics 1983, 2, 1905.

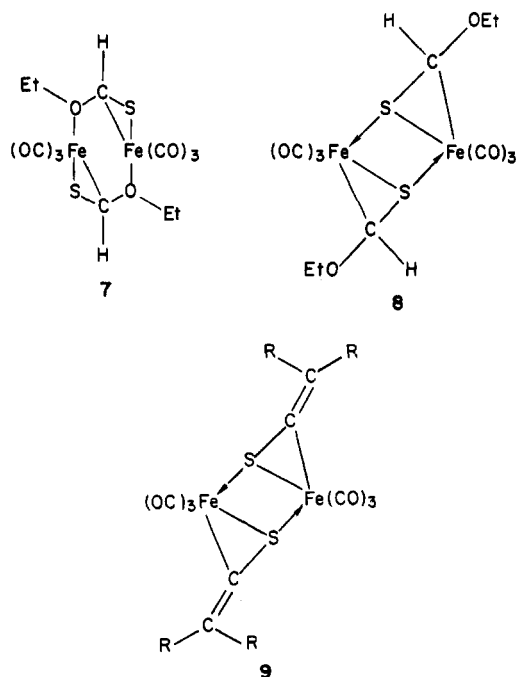
Table III. Atomic Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters^a

atom	x	y	z	B_{eq} , Å ²
Fe(1)	1775.4 (4)	857.6 (4)	2441.5 (6)	2.93
S(1)	-369.9 (8)	-1274.9 (7)	872 (1)	3.04
O(1)	807 (4)	3524 (3)	5167 (5)	7.04
O(2)	5056 (3)	2172 (3)	2130 (5)	5.93
O(3)	3330 (3)	272 (3)	6652 (4)	5.19
O(4)	2662 (2)	-2068 (2)	1747 (4)	3.61
C(1)	1140 (4)	2493 (3)	4096 (5)	4.18
C(2)	3798 (4)	1676 (3)	2292 (5)	3.90
C(3)	2723 (3)	472 (3)	5010 (5)	3.58
C(4)	1725 (3)	-1265 (3)	614 (5)	3.14
C(5)	2324 (4)	-3644 (3)	414 (6)	4.41
C(6)	3346 (6)	-4417 (4)	1798 (9)	7.86

^a Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits.

In the present study, a reaction of *O*-ethyl thioformate, HC(S)OEt, with diiron nonacarbonyl was carried out in toluene solution at 70 °C under nitrogen for 3 h. Removal of solvent left a red solid that was recrystallized from pentane at -20 °C to give a red-brown, air-stable crystalline solid, mp ~100 °C dec, in 54% yield. This product was quite different from those of type 5. In its IR spectrum (in pentane) only *three* bands were observed in the terminal CO region; in its ¹³C NMR spectrum there were *three* signals due to CO ligand carbon atoms. Of special significance was the field desorption mass spectrum of the product that showed $M^+ = 460$. This corresponds to a formulation of [HC(S)OEt]₂Fe₂(CO)₆. The combustion analysis agreed with this formulation as well.

Two structural possibilities, 7 and 8, seemed most likely for [HC(S)OEt]₂Fe₂(CO)₆. In 7 the ethoxy group is coordinated to iron; in 8 it is not. Structure 8 has precedent: reactions of dialkyl thioketenes with Fe₂(CO)₉ give products of type 9.^{4b}



An X-ray diffraction study of the HC(S)OEt/Fe₂(CO)₉ reaction product confirmed its structure to be of type 8.

Description of Structure. The X-ray structure determination of [HC(S)OEt]₂Fe₂(CO)₆ unambiguously establishes that the compound has a geometry corresponding to formulation 8, shown earlier, and not that of 7 (see

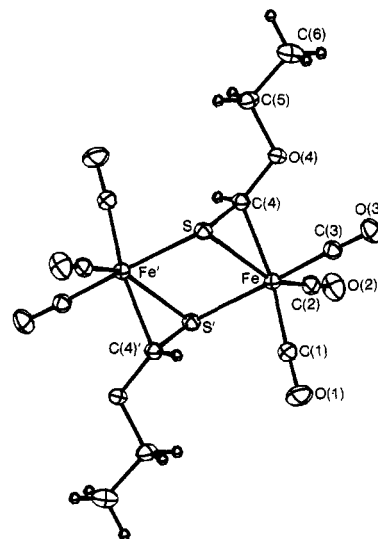


Figure 1. Perspective view of [HC(S)OEt]₂Fe₂(CO)₆ showing the numbering scheme. Primed atoms are related to unprimed ones by the inversion center at the center of the complex. Unlabeled atoms on C(4), C(5), and C(6) are hydrogens. Twenty percent thermal ellipsoids are shown except for the hydrogen atoms, which are shown artificially small.

Table IV. Selected Interatomic Distances (Å) for [HC(S)OEt]₂Fe₂(CO)₆

(i) Bond Lengths			
Fe-S	2.2810 (9)	C(1)-O(1)	1.122 (3)
Fe-S'	2.3146 (9)	C(2)-O(2)	1.125 (3)
S-C(4)	1.774 (3)	C(3)-O(3)	1.125 (4)
Fe-C(1)	1.813 (3)	C(4)-O(4)	1.374 (3)
Fe-C(2)	1.785 (3)	O(4)-C(5)	1.429 (3)
Fe-C(3)	1.794 (3)	C(5)-C(6)	1.479 (5)
Fe-C(4)	1.987 (3)		
(ii) Non-Bonded Contacts			
Fe-Fe'	3.483 (1)	Fe-C(4')	3.188 (3)
S-S'	2.999 (1)	H(C4)-C(1)'	2.59 ^a

^a H(C4) is the hydrogen atom on C(4).

Figure 1). In the observed geometry the two inversion-related iron centers are not bonded to each other but are held together by the bridging *O*-ethyl thioformate groups. The very long Fe-Fe separation of 3.483 (1) Å (see Table IV) is clearly outside the range of normal iron-iron interactions and can be contrasted, for example, to the Fe-Fe distances in four closely related, but iron-iron bonded complexes, which range from 2.485 (1) to 2.627 (1) Å.^{4b,9,14} Each bridging HC(S)OEt group is side-on bound through the C-S moiety to a different iron center and is attached to the other metal by a dative bond from the sulfur atom. These bridging groups each function as four-electron donors, giving each metal an 18-electron configuration and a quasioctahedral geometry, in which three of the coordination sites are occupied by terminal carbonyl groups, two by the side-on bond C-S moiety, and the last by the dative bond from the sulfur atom. Distortions from idealized octahedral geometry arise mostly from the strain imposed by the η²-bound C-S group, which results in an acute C(4)-Fe-S angle of 48.51 (7)° (see Table V).

The three carbonyl groups on each metal are chemically distinct, as shown by the spectroscopic data given earlier, and are normal for such groups. All are close to linear and have C-O distances that are essentially indistinguishable. However, there is a significant difference in the Fe-C

Table V. Selected Angles (deg) in $[\text{HC}(\text{S}(\text{OEt})_2)_2\text{Fe}_2(\text{CO})_6]$

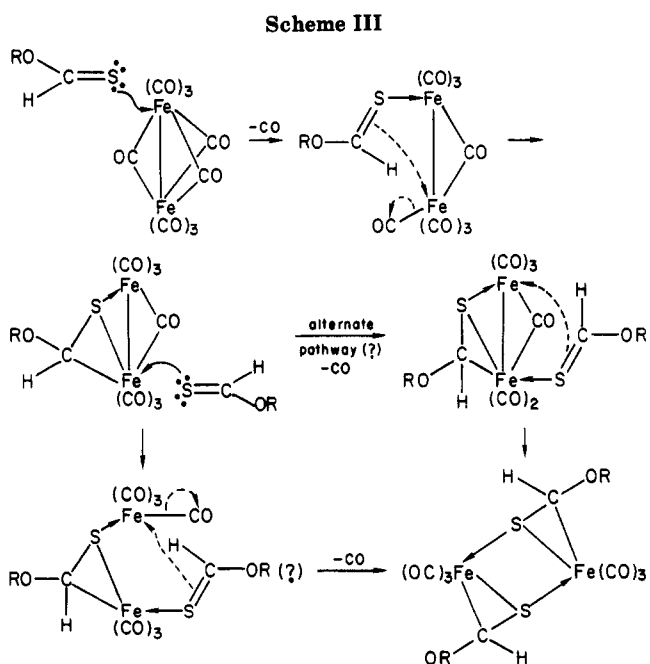
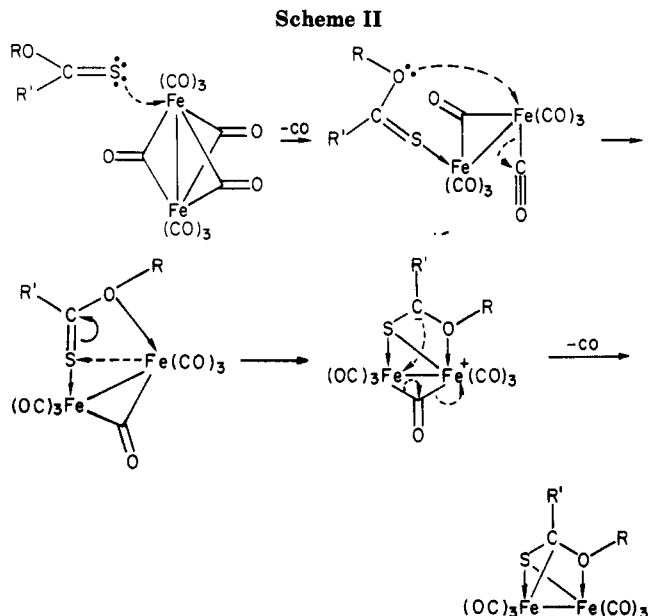
C(1)-Fe-C(2)	102.6 (1)	C(3)-Fe-C(4)	88.8 (1)	Fe-S-Fe'	98.55 (3)
C(1)-Fe-C(3)	90.7 (1)	C(3)-Fe-S	95.23 (9)	Fe-S-C(4)	57.06 (8)
C(1)-Fe-C(4)	161.2 (1)	C(3)-Fe-S'	176.05 (9)	Fe'-S-C(4)	101.67 (9)
C(1)-Fe-S	112.8 (1)	C(4)-Fe-S	48.51 (7)	Fe-C(4)-S	74.4 (1)
C(1)-Fe-S'	88.6 (1)	C(4)-Fe-S'	90.57 (8)	Fe-C(4)-O(4)	116.9 (2)
C(2)-Fe-C(3)	93.5 (1)	S-Fe-S'	81.45 (3)	S-C(4)-O(4)	115.4 (2)
C(2)-Fe-C(4)	96.2 (1)	Fe-C(1)-O(1)	177.5 (3)	C(4)-O(4)-C(5)	112.8 (2)
C(2)-Fe-S	143.3 (1)	Fe-C(2)-O(2)	178.0 (3)	O(4)-C(5)-C(6)	108.8 (3)
C(2)-Fe-S'	90.5 (1)	Fe-C(3)-O(3)	178.1 (3)		

distances in these groups, with that of Fe-C(1) (1.813 (3) Å) being longer than the other two (1.785 (3), 1.794 (3) Å). The longer distance is consistent with the higher trans influence of C(4) compared to sulfur. Such differences in carbonyl parameters have also been recognized in two other closely related molecules. In $(\text{SCSMe}_2)_2\text{Fe}_2(\text{CO})_6$ ¹⁴ the two carbonyl groups that are almost trans to the coordinated carbon of the SCSMe₂ group have Fe-C distances (1.795 (3), 1.811 (4) Å) that are significantly longer than the others (range 1.759 (3)-1.777 (3) Å), and in $[\text{HC}(\text{S})\text{SCH}_2\text{C}(\text{O})\text{Me}]_2\text{Fe}_2(\text{CO})_6$ ⁹ the analogous Fe-C distances are 1.810 (5) Å for the carbonyl group trans to carbon with the others ranging from 1.781 (6) to 1.798 (5) Å.

Within the *O*-ethyl thioformate ligand the C(4)-S distance, at 1.774 (3) Å, approaches that of a single bond (1.81 Å),¹³ showing the expected lengthening from a double bond, owing to its π -coordination to iron. The C(4)-O(4) distance (1.374 (3) Å) on the other hand displays some multiple-bond character and can be contrasted with the O(4)-C(5) distance of 1.429 (3) Å, which exactly corresponds to a normal single bond.¹⁵ Significantly, the oxygen atom of this group (O(4)) is not in a position to be coordinated to either metal and is in fact oriented away from the bridging position; we will return to this important detail later. Although the Fe-S-C(4) and Fe-C(4)-S angles (57.06 (8)° and 74.4 (1)°) are rather acute, they are not unexpected for the η^2 -coordination mode; all other angles are essentially as expected.

The present complex bears a remarkable resemblance to that of the thioketene-bridged dimer $[\text{SCC}_{10}\text{H}_{18}]_2\text{Fe}_2(\text{CO})_6$, reported recently by Behrens and co-workers.^{4a} Replacement of the thioketene unit by the *O*-ethyl thioformate ligand has led to only minor differences in the bonding parameters in the analogous parts of the molecules. Thus, the Fe-C(4) distance in our species (1.987 (3) Å) is close to that reported by Behrens et al. (2.010 (3) Å), both falling within the range previously reported for related species^{4b,9,14} (1.921 (3)-2.064 (9) Å). Similarly, the Fe-S distances in the two compounds are in close agreement and show that those involving the η^2 -bound C-S group (2.2810 (9) and 2.261 (1) Å^{4a}) are shorter than the dative S→Fe bonds (2.3146 (9) and 2.349 (1) Å^{4a}). Again these Fe-S contacts are normal, although they are at the longer end of those reported for the compounds above^{4b,9,14} (2.220 (3)-2.304 (1) Å); it seems that in the dimers containing Fe-Fe bonds the distances between iron and the sulfur atoms in the bridging groups tend to be shorter than those in which there are no Fe-Fe bonds.

The formation of complexes of type 5 in the reaction of $\text{ArC}(\text{S})\text{OEt}$ with $\text{Fe}_2(\text{CO})_9$ has been rationalized as shown in Scheme II.² However, the mechanism that leads to 8 is clearly different, although the first step, nucleophilic attack by sulfur at an iron atom of $\text{Fe}_2(\text{CO})_9$, very likely is the same. We believe that the difference in the two mechanisms can be related both to the preference of the



Fe(0) centers to coordinate to either the softer sulfur center or the C=S bond rather than to the harder oxygen atom, and to the steric bulk of R'. It is our contention that with $\text{R}'\text{C}(\text{S})\text{OR}$ molecules, the electronically favored second step (after nucleophilic attack of sulfur at an iron center) is coordination of the C=S π -bond at the second metal (see Scheme III). However, the result of such coordination can be seen in the structure of $[\text{HC}(\text{S}(\text{OEt})_2)_2\text{Fe}_2(\text{CO})_6]$ (Figure 1). In this structure, a rather short contact of 2.59 Å between the hydrogen atom on C(4) and C(1)' results. Clearly with R' groups bulkier than hydrogen, π -coordi-

(15) MacGillavry, C. H.; Rieck, G. D., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. III, Table 4.2.

nation of the C=S bond, with the ligand conformations observed in **8**, will not be possible owing to the highly unfavorable nonbonded contact that would result between the R' group and the carbonyl group C(1)'O(1)'. Of course, the R' substituent could be directed away from C(1)'O(1)'. However, this would result in unfavorable contacts between C(1)'O(1)' and the OEt moiety. Therefore, for R' groups bulkier than hydrogen (CH₃, Et, Ar) π -coordination by C=S is not possible so coordination by the harder oxygen atom results and other products are produced as shown in Scheme II. If this suggestion is correct, substitution of the oxygen atom in HC(S)OEt by the softer sulfur atom should tend to favor reaction via Scheme II, and in agreement with this, the compound [HC(S)SEt]Fe₂(CO)₆ has been shown to have a structure of type **2**, having both sulfur atoms coordinated to iron, in spite of having the small H substituent on carbon.⁹

When coordination of the RC(S)OEt group via the oxygen atom occurs (Scheme II), the ligand ultimately functions as a 6-electron donor, which together with the Fe-Fe bond and the carbonyl ligands gives the metals their favored 18-electron configurations. However, when π -coordination via the C=S moiety occurs the ligand functions as only a 4-electron donor, presumably giving the 1:1 adduct shown in Scheme III. This species is capable of coordinating an additional O-alkyl thio ester ligand to give, after carbonyl loss, the final 2:1 product without an accompanying metal-metal bond.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified, tank nitrogen. Tetrahydrofuran and toluene were distilled from sodium/benzophenone ketyl. Reagent-grade acetone, pentane, dichloromethane, and methylcyclohexane 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. Chromatography was done under atmospheric conditions; all solid products were recrystallized from deoxygenated solvents at -20 °C.

Infrared spectra were obtained by using a Perkin-Elmer Model 457A or Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either JEOL FX-90Q, Bruker 250 or Bruker 270 NMR spectrometers operating at 90, 250, and 270 MHz, respectively. ¹³C NMR spectra were obtained by using a Bruker 270 instrument operating at 67.9 MHz. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Field desorption mass spectra were obtained by using a MAT-731 instrument. Melting points were determined on analytically pure samples using a Büchi capillary melting point apparatus and are uncorrected.

Preparation of (μ -Alkyl dithioformate)diiron Hexacarbonyl Complexes. The preparation of the [HCS₂CH₃]Fe₂(CO)₆ complex is described in detail to illustrate the procedure used.

A 300-mL, three-necked, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 3.3 g (9.0 mmol) of Fe₂(CO)₉ and flushed with nitrogen. Subsequently, 50 mL of THF was added.

In a separate 100-mL, round-bottomed flask, 8 mL (8.0 mmol) of a 1 M LiBEt₃H solution (Aldrich) was added dropwise to 0.5 mL (8.0 mmol) of CS₂ (MCB) in 15 mL of THF. The reaction mixture immediately turned orange. It was stirred for 0.5 h, and then 1.0 mL (16.1 mmol) of MeI (Aldrich) was added. The resulting solution was cannulated into the Fe₂(CO)₉/THF solution, and the reaction mixture was refluxed gently for 1 h. Subsequently, the solvent was removed under reduced pressure, leaving a brown tar which was extracted with pentane/CH₂Cl₂ (4:1, v/v). The extracts were filtered through a pad of silicic acid. After removal of the solvent, the red oil that remained was applied to

filtration chromatography (silicic acid/pentane). Pentane/CH₂Cl₂ (9/1, v/v) eluted an orange band that yielded 0.90 g (2.42 mmol, 30% yield based on CS₂) of (μ -SCHSCH₃)Fe₂(CO)₆, **2a**, as a slightly air-sensitive red oil. Anal. Calcd for C₈H₄Fe₂O₆S₂: C, 25.83; H, 1.08. Found: C, 26.09; H, 1.16. IR (pentane) (terminal carbonyl region): 2076 (s), 2031 (vs), 2006 (vs), 1994 (s), 1982 (m), 1975 (m) cm⁻¹. ¹H NMR (CDCl₃, 90 MHz): δ 2.33 (s, 3 H, CH₃), 3.89 (s, 1 H, S₂CH). ¹³C NMR (CDCl₃): δ 35.4 (q, J = 141 Hz, CH₃), 55.4 (d, J = 188 Hz, S₂CH), 208.0 (br, CO), 211.2 (s, CO).

A similar reaction in which HCS₂C₂H₅ was formed in situ (8.0 mmol each of LiBEt₃H and CS₂; 16.1 mmol of C₂H₅I) and added to 9.0 mmol of Fe₂(CO)₉ in THF gave (μ -SCHSEt)Fe₂(CO)₆, **2b**, as a red oil (2.44 mmol, 30% yield). Anal. Calcd for C₉H₆Fe₂O₆S₂: C, 28.00; H, 1.57. Found: C, 28.31; H, 1.67. IR (pentane) (terminal carbonyl region): 2075 (s), 2027 (vs), 2003 (vs), 1992 (s), 1980 (m), 1974 (m) cm⁻¹. ¹H NMR (CDCl₃, 90 MHz): δ 1.25 (t, J = 7.3 Hz, CH₃), 2.63 (m, 2 H, SCH₂), 3.97 (s, 1 H, S₂CH). ¹³C NMR (CDCl₃): δ 11.8 (q, J = 128 Hz, CH₃), 46.2 (t, J = 141 Hz, SCH₂), 52.2 (d, J = 188 Hz, S₂CH), 208.8 (br, CO), 211.3 (s, CO). mass spectrum: m/z (relative intensity) 386 (M⁺, 15), 358 (M⁺ - CO, 12), 330 (M⁺ - 2CO, 29), 302 (M⁺ - 3CO, 24), 274 (M⁺ - 4CO, 29), 246 (M⁺ - 5CO, 67), 218 (M⁺ - 6CO, 89), 190 (Fe₂S₂CH₂, 39), 189 (Fe₂S₂CH, 46), 188 (Fe₂S₂C, 26), 176 (Fe₂S₂, 63), 144 (Fe₂S, 100), 112 (Fe₂, 24), 88 (FeS, 12), 56 (Fe, 61).

In another experiment, a THF solution of HCS₂CH₂CH=CH₂ was prepared in situ (8.0 mmol each of LiBEt₃H and CS₂; 16.1 mmol of CH₂=CHCH₂Cl). In the filtration chromatography, pentane eluted a small amount (0.127 g, 0.3 mmol) of (μ -CH₂=CHCH₂S)₂Fe₂(CO)₆, a red oil and a known compound.¹⁶ A 9:1 (v/v) pentane/CH₂Cl₂ solution eluted (μ -SCHSCH₂CH=CH₂)Fe₂(CO)₆, **2** (R = allyl), a slightly air-sensitive red oil (0.374 g, 0.94 mmol, 12% yield). Anal. Calcd for C₁₀H₆Fe₂O₆S₂: C, 30.18; H, 1.52. Found: C, 30.38; H, 1.60. IR: (CHCl₃) 1631 (m), 1424 (m), 1400 (w), 1155 (w), 1067 (w), 984 (s), 929 (s), 605 (s), 585 (s), 561 (s), 550 (s) cm⁻¹; terminal carbonyl region (pentane) 2078 (s), 2030 (vs), 2007 (vs), 1994 (s), 1983 (m), 1976 (m) cm⁻¹. ¹H NMR (CDCl₃, 270 MHz): δ 3.22 (d, J = 7.35 Hz, 2 H, SCH₂), 3.94 (s, 1 H, S₂CH), 5.33 (d, 1 H, J = 16.45 Hz, vinyl), 5.34 (d, 1 H, J = 10.33 Hz, vinyl), 5.71 (m, 1 H, CH=). ¹³C NMR (CDCl₃, 67.9 MHz): δ 52.0 (d, J = 187 Hz, S₂CH), 55.2 (t, J = 143 Hz, SCH₂), 121.9 (t, J = 159 Hz, =CH₂), 128.9 (d, J = 158 Hz, CH=), 208.5 (br, CO), 211.2 (s, CO). mass spectrum: m/z (relative intensity) 398 (M⁺, 3), 370 (M⁺ - CO, 3), 357 (M⁺ - C₃H₅, 67), 342 (M⁺ - 2CO, 6), 314 (M⁺ - 3CO, 11), 329 (M⁺ - C₃H₅ - CO, 15), 301 (M⁺ - C₃H₅ - 2CO, 6), 286 (M⁺ - 4CO, 14), 273 (M⁺ - C₃H₅ - 3CO, 4), 258 (M⁺ - 5CO, 45), 245 (M⁺ - C₃H₅ - 4CO, 7), 230 (M⁺ - 6CO, 100), 217 (M⁺ - C₃H₅ - 5CO, 21), 189 (Fe₂S₂CH, 58), 188 (Fe₂S₂C, 25), 176 (Fe₂S₂, 91), 144 (Fe₂S, 41), 112 (Fe₂, 11), 56 (Fe, 17).

Reaction between Cyclopentadienyliron Dicarboxylate and Lithium Dithioformate. A 100-mL, round-bottomed flask equipped with a stir bar and serum cap was flushed with nitrogen and charged with 15 mL of THF and 0.4 mL (6.6 mmol) of CS₂ (MCB). To this solution was added 4.0 mL (4.0 mmol) of a 1 M LiBEt₃H solution (Aldrich), and the resulting solution was stirred for 0.5 h. The dithioformate anion solution thus formed was cannulated into a solution of (η^5 -C₅H₅)Fe(CO)₂I [1.22 g (4.0 mmol)] in 50 mL of THF, and this mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure, leaving a red oil which was extracted with CH₂Cl₂. The extracts were filtered through a pad of silicic acid. After removal of the solvent, the residue was applied to a filtration chromatography funnel (silicic acid/pentane). Pentane/CH₂Cl₂ (1.4, v/v) eluted an orange band which yielded 0.78 g (3.07 mmol, 77% yield) of (η^5 -C₅H₅)Fe(CO)₂SC(S)H as a red-brown, air-stable solid, mp 61-63 °C after crystallization from CH₂Cl₂/pentane. Anal. Calcd for C₈H₆FeO₂S₂: C, 37.81; H, 2.38. Found: C, 37.89; H, 2.48. IR: (CHCl₃): 3058 (w), 2995 (m), 1425 (m), 1230 (s), 1016 (s), 841 (m), 730 (br), 600 (m), 567 (s), 534 (m) cm⁻¹. Terminal carbonyl region (pentane) 2051 (vs), 2010 (vs) cm⁻¹. ¹H NMR (CDCl₃, 90 MHz): δ 5.08 (s, 5 H, C₅H₅ ring), 11.27 (s, 1 H, HC(S)). ¹³C NMR (CDCl₃, 67.9 MHz): δ 85.5 (d, J = 183 Hz, C₅H₅), 210.5 (s, CO), 233.1 (d, J = 174 Hz, S₂CH). Mass spectrum: m/z

(relative intensity) 254 (M^+ , 2), 226 ($M^+ - CO$, 24), 198 ($M^+ - 2CO$, 43), 154 ($CpFeSH$, 9), 122 ($CpFeH$, 68), 121 ($CpFe$, 65), 56 (Fe , 100).

Reaction between *O*-Ethyl Thioformate and Diiron Nonacarbonyl. A 300-mL, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 3.0 g (8.25 mmol) of $Fe_2(CO)_9$ and flushed with nitrogen. Toluene (50 mL) and 0.45 g (5.0 mmol) of *O*-ethyl thioformate¹⁷ were added by syringe. The reaction mixture was stirred in an oil bath at 70 °C for 3 h. Subsequently, the solvent was removed under reduced pressure, leaving a red solid which was dissolved in pentane and filtered. The filtrate was concentrated and cooled to -20 °C. The crystals that formed were collected, washed with a small amount of pentane, and dried to yield 0.62 g (1.35 mmol, 54% yield based on $HC(S)OEt$) of $[\mu-SCH(OEt)]_2Fe_2(CO)_6$, **8**, as a red-brown, air-stable solid, mp ~100 °C dec. Anal. Calcd for $C_{12}H_{12}Fe_2O_8S_2$: C, 31.33; H, 2.63. Found: C, 31.53; H, 2.68. FD mass spectrum: $M^+ = 460$ (calcd for 8 460.04). IR: ($CHCl_3$) 2985 (s), 2940 (m), 2905 (w), 2890 (m), 1471 (w), 1445 (m), 1391 (m), 1290 (m), 1206 (w), 1166 (m), 1115 (sh), 1085 (vs), 1024 (m), 960 (m), 938 (m), 865 (m), 816 (w), 725 (m), 615 (s), 585 (s), 560 (s) cm^{-1} . Terminal carbonyl region (pentane) 2059 (s), 2011 (s), 1988 (s) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.31 (t, $J = 7.0$ Hz, CH_3), 4.05 (m, 2 H, OCH_2 ; collapses to AXq, δ 4.13 and 3.96 ($J_{gem} = 9.2$ Hz)), 7.18 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$): δ_C 14.8 (q, $J = 127$ Hz, CH_3), 72.5 (t, $J = 141$ Hz, OCH_2), 114.3 (d, $J = 187$ Hz, CH), 202.0, 207.9, 210.1 (all s, $Fe(CO)$).

Reaction between *O*-Ethyl Thio Esters and Diiron Nonacarbonyl. A 300-mL, three-necked, round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 3.0 g (8.25 mmol) of $Fe_2(CO)_9$ and flushed with nitrogen. Toluene (50 mL) and 0.73 g (7.0 mmol) of *O*-ethyl thioacetate¹⁸ were added by syringe, and the reaction mixture was heated at 70 °C in an oil bath for 30 min. Subsequently, the solvent was removed and the red oil that remained was taken up in pentane and filtered through a pad of silicic acid. The solvent was again removed and the red oil applied to a filtration chromatography funnel (silicic acid/pentane). Pentane eluted a minor red band of $S_2Fe_3(CO)_9$. Further elution with pentane moved a second orange-red band, which, after removal of solvent, yielded 0.80 g (2.08 mmol, 30% yield based on the thio ester) of $[\mu-SC(Me)OEt]Fe_2(CO)_6$, **5a**, as a black-red, slightly air-sensitive solid, mp 53–54 °C after crystallization from pentane. Anal. Calcd for $C_{10}H_8Fe_2O_7S$: C, 31.28; H, 2.10. Found: C, 31.21; H, 2.14. FD mass spectrum: $M^+ = 384$ (calcd for **5a** 383.93). IR: ($CHCl_3$) 2987 (m), 2912 (m), 1463 (m), 1442 (m), 1387 (s), 1371 (m), 1359 (m), 1168 (m), 1096 (w), 1067 (s), 1021 (s), 1010 (s), 913 (s), 896 (s), 823 (w), 725 (s), 628 (w), 613 (w), 608 (s), 580 (s), 552 (s) cm^{-1} . Terminal carbonyl region (pentane) 2074 (s), 2026 (vs), 2003 (s), 1997 (vs), 1981 (s), 1969 (vs), 1957 (s) cm^{-1} . 1H NMR ($CDCl_3$): δ 0.87 (t, $J = 7.1$ Hz, CH_3 of Et), 1.76 (s, 3 H, CH_3), 3.02 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ_C 12.4 (q, $J = 128$ Hz, CH_3), 33.9 (q, $J = 128$ Hz, CH_3), 71.3 (t, $J = 146$ Hz, OCH_2), 122.7 (s, SCO), 212.1, 208.9 (both broad, $Fe(CO)$).

The same procedure was used in the reaction of 8.25 mmol of $Fe_2(CO)_9$ and 0.83 g (7.0 mmol) of *O*-ethyl thiopropanoate¹⁸ in 50 mL of toluene (30 min at 70 °C).

The solvent was removed, and the red oil that remained was taken up in pentane and filtered through a pad of silicic acid. The solvent was again removed and the red oil subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band of $S_2Fe_3(CO)_9$. Pentane/ CH_2Cl_2 (10% CH_2Cl_2 by volume) eluted a second orange-red band, which, after removal of solvent, yielded 0.84 g (2.11 mmol, 30% yield based on the thioester) of $[\mu-SC(Et)OEt]Fe_2(CO)_6$, **5b**, as a black-red, slightly air-sensitive solid, mp 67.5–68.5 °C after crystallization from pentane. Anal. Calcd for $C_{11}H_{10}Fe_2O_7S$: C, 33.20; H, 2.53. Found: C, 33.33; H, 2.60. FD mass spectrum: $M^+ = 398$ (calcd for **5b** 397.95). IR: ($CHCl_3$) 2976 (m), 2941 (w), 1445 (m), 1385 (m), 1254 (w), 1207 (m), 1160 (m), 1142 (w), 1098 (m), 1066 (m), 1021 (m), 1010 (m), 907 (m), 830 (w), 721 (m), 662 (m), 621 (m), 584 (s), 554 (s) cm^{-1} . Terminal carbonyl region (pentane) 2072 (vs), 2025 (vs),

2003 (s), 1995 (vs), 1978 (s), 1967 (s), 1956 (s) cm^{-1} . 1H NMR ($CDCl_3$): δ 0.89 (t, $J = 7.1$ Hz, 6 H, CH_3), 1.55, 2.20, 2.83, 3.18 (all m, 4 H, methylene protons). ^{13}C ($CDCl_3$): δ 12.2 (q, $J = 127$ Hz, CH_3), 39.2 (t, $J = 130$ Hz, CH_2), 71.5 (t, $J = 145$ Hz, OCH_2), 128.8 (s, SCO), 212.1, 209.0 (both broad, $Fe(CO)$).

X-ray Data Collection. A suitable quality, red-brown crystal of $[HC(S)OEt]_2Fe_2(CO)_6$, which had been grown from pentane at -20 °C, was mounted on a glass fiber using epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 24 reflections in the range $8.0^\circ \leq 2\theta \leq 30.6^\circ$, which were accurately centered at 22 °C on an Enraf-Nonius CAD4 diffractometer using $Mo K\alpha$ radiation. The $\bar{1}$ diffraction symmetry and the lack of systematic absences were consistent with the space groups $P\bar{1}$ and $P\bar{1}$, the latter of which was ultimately established as the more probable one. A cell reduction¹⁹ failed to show the presence of a higher symmetry cell.

Intensity data were collected at 22 °C on the CAD4 diffractometer in the bisecting mode employing the ω -2 θ scan technique and using graphite-monochromated $Mo K\alpha$ radiation. 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 possible crystal decomposition or movement. No significant variation in these standards was noted so no correction was applied. A total of 2260 unique reflections were measured and processed in the usual manner²⁰ using a value of 0.04 for p . Of these, 1533 were considered to be observed and were used in subsequent calculations. See Table II for pertinent crystal data and details of intensity collection.

Structure Solution and Refinement. The structure was solved in the space group $P\bar{1}$, by using MULTAN 80²¹ to locate the Fe and S atoms and subsequent difference Fourier calculations to locate all other atoms. The dimer occupies the inversion center at the origin of the unit cell such that the two $[HC(S)OEt]Fe(CO)_3$ halves of the molecule are inversion related. Full-matrix, least-squares techniques were used for the refinements, utilizing the usual atomic scattering factors for hydrogen²² and the other atoms;²³ anomalous dispersion terms²⁴ for Fe and S were included in the calculation of F_c . The non-hydrogen atoms were all refined anisotropically. Hydrogens, although all were located, were not refined but were input to the least-squares program as fixed contributions in their idealized positions using C-H distances of 0.95 Å. These atoms were assigned isotropic thermal parameters of 1 \AA^2 greater than the equivalent isotropic thermal parameter of their attached atom. Absorption corrections were applied to the data by using Gaussian integration.²⁵

The structure, in space group $P\bar{1}$, refined to $R = 0.029$ and $R_w = 0.039$ ²⁶ based on 109 parameters varied and 1533 unique observations. On the final difference Fourier map the highest ten residuals were in the range 0.23–0.27 $e \text{ \AA}^{-3}$; this can be compared to peaks corresponding to carbon atoms on earlier Fourier maps that had intensities of ca. 4.0–6.0 $e \text{ \AA}^{-3}$. The alternate space group $P1$ was rejected owing to the satisfactory refinement in $P\bar{1}$; even the hydrogen atoms in this structure are clearly defined.

The positional parameters and the equivalent isotropic B 's of the non-hydrogen atoms are given in Table III; tables of anisotropic thermal parameters and hydrogen atom parameters and

(19) The cell reduction was performed by using a modification of TRACER II by S. L. Lawson. See: Lawson, S. L.; Jacobsen, R. A. "The Reduced Cell and Its Crystallographic Applications", Ames Laboratory Report IS-1141; USAEC: Iowa State University, Ames, IA, April 1965.

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(25) In addition to local programs, the following were used: FASTFO, an adapted version of Zalkin's FORADP by R. J. Dellaca; BUCILS, the least-squares program, adapted from the Northwestern program NUCLS; AGNOST, the absorption and extinction program from Northwestern University; ORFFE, for calculating bond lengths and angles and associated standard deviations by W. Busing and H. A. Levy; ORTEP, plotting program by L. K. Johnson.

(26) $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

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a listing of observed and calculated structure factor amplitudes are available.²⁷

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(27) Supplementary material.

Registry No. 2 (R = allyl), 91993-58-7; 2a, 85534-04-9; 2b, 85534-05-0; 5a, 91993-59-8; 5b, 91993-60-1; 8, 91993-61-2; (μ -CH₂=CHCH₂S)₂Fe₂(CO)₆, 74438-37-2; (η^5 -C₅H₅)Fe(CO)₂SC(S)H, 91993-62-3; (η^5 -C₅H₅)Fe(CO)₂I, 12078-28-3; S₂Fe₃(CO)₉, 22309-04-2; Fe₂(CO)₉, 15321-51-4; LiBEt₃H, 22560-16-3; CS₂, 75-15-0; MeI, 74-88-4; C₂H₅I, 75-03-6; CH₂=CHCH₂Cl, 107-05-1; CH₃C(S)OEt, 926-67-0; C₂H₅C(S)OEt, 924-45-8; HC(S)OEt, 29392-46-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen parameters, and observed and calculated structure amplitudes (8 pages). Ordering information is given on any current masthead page.

Silacyclopropenes. 2. "Two-Atom" Insertion Reactions of 1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene^{1,2}

Dietmar Seyferth,* Steven C. Vick, and Mark L. Shannon

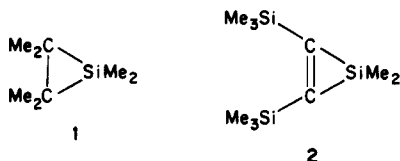
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received May 14, 1984

The silacyclopropene 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene reacts with aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzyne, terminal 1,3-dienes, and a conjugated imine to give five-membered cyclic organosilicon products in which the C=O, C=C, C≡C, or C=N bonds of the organic reactants have inserted into the Si—C bond of the silirene ring. In the case of the C=C and C≡C insertions, acyclic products, isomeric with the cyclic products, are formed as well. The available evidence suggests that a radical mechanism is operative.

Introduction

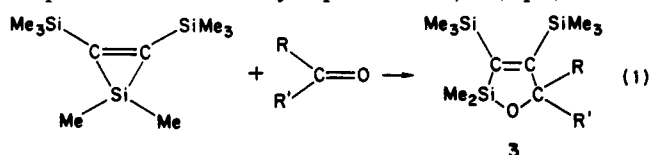
A characteristic reaction of the hyperreactive hexamethylsilirane, 1, is the "two-atom" insertion that it undergoes with aryl olefins such as styrene, terminal 1,3-dienes, terminal conjugated acetylenes, aldehydes, ketones, imines, and *cis*-azobenzene.^{3,4} Some of these reactions occur at room temperature; most require mild heating; those involving aliphatic aldehydes and ketones require UV irradiation. We have prepared and isolated a number of silacyclopropenes (silirenes) that appeared to be even more reactive than hexamethylsilirane, and it was of interest to see if these too would undergo such two-atom insertion reactions. We describe here such reactions of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene, 2.



Results and Discussion

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene, 2, was found to react exothermally with a number of aromatic, heterocyclic, and α,β -unsaturated aldehydes and ketones when the reactants were mixed in benzene solution. According to their spectroscopic properties, the products were the

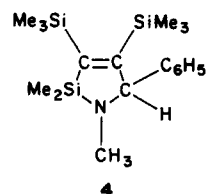
respective 1-oxa-2-silacycloprop-3-enes, 3 (eq 1). The



reactions proceeded well in normal laboratory lighting in benzene and diethyl ether solution and only poorly or not at all in pentane. The reaction with 2-acetylfuran was carried out in the dark to check whether normal laboratory fluorescent lighting was a requirement. An 18-h reaction at room temperature with complete exclusion of light gave the expected two-atom insertion product in 89% yield. Acetaldehyde and acetone did not react with 2 at room temperature, but low yields of products of type 3 were obtained when the respective reaction mixtures were heated at $\sim 70^\circ\text{C}$ for 18 h. Results are given in Table I.

The insertion of aliphatic aldehydes and ketones into the Si—C bond of silirene 2 was facilitated by UV irradiation (100-W UV lamp, quartz flask) for ~ 2 h in pentane. Longer irradiation times resulted in diminished yields. The results of these experiments are given in Table II.

One compound with a C=N bond, benzaldehyde *N*-methylimine, also underwent insertion into the SiC₂ ring of silirene 2 at room temperature, giving 4 in 77% yield.



Inspection of the results in Tables I and II shows that the nature of the carbonyl substrate in these two-atom insertions into silirene 2 is of great importance. The most

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