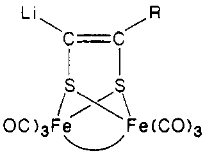
Construction of Bidentate Organosulfur Ligands via (μ-RC≡CS)(μ-SLi)$Fe_2(CO)_6$ Intermediates

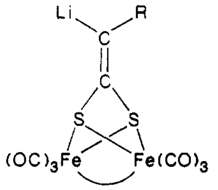
Dietmar Seyferth* and Gary B. Womack

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

Received February 4, 1986

(μ-Dithio)bis(tricarbonyliron) reacts with alkynyllithium reagents in THF at −78 °C to give initially (μ-RC≡CS)(μ-LiS)$Fe_2(CO)_6$. This species appears to be in equilibrium with either one or, in at least one case (R = Me_3Si), both of two possible products of intramolecular thiolate addition to the C≡C bond:



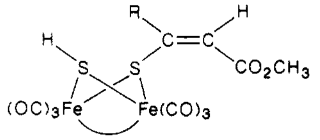


The products from such RC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reactions depend on the electrophilic substrate used. Alkylating and acylating agents yield products derived from the "open" reagent, while protonation and reactions with aldehydes and with group IV (14^{20}) organometallic halides give "closed" 1,2- or 1,1-dithiolene products.

Introduction

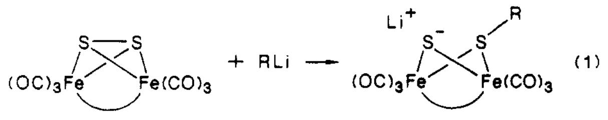
In a previous paper we have described base-catalyzed addition reactions of (μ-HS)$_2$$Fe_2(CO)_6$ to α,β-unsaturated acetylenes (Scheme I).[1]

The intermediates in such reactions were of type 1 and intramolecular addition of the HS function to the C=C bond, to either the α- or the β-carbon, gave the observed products. Such in situ construction of bidentate organosulfur ligands seemed of interest, especially since there was a possibility that they could be released from their $Fe_2(CO)_6$ complexes. Such ligand release in simple (μ-RS)$_2$$Fe_2(CO)_6$ systems can be effected oxidatively (to give R_2S or RSSR) or reductively (to give RS^-).[2]

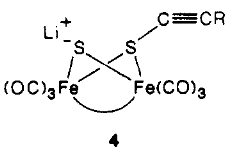


1

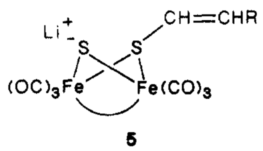
In earlier studies we had found the S–S bond of (μ-S_2)$Fe_2(CO)_6$ (2) to be readily cleaved by organometallic nucleophiles (eq 1).[3] The intermediate lithium thiolate 3 then could be protonated, alkylated, acylated, etc. In the case of an unsaturated organometallic reagent, RC≡CLi or RCH=CHLi, such cleavage would give 4 and 5, respectively. In both cases, there then is the possibility of intramolecular lithium thiolate addition to the carbon–carbon multiple bond in reactions analogous to the base-catalyzed intramolecular ring closure of intermediate 1.



2 3

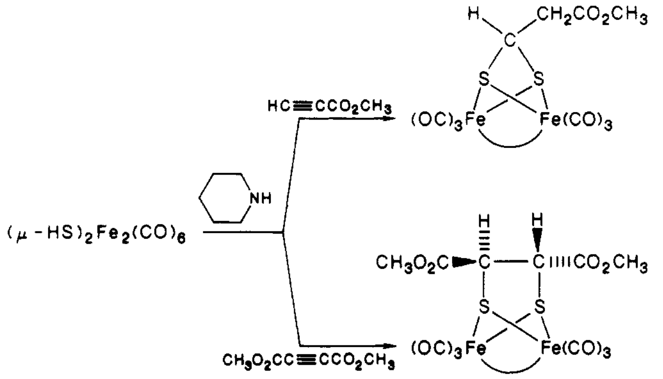


4

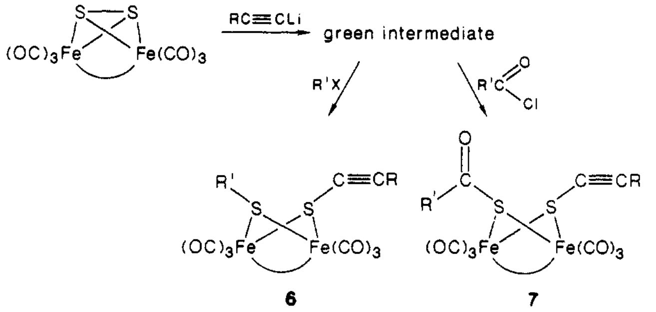


5

Scheme I



Scheme II



We report here our investigations of the reactions of alkynyllithium and Grignard reagents with (μ-S_2)$Fe_2(CO)_6$ and the chemistry of the resulting intermediates 4.

Results and Discussion

Our initial experiments were disappointing in that products containing one- or two-carbon bridges between the sulfur atoms were not observed. Alkynyllithium reagents, prepared by treatment of the alkyne with an equimolar quantity of *n*-butyllithium, did react with (μ-S_2)$Fe_2(CO)_6$ in THF at −78 °C, as evidenced by the red-

---

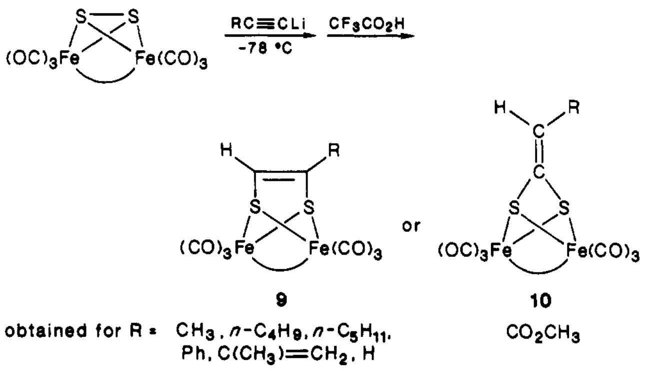
[1] Seyferth, D.; Womack, G. M.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 1568.

[2] Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

[3] Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9.

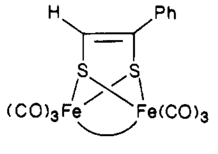
0276-7333/86/2305-2360$01.50/0

Scheme III



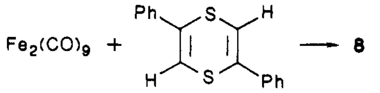
to-green color change which occurs in reactions of the type shown in eq 1. However, alkylation (with methyl iodide, ethyl iodide, benzyl chloride, and bromoacetone) or acylation (with acetyl and pivaloyl chloride) gave only "open" products (Scheme II). It made no difference whether the organic electrophile was added at −78 °C or at room temperature. The R substituent in RC≡CLi did not affect the reaction course. In the reactions carried out there were examples where R = alkyl, phenyl, isopropenyl, trimethylsilyl, and hydrogen (in the case of HC≡CMgBr). The product yields (Scheme II) were in the 75%->90% range. All of these results suggested that the intermediates formed in the (μ-S_2)$Fe_2(CO)_6$/RC≡CM reactions are of type 4 and that intramolecular thiolate addition to the C≡C bond to give a bridged species does not take place.

This initial conclusion was shown to be incorrect by further experiments in which electrophiles other than organic halides were added to the RC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixtures. Thus protonation of the PhC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixture at −78 °C did not give (μ-HS)(μ-PhC≡CS)$Fe_2(CO)_6$ but rather a dithiolene complex, 8, was isolated in 87% yield after hydrolytic workup.



8

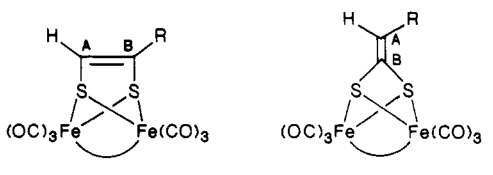
Complex 8 was a known compound, having been prepared earlier by another procedure by Bird and Hollins[4] (eq 2).



(2)

The identity of our product with that of Bird and Hollins was confirmed by ^{1}H NMR and IR spectroscopy and by a mixed melting point. Further experiments showed that such bridge formation between the sulfur atoms was a general process when RC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixtures were protonated. In all of these reactions in which the anionic intermediate was quenched with trifluoroacetic acid the alkynyllithium reagent was generated by the action of lithium diisopropylamide on the acetylene. Thiolate addition to the β-carbon atoms of the RC≡CS$^-$ group was the usual reaction, but some cases of addition to the α-carbon atom also were observed (Scheme III). Both types of products, 9 and 10, were obtained in the case of Me_3SiC≡CLi in yields of 45% and 29%, respectively. The reaction of HC≡CMgBr with (μ-S_2)$Fe_2(CO)_6$ followed by protonation with CF_3CO_2H gave 9 (R = H), also a known compound.[5]

Table I. ^{13}C NMR Spectra of Complexes of Types 9 and 10



type 9 type 10

R	type	δ carbon A	δ carbon B
H_b	9	146.3 (d, J = 190 Hz)	
CH_3	9	134.2 (d, J = 183 Hz)	159.5
n-C_4H_9	9	133.4 (d, J = 183 Hz)	164.4
n-C_5H_{11}	9	133.4 (d, J = 183 Hz)	164.4
C_6H_5	9	134.4 (d, J = 183 Hz)	161.7
$C(CH_3)$=CH_2^{c}	9	135.7 (d, J = 183 Hz)	162.8
$(CH_3)_3Si$	9	150.8 (d, J = 184 Hz)	159.7
$(CH_3)_3Si$	10	115.4 (d, J = 142 Hz)	157.9
CO_2CH_3^{c}	10	108.4 (d, J = 169 Hz)	165.3

[a] Solvent used was $CDCl_3$ unless stated otherwise. [b] Solvent was CD_3CN. [c] Solvent was CD_2Cl_2.

The ^{13}C NMR spectra of the products of types 9 and 10 served to establish their structures (Table I). The key compounds were the products of the Me_3SiC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction in which both type 9 and type 10 complexes had been obtained on protonation. It is reasonable to assign structure 9 to that compound in the ^{13}C NMR spectrum of which the vinylic carbon atom chemical shifts differ less (δ_C 150.8 and 159.7) and structure 10 to that compound for which this difference is greater (δ_C 115.4 and 157.9). Furthermore, the $J(^1H-^{13}C)$ coupling constants are indicative of the structures: 184 Hz in the case of 9 (R = Me_3Si) and 142 Hz in the case of 10 (R = Me_3Si) (cf. J values in Table I). These data, as well as those for the known 9, R = H, and R = Ph complexes, serve to establish the structures of the new complexes of types 9 and 10. Additionally, in the proton NMR spectra of 9 (R = alkyl) vicinal coupling between the vinylic and allylic protons, expected for the 1,1-dithiolene structure 10, was absent. Allylic coupling, J = 1.7 Hz, was observed for 9, R = CH_3.

Since these experiments showed the products of RC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reactions to depend on the electrophile added to react with the anionic intermediates present in solution, we examined the effect of other types of electrophiles on the nature of the products isolated, i.e., "open" (e.g., 6 and 7), 2-carbon-bridged (e.g., 9), or 1-carbon-bridged (e.g., 10).

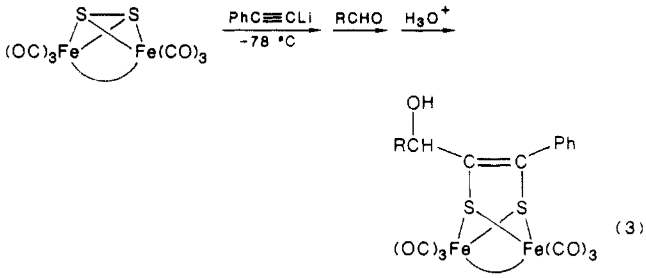
The formation of bridged products of types 9 and 10 suggested the intermediacy of vinylic lithium reagents, and so the PhC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixture was treated with some organic carbonyl compounds. Ketones (acetone and benzophenone) and an ester (methyl acetate) did not appear to react, but the more reactive aldehydes did (eq 3), giving allylic alcohol derivatives 11.

Group IV (14) organometallic halides reacted with RC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixtures to give "bridged" products (Scheme IV). With most alkynyllithium reagents and with HC≡CMgBr products of type 12 were isolated (Table II). Only in the case of LiC≡CCO_2Me were products of type 13 (R'_3M=Me_3Si and Me_3Sn) obtained. Structure assignments were made on the basis of ^{13}C NMR spectra (Table III). In the case of complexes of type 12 the high-field ^{13}C NMR signals were

---

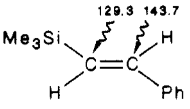
[4] Bird, C. W.; Hollins, E. M. *J. Organomet. Chem.* **1965**, *4*, 245.

[5] Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 4604.

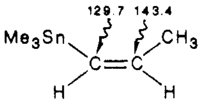


11a, R = CH$_3$
b, R = *t*-Bu
c, R = Ph

assigned to the group IV (14) element-substituted vinyl carbon atoms; this is generally the case for vinylic silanes and stannanes (e.g., **14**[6] and **15**;[7] other examples.[8] In the ^{13}C NMR spectra of the two type **12** complexes, the C$_A$ resonances again are at higher field than the C$_A$ resonances of the type **13** complexes.

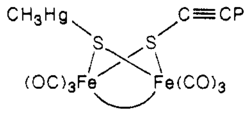


14

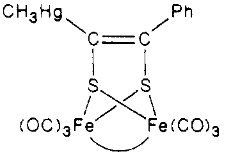


15

The PhC≡CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ reaction mixture also was treated with methylmercuric chloride. This reaction was of special interest since it demonstrated additional complexities of the RC≡CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ system. When CH$_3$HgCl was added to the PhC≡CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ reaction mixture at -78 °C, an immediate reaction was observed, signal by a color change from green to red. TLC analysis of the mixture indicated the formation of a single red product. After the reaction mixture had been stirred at -78 °C for 30 min, it was allowed to warm. As it warmed, TLC showed that a second product was beginning to form. Thirty minutes after the cold bath had been removed, the solvent was evaporated at reduced pressure and the residue chromatographed. Two products, **16** and **17**, as identified by NMR spectroscopy, were isolated in yields of 52% and 16%, respectively. Complex **16** was the product formed initially at low temperature. In another experiment the reaction mixture was stirred at -78 °C for 4.5 h; only **16** was present (by TLC). Rapid workup, with minimal exposure of the solution to higher temperatures, increased the yield of **16** to 79% and decreased that of **17** to 6%. In contrast, an experiment in which the -78 °C bath was removed from the PhC≡CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ reaction mixture and the solution was stirred for 35 min thereafter gave only **17** in 67% yield. It is clear that **16** is formed at -78 °C and that **16** is converted to **17** as the reaction mixture is allowed to warm. However, it is not a matter of a simple isomerization of **16** to **17**. Pure **16** is indefinitely stable in THF solution at room temperature, but conversion of **16** to **17** can be effected by addition of a stoichiometric quantity of anhydrous lithium chloride to a THF solution of **16**.



16



17

Scheme IV

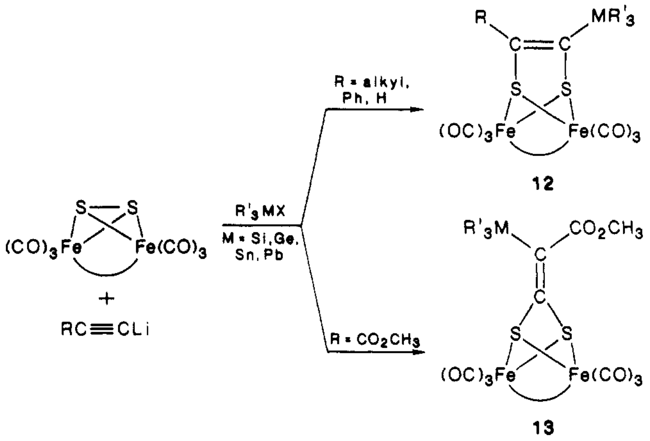
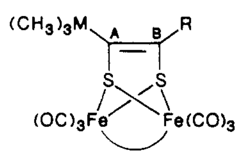


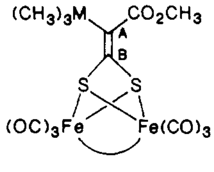
Table II. Products of Reactions

12	R	M	R′	% yield
a	H	Si	Me	40
b	Me	Sn	Me	75
c	Ph	Si	Me	66
d	Ph	Sn	Me	91
e	Ph	Sn	Ph	86
f	Ph	Ge	Ph	41
g	Ph	Pb	Ph	70
h	*n*-C$_4$H$_9$	Si	Me	82
2	*n*-C$_4$H$_9$	Sn	Me	86

Table III. ^{13}C NMR Data for Complexes of Types 12 and 13



type 12



type 13

R	M	type	δ carbon A	δ carbon B
H	Si	12	159.7	150.8
n-C$_4$H$_9$	Si	12	143.7	170.3
C$_6$H$_5$	Si	12	148.6	167.2
CH$_3$	Sn	12	143.7	163.8
n-C$_4$H$_9$	Sn	12	143.8	169.2
C$_6$H$_5$	Sn	12	149.5	167.7
CO$_2$Me	Si	13	121.8	165.4
CO$_2$Me	Sn	13	121.7	165.5

[a] Solvent used was CDCl$_3$.

At this point there is enough evidence to make a consideration of the mechanisms of product formation worthwhile. The initially formed intermediate when an alkynyllithium reagent cleaves the S–S bond of (μ-S$_2$)Fe$_2$(CO)$_6$ must be **18**. In view of the diversity of products which can be formed, **18** must be in equilibrium with the vinylic lithium reagents **19** and **20**, obtained by lithium thiolate addition to the C≡C bond of **18** (Scheme V). Which of the "closed" forms, **19** or **20**, is present will be determined by the nature of the substituent R in RC≡CLi. If R is a group which strongly stabilizes an adjacent full or partial negative charge, such as CO$_2$CH$_3$,[9] than **20** will

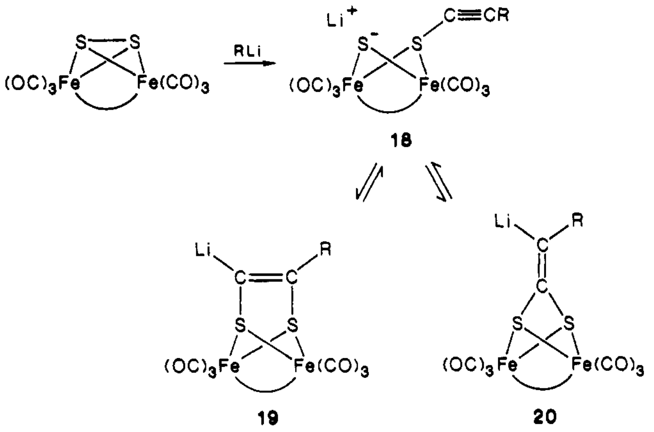
---

[6] Glukhikh, V. I.; Yarosh, O. G.; Glukhikh, N. G.; Pensionerova, G. A.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1979**, *247*, 1405.

[7] Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179.

[8] (a) Mitchell, T. N., Kummetat, C. *J. Organmet. Chem.* **1978**, *157*, 275. (b) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177.

Scheme V

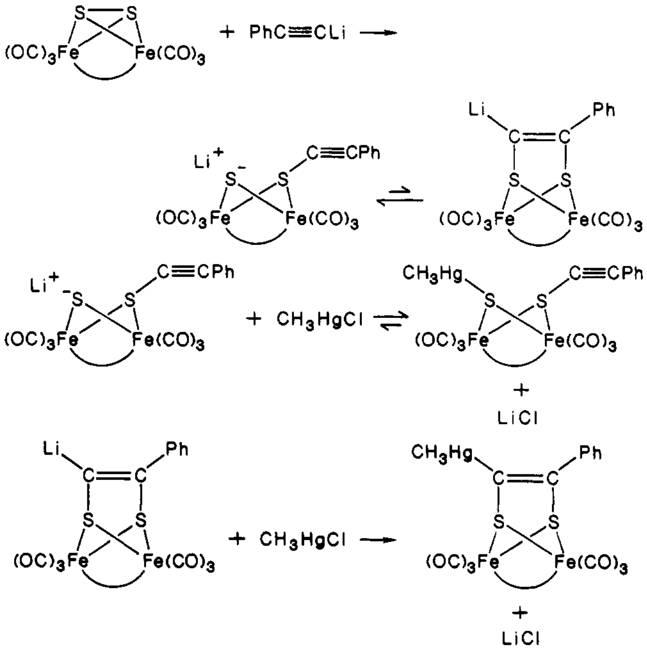


be formed, even though it is more strained than **19**. If R is not a group which strongly stabilizes a carbanion (vs. the stabilization it would experience from an adjacent sulfur atom),[10] e.g., alkyl, H, vinyl, and aryl, then **19** will be the more important C–Li species. The trimethylsilyl group is well-known for its ability to stabilize an adjacent carbanionic center,[11] and so the formation of a mixture of type **19** and type **20** products is not surprising. Thus the regiochemistry of the bridge construction is due to electronic factors.

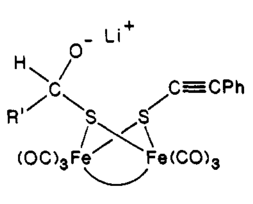
Another question of interest is why are "open" products formed in some cases and "bridged" products in others. Since the formation of "bridged" and "open" products is electrophile-dependent, it is *not* a reflection of the species actually present in solution and their relative concentrations.

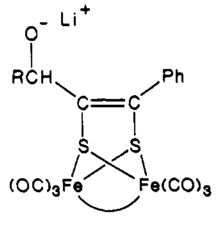
The question as to the species present in solution we have attempted to investigate by low-temperature ^{13}C NMR spectroscopy in THF-d_8. Examination of the n-$C_5H_{11}C{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ and the $Me_3SiC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixtures failed to provide evidence for vinyl carbanion intermediates. The ^{13}C NMR spectrum of the former system showed two resonances at δ_C 82.0 and 80.8 at −68 °C. These did not change with increasing temperature (−38, −13, +12 °C). These peaks are shifted, one to higher and the other to lower field, from those due to the alkyne carbon atoms of the neutral compounds $(\mu\text{-}C_5H_{11}C{\equiv}CS)(\mu\text{-}RS)Fe_2(CO)_6$ (R = CH_3, $CH_2C(O)CH_3$), δ_C 70 and 90. The same trend was found in the ^{13}C NMR spectra of the $Me_3SiC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ system, in which two resonances were observed at δ_C 109.5 and 83.3 at −63, −43, and 0 °C. The observation of just two peaks in the alkene/alkyne carbon shift region of these spectra indicates either that just one major intermediate was detected or that the time-averaged spectra of the interconverting intermediates (Scheme V) were obtained. Since these signals appear in the general region in which the alkyne carbon atom signals of $(\mu\text{-}RC{\equiv}CS)(\mu\text{-}R'S)Fe_2(CO)_6$ complexes occur, we conclude that the major species present in the $RC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reactions are of type **18**. If the equilibrium concentrations of **19** and **20** are low, there are two possible explanations for the formation of the one-carbon- and two-carbon-bridged products. It may be that in those cases where they are formed, the rate of reaction of **19** and/or **20** with the particular electrophile is so much faster than the rate of reaction of **18** with the electrophile so that there is preferential formation of the bridged product. This assumes that the **18** ⇌ **19**/**20** equilibria also are very rapidly established. On the other hand, it may be thermodynamic factors which determine product formation. The case of the reaction of the $PhC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture with methylmercuric chloride provides evidence for this possibility: the Hg–S bonded complex **16** clearly is the kinetic product. Its formation, however, is a reversible process, and the stable end product is the C-bonded organomercurial **17**. The kinetic product can be intercepted and isolated under appropriate reaction conditions. It is stable in solution, but in the presence of LiCl, the other product of the coupling reaction, it reverts to **17**. Lithium chloride must attack **16** to regenerate CH_3HgCl and the originally formed anion (Scheme VI). Because of the high thiophilicity of mercury, **16** is stable in the presence of LiCl at lower temperatures and the **16** → **17** conversion becomes important only at higher temperatures.

Scheme VI



It would seem reasonable that a similar explanation, i.e., kinetic vs. thermodynamic product formation, is applicable in the reactions of the $RC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ systems with other electrophiles. In the case of aldehydes, the formation of the "open" S-bonded adduct **21** would be expected to be reversible,[12] so that the stable **22** could accumulate in solution.


21


22

However, in the case of the Group IV (14) organometallic halides, the picture is not clear. In THF solution, there was no evidence of metal–sulfur bonded intermediates in their reactions with the $PhC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ system.

---

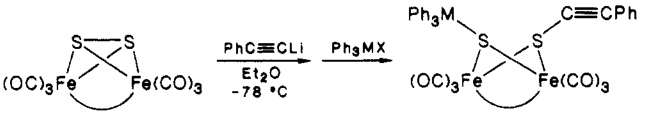
(9) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum: New York, 1977; Part B, Chapter 1.

(10) (a) Streitwieser, A.; Ewing, S. P. *J. Am. Chem. Soc.* **1975**, *97*, 190. (b) Streitwieser, A.; Williams, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 192.

(11) Magnus, P. D.; Sarkar, T.; Djuric, S. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, p 519, and references cited therein.

(12) Campaigne, E. In *Organic Sulfur Compounds*; Kharasch, N., Ed.; Pergamon: New York, 1961; Vol. 1, pp 134–140.

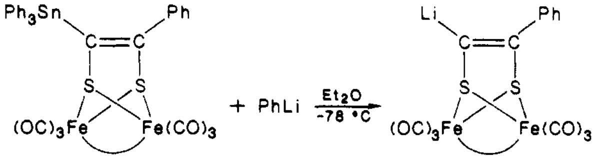
However, it was possible to isolate two sulfur-metalated compounds, **23a** and **23b**, when the reactions were carried out in diethyl ether solution (eq 4). The PhC≡CLi was prepared in Et_2O solution and (μ-S_2)$Fe_2(CO)_6$ added at −78 °C. The solution became brown (not green as in the reactions carried out in THF). A color change to red was noted upon addition of the group IV (14) halide. The reaction mixtures in each case were allowed to warm to room temperature prior to solvent removal, but this did not affect the initially formed products which were isolated. Complex **23a** could not be chromatographed; it decomposed on silica and alumina columns. Crystallization of the reaction residue from pentane gave **23a**, but only in 26% yield. The Ph_3Pb derivative **23b** was less sensitive and was isolated in 71% yield as a red, glassy solid after filtration chromatography. Assignment of structure **23** was based on spectroscopic data: observation if ν(C≡C) at 2172 (**23a**) and 2175 cm^{-1} (**23b**) in their IR spectra and of alkyne carbon atom signals in their ^{13}C NMR spectra (δ_C 86.6 and 86.9 for **23a** and δ_C 86.1 and 87.0 for **23b**), which are in good agreement with the range of δ_C 82–93 for other "open" (μ-R′S)(μ-RC≡CS)$Fe_2(CO)_6$ complexes. Complexes **23a** and **23b** were stable in THF solution. An attempt to obtain evidence for an equilibrium of the type found for the CH_3Hg derivative (Scheme VI) gave ambiguous results. When **23b** was added to a THF solution containing 1 molar equiv of anhydrous LiBr at −78 °C, the mixture became brown. After 2 h at −78 °C and 3 h at room temperature TLC analysis showed **23b** no longer was present. However, the only product which could be isolated (in low yield) was the protonated complex **8**. A similar result was observed when anhydrous LiCl was added to a THF solution of **23a**. It would appear that **23a** and **23b** are not stable in THF in the presence of lithium halides, and this leads us to the *tentative* conclusion that the bridged complexes **12** (R'_3M=Ph_3Sn, Ph_3Bp) are formed directly rather than by isomerization of initially formed **23a** and **23b**, respectively. In this connection we note that in previous work with anions derived from (μ-S_2)$Fe_2(CO)_6$ we had been unable to prepare complexes of type (μ-R_3MS)$_2Fe_2(CO)_6$ and (μ-R_3MS)(μ-R′S)$Fe_2(CO)_6$ by reactions of group IV (14) organometallic halides with (μ-LiS)$_2Fe_2(CO)_6$ and (μ-LiS)(μ-R′S)$Fe_2(CO)_6$ in THF.[13] Only decomposition was observed. However, we had been able to prepare analogous mercurials, (μ-RHgS)$_2Fe_2(CO)_6$ and (μ-RHgS)(μ-R′S)$Fe_2(CO)_6$, by such reactions. These results and the relevant observations of the present investigation possibly are related.



23a, M = Sn
b, M = Pb
(4)

In the case of the protonation reaction (Scheme III) we have no clear-cut evidence as to how the isolated product was formed, i.e., via an initial open product, (μ-HS)(μ-RC≡CS)$Fe_2(CO)_6$, with subsequent intramolecular SH addition to the C≡C bond to give the dithiolene complex or direct, preferred protonation of the "closed" species **19** (Scheme V). In any case, it seems unlikely that any base-catalyzed SH addition process is operative since the dithiolene complex was the only product obtained when a PhC≡CLi/(μ-S_2)$Fe_2(CO)_6$ reaction mixture was *added to* a THF solution containing an excess of trifluoroacetic acid.

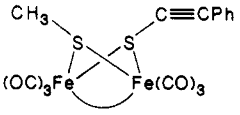
In the equilibrium shown in Scheme 5 the initially formed species is the "open" complex **18**. This equilibrium may be generated by means of alternate chemistry in which **19** is the initially formed species. Reaction of triphenyltin chloride with the PhC≡CLi/(μ-S_2)$Fe_2(CO)_6$ system had given complex **22**. This compound is a vinylic tin compound, and it could be converted to the bridged vinylic lithium reagent **23** by transmetalation with phenyllithium, a useful synthetic procedure developed in 1959 in these laboratories[14] (eq 4). If the equilibrium shown in Scheme V did indeed obtain, then addition of methyl iodide to this mixture should give the "open" product **24**. In this experiment, a methyl iodide quench gave **24** as the sole organoiron product.



22

23
+
Ph_4Sn

(5)



24

In conclusion, this new chemistry of (μ-S_2)$Fe_2(CO)_6$ has provided a simple and quite general route to dithiolene complexes. Mono- and dinuclear dithiolene complexes have been the subject of interesting investigations.[15] In our new chemistry we are constructing novel dithiolene ligands on the $Fe_2(CO)_6$ unit, and it will be of interest to see if these ligands can be released as the neutral 1,2-dithiete or as the $^-$SC(R)=C(R′)S$^-$ dianion and then transferred to another metal unit. Such studies are in progress. It may be noted that such dithiolene ligand transfer from mononuclear titanium complexes to other metals (e.g., Ni, Pt, and Rh) has been reported by Bolinger and Rauchfuss.[15c]

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, dichloromethane, and absolute ethanol were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Acetylene was pretreated by passing it through a −78 °C trap, bubbling through concentrated sulfuric acid, and then passing it through a column of activated alumina (MCB, 8–14 mesh). 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 chromatographs were performed with a 350 × 25 mm column using either silicic acid or Florisil (Fisher, 100–200 mesh). All chromatography was done without exclusion of atmospheric oxygen or moisture; all solid products were recrystallized from deoxygenated solvents at −20 °C.

---

[13] (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (b) Henderson, R. S. Ph.D. Thesis, MIT, 1981.

[14] Seyferth, D.; Weiner, M. A. *Chem. Ind. (London)* **1959**, 402; *J. Am. Chem. Soc.* **1961**, *83*, 3583.

[15] (a) Burns, R. P., McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (b) Lindoy, L. F. *Coord. Chem. Rev.* **1969**, *4*, 41. (c) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

Infrared spectra were obtained by using a Perkin-Elmer Model 457A or Model 283 double-beam grating infrared spectrophotometer. Chloroform solutions of the samples were used unless otherwise specified. Proton NMR spectra were recorded on either a Varian Associates T60, JEOL FX-90Q, 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 by using a Büchi capillary melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Lithium diisopropylamide was prepared just prior to use by adding 1 equiv of *n*-butyllithium (Alfa) to a THF solution of diisopropylamine at 0 °C and then stirring at room temperature for 1 h. (μ-Dithio)bis(tricarbonyliron) was prepared as described in the literature.[13,16] Isomer ratios of the (μ-RS)(μ-R′S)Fe$_2$(CO)$_6$ type complexes were determined by integration of the appropriate signals in the ^{1}H NMR spectrum. Isomer ratios of solid products were obtained from recrystallized samples.

Reactions of Alkynyllithium Reagents with (μ-S$_2$)Fe$_2$(CO)$_6$. A. Alkylation and Acylation of Intermediates. 1. PhC$\equiv$CLi Reactions. a. Iodomethane Quench. A dry, three-necked, 300-mL round-bottomed flask equipped with serum caps and a magnetic stir bar was flushed with nitrogen and charged with 40 mL of THF and 0.35 mL (3.19 mmol) of phenylacetylene (Aldrich). This was cooled to −78 °C and 1.45 mL (3.19 mmol) of a 2.2 M *n*-butyllithium in hexane solution (Alfa) was added by syringe. The mixture then was removed from the cold bath and stirred for 1 h to form the PhC$\equiv$CLi. The reagent solution then was cooled to −78 °C, and 1.0 g (2.91 mmol) of (μ-S$_2$)Fe$_2$(CO)$_6$ dissolved in 10 mL of THF was cannulated into it, resulting in a green reaction mixture. This was stirred for 30 min at −78 °C, then 1.5 mL (24.1 mmol) of iodomethane (Aldrich) was added by syringe. The solution was stirred for 1 h at −78 °C and 1 h at room temperature during which time a color change from green to red occurred. The solvent was removed on a rotary evaporator leaving a red oil which was purified by filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after removal of solvent yielded 1.13 g (2.46 mmol, 85% yield) of (μ-PhC$\equiv$CS)(μ-MeS)Fe$_2$(CO)$_6$ as an air-stable red solid. After recrystallization from pentane, mp 80–100 °C dec, it was identified as a mixture of two isomers, 1.3:1 CH$_3$(a)/CH$_3$(e).

IR: ν(C$\equiv$C) 2193 cm^{-1}; terminal CO, 2085 (s), 2051 (vs), 2000 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 270 MHz): δ 1.63 [s, CH$_3$(a)], 2.15 [s, CH$_3$(e)], 7.38 (m, Ph). ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ$_C$ 8.7 (q, *J* = 141 Hz, CH$_3$), 19.6 (q, *J* = 141 Hz, CH$_3$), 82.2, 84.3, 88.1, 88.9 (all s, alkynyl), 122.2 (t, ^2J = 8 Hz, ipso Ph), 128.3 (d, *J* = 162 Hz, Ph), 129.0 (d, *J* = 163 Hz, Ph), 132.0 (d, *J* = 161 Hz, Ph), 208.7 and 207.8 (both s, CO). Anal. Calcd for C$_{15}$H$_8$Fe$_2$O$_6$S$_2$: C, 39.16; H, 1.75. Found: C, 39.16; H, 1.89.

The same product was obtained in 84% yield in an experiment in which the PhC$\equiv$CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ reaction mixture was allowed to warm to room temperature and kept at room temperature for 30 min before the CH$_3$I was added. The product yield dropped to 33% when the PhC$\equiv$CLi/(μ-S$_2$)Fe$_2$(CO)$_6$ reaction mixture was kept at room temperature for 1.5 h before the CH$_3$I was added.

b. Iodoethane Quench. The product (μ-C$_2$H$_5$S)(μ-PhC$\equiv$CS)Fe$_2$(CO)$_6$ (75% yield) was a red oil which was purified by filtration chromatography (silicic acid, 9:1 (v/v) pentane/CH$_2$Cl$_2$) to give a mixture of isomers (3:1.7:1 Et(a)/Et(e)/Et(e)).

IR: ν(C$\equiv$C) 2182 cm^{-1}; terminal CO, 2079 (s), 2044 (vs), 1996 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.16 [t, *J* = 7.4 Hz, CH$_3$(a)], 1.35 [t, *J* = 7.4 Hz, CH$_3$(e)], 1.46 [t, *J* = 7.2 Hz, CH$_3$(e)], 2.04 (q, *J* = 7.4 Hz, CH$_2$(a)), 2.49 [q, *J* = 7.4 Hz, CH$_2$(e)], 2.81 [q, *J* = 7.2 Hz, CH$_2$(e)], 7.2–7.5 (m, Ph). ^{13}C{^{1}H} (CD$_2$Cl$_2$, 67.9 Hz): δ$_C$ 19.4, 22.0, 22.5, 24.9, 36.9, 38.5 (Et), 89.4, 92.6, 93.4 (alkynyl), 127.1, 129.9, 132.8, 133.3, 133.6, 133.9, 136.1, 136.8, 139.5 (Ph), 212.6, 213.0, 213.8 (CO). Anal. Calcd for C$_{16}$H$_{10}$Fe$_2$O$_6$S$_2$: C, 40.54; H, 2.13. Found: C, 40.68; H, 2.27.

c. Benzyl Chloride Quench. The product (μ-PhCH$_2$S)(μ-PhC$\equiv$CS)Fe$_2$(CO)$_6$ (28% yield) was an air-stable red solid, mp 122–125 °C, after recrystallization from pentane/CH$_2$Cl$_2$. A mixture of two isomers was present, 9:1 PhCH$_2$(a)/PhCH$_2$(e).

IR: ν(C$\equiv$C) 2190 cm^{-1}; terminal CO, 2078 (s), 2044 (vs), 2006 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 3.19 [s, CH$_2$(a)], 3.62 [s, CH$_2$(e)], 7.0–7.6 (m, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, 67.9 MHz): δ 29.4 [CH$_2$(a)], 41.2 [CH$_2$(e)], 89.0, 84.3 (alkynyl) 122.2, 127.8, 128.4, 128.8, 129.1, 129.2, 132.1, 138.1 (Ph), 207.7 and 208.8 (CO). Anal. Calcd for C$_{21}$H$_{12}$Fe$_2$O$_6$S$_2$: C, 47.05; H, 2.26. Found: C, 47.28; H, 2.40.

d. Bromoacetone Quench. The product (μ-CH$_3$C(O)CH$_2$S)(μ-PhC$\equiv$CS)Fe$_2$(CO)$_6$ (75% yield) was an air-stable, red solid, mp 88–91 °C (from pentane/CH$_2$Cl$_2$), a 13:1 CH$_3$C(O)CH$_2$(a)/CH$_3$C(O)CH$_2$(e) isomer mixture.

IR: ν(C$\equiv$C) 2174 cm^{-1} ν(C$=$O) 1713 cm^{-1}; terminal CO, 2084 (s), 2047 (vs), 2011 (vs), 1999 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 2.22 [s, CH$_3$(a)], 2.28 (s, CH$_3$(e)], 2.79 [s, CH$_2$(a)], 3.33 [s, CH$_2$(e)], 7.5–7.1 (m, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, 67.9 MHz): δ$_C$ 29.2 [CH$_3$(a)], 34.3 [CH$_3$(e)], 46.6 [CH$_2$(a)], 48.5 [CH$_2$(e)], 83.4, 89.5 (alkynyl), 122.0, 128.4, 129.2, 132.1 (Ph), 201.9 (ketone CO), 207.3 and 208.4 (CO). Anal. Calcd for C$_{17}$H$_{10}$Fe$_2$O$_7$S$_2$: C, 40.67; H, 2.01. Found: C, 40.86; H, 2.19.

e. Acetyl Chloride Quench. The product (μ-CH$_3$C(O)S)(μ-PhC$\equiv$CS)Fe$_2$(CO)$_6$ (92% yield) was an air-stable, red solid, mp 74–75 °C dec (from pentane/CH$_2$Cl$_2$). Only one isomer appeared to be present in the recrystallized product.

IR: ν(C$\equiv$C) 2179 cm^{-1}; ν(C$=$O) 1728 cm^{-1}; terminal CO, 2088 (s), 2059 (vs), 2021 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 90 MHz): δ 2.40 (s, 3 H, CH$_3$), 7.34 (s, 5 H, Ph). ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ$_C$ 35.5 (q, *J* = 131 Hz, CH$_3$), 84.0, 89.4 (both s, alkynyl), 122.1 (s, ipso Ph), 128.3 (d, *J* = 156 Hz, Ph), 129.1 (d, *J* = 154 Hz, Ph), 132.0 (d, *J* = 162 Hz, Ph), 198.9 (s, organic CO), 207.5 (s, CO). Anal. Calcd for C$_{16}$H$_8$Fe$_2$O$_7$S$_2$: C, 39.38; H, 1.65. Found: C, 39.57; H, 1.84.

f. Pivaloyl Chloride Quench. The product (μ-Me$_3$CC(O)S)(μ-PhC$\equiv$CS)Fe$_2$(CO)$_6$ (67% yield) was a red solid, mp 80–82 °C (from pentane/CH$_2$Cl$_2$). The recrystallized product appeared to contain a single isomer.

IR: ν(C$\equiv$C) 2164 cm^{-1}; ν(C$=$O) 1714 cm^{-1}; terminal CO, 2076 (s), 2042 (vs), 2007 (vs) cm^{-1}. ^{1}H NMR (acetone-*d*$_6$, 90 MHz): δ 1.28 (s, 9 H, CH$_3$), 7.40 (s, 5 H, Ph). ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ$_C$ 28.0 (q, *J* = 128 Hz, CH$_3$), 89.5 and 84.6 (both s, alkynyl), 122.1 (s, ipso Ph), 128.4 (d, *J* = 162 Hz, Ph), 129.1 (d, *J* = 161 Hz, Ph), 132.1 (d, *J* = 163 Hz, Ph), 207.2 (s, organic CO), 207.6 (s, CO). Anal. Calcd for C$_{19}$H$_{14}$Fe$_2$O$_7$S$_2$: C, 43.05; H, 2.66. Found: C, 43.23; H, 2.81.

2. *n*-C$_4$H$_9$C$\equiv$CLi Reactions. Iodomethane Quench. The product (μ-CH$_3$S)(μ-*n*-C$_4$H$_9$C$\equiv$CS)Fe$_2$(CO)$_6$ (93% yield), a slightly air-sensitive, red oil, was purified by filtration chromatography (silicic acid/pentane). Two isomers were present (by ^{1}H NMR), but their ratio could not be determined due to overlapping CH$_3$ and *n*-butyl proton signals.

IR: ν(C$\equiv$C) 2201 cm^{-1}; terminal CO, 2080 (s), 2048 (vs), 2000 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 90 MHz): δ 0.84, 1.30, and 2.10 (all complex multiplets). ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ$_C$ 8.4 (q, *J* = 141 Hz, CH$_3$), 13.4 (q, *J* = 126 Hz, CH$_3$), 19.6 (t, *J* = 133 Hz, CH$_2$), 21.9 (t, *J* = 130 Hz, CH$_2$), 30.3 (t, *J* = 121 Hz, CH$_2$), 70.8, 73.1, 91.4, 92.2 (all s, alkynyl carbons), 208.0 and 208.9 (both s, CO). Anal. Calcd for C$_{13}$H$_{12}$Fe$_2$O$_6$S$_2$: C, 35.48; H, 2.75. Found: C, 35.63; H, 2.84.

3. *n*-C$_5$H$_{11}$C$\equiv$CLi Reactions. a. Iodomethane Quench. The product (μ-CH$_3$S)(μ-*n*-C$_5$H$_{11}$C$\equiv$CS)Fe$_2$(CO)$_6$ (89% yield), a red oil (slightly air-sensitive), was eluted by pentane on filtration chromatography (silicic acid). A mixture of three isomers (by NMR) was present, but due to overlapping CH$_3$ and *n*-pentyl proton signals, their ratio could not be determined.

IR: ν(C$\equiv$C) 2190 cm^{-1}; terminal CO, 2077 (s), 2038 (vs), 2002 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 90 MHz): δ 0.86, 1.32, 2.19 (all multiplets), 1.52 [s, CH$_3$(a)], 2.07 [s, CH$_3$(e)]. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 67.9 MHz): δ$_C$ 8.1, 14.0, 19.2, 20.0, 20.2, 21.5, 22.4, 24.3, 28.2, 29.5, 30.1, 31.2 (SCH$_3$ and *n*-pentyl), 64.6, 71.3, 73.6, 90.4, 91.9, 92.7 (alkynyl), 208.4 and 209.3 (CO). Anal. Calcd for C$_{14}$H$_{14}$Fe$_2$O$_6$S$_2$: C, 37.03; H, 3.11. Found: C, 37.43; H, 3.32.

b. Bromoacetone Quench. The product (μ-CH$_3$C(O)CH$_2$S)(μ-*n*-C$_5$H$_{11}$C$\equiv$CS)Fe$_2$(CO)$_6$ (77% yield), a slightly air-

---

[16] (a) Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91. (b) Brendel, G. Ph.D. Dissertation, Technische Hochschule München, 1956, pp 47–55.

sensitive, red oil, was eluted with 9:1 (v/v) pentane/CH_2Cl_2 (silicic acid). A mixture of three isomers was present: 2.7:1:0.3 $CH_3C(O)CH_2$(a)/$CH_3C(O)CH_2$(e)/$CH_3C(O)CH_2$(e).

IR: ν(C≡C) 2190 cm^{-1}; ν(C=O) 1715 cm^{-1}; terminal CO, 2079 (s), 2043 (vs), 2005 (vs), 1997 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 0.84, 1.30 (both m, pentyl), 2.16 [s, CH_3(a)], 2.23 [s, CH_3(e)], 2.30 [s, CH_3(e)], 2.71 [CH_2(a)], 3.25 [CH_2(e)], 3.35 [CH_2(e)]. $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz): δ 13.9, 20.0, 22.3, 28.2, 28.5, 31.2, 33.8, 46.3 (pentyl, CH_2 and CH_3), 70.9, 72.9, 92.4, 93.2, (alkynyl), 199.5, 200.3 (ketone CO), 208.1 and 209.1 (CO). Anal. Calcd for $C_{16}H_{16}Fe_2O_7S_2$: C, 38.74; H, 3.25. Found: C, 38.84; H, 3.46.

4. CH_2=C(CH_3)C≡CLi Reactions. Iodomethane Quench. The lithium reagent was prepared by treating CH_2=C(CH_3)C≡CH (Farchan) in THF with an equimolar quantity of *n*-butyllithium in hexane.

The product (μ-CH_3S)(μ-CH_2=C(CH_3)C≡CS)$Fe_2(CO)_6$ (91% yield), an air-stable, red solid, mp 83–90 °C (from pentane), was a mixture of two isomers, 5:1 CH_3(a)/CH_3(e).

IR: terminal CO, 2077 (s), 2041 (vs), 2008 (vs), 1998 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.54 [SCH_3(a)], 1.80 (CH_3), 2.09 [SCH_3(e)], 5.26 and 5.32 (both s, vinyl). $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz): δ_C 8.39 [SCH_3(a)], 18.9 [SCH_3(e)], 22.6, 21.3 (CH_3), 81.5, 90.0 (alkynyl), 123.8, 124.4, 126.5 (vinyl), 208.2 and 209.1 (CO). Anal. Calcd for $C_{12}H_8Fe_2O_6S_2$: C, 33.99; H, 1.93. Found: C, 34.13; H, 2.00.

5. $(CH_3)_3$SiC≡CLi Reactions. a. Iodomethane Quench. The product (μ-CH_3S)(μ-Me_3SiC≡CS)$Fe_2(CO)_6$ (86% yield), an air-stable, red solid, mp 62–78 °C (from pentane), was a mixture of two isomers, 4:1 CH_3(a)/CH_3(e).

IR: ν(C≡C) 2108 cm^{-1}; Me_3Si, 1250 cm^{-1}; terminal CO, 2079 (s), 2048 (vs), 2008 (vs), 1967 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 2.08 [s, CH_3(e)], 1.53 [s, CH_3(a)], 0.10 (s, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz): δ_C −0.5 ($SiCH_3$), 8.4 [SCH_3(a)], 1.90 [SCH_3(e)], 96.7, 97.0, 97.4, 99.3 (alkynyl), 208.1 and 209.0 (CO). Anal. Calcd for $C_{12}H_{12}Fe_2O_6S_2Si$: C, 31.60; H, 2.65. Found: C, 31.50; H, 2.66.

b. Iodoethane Quench. The product (μ-C_2H_5S)(μ-Me_3SiC≡CS)$Fe_2(CO)_6$ (85% yield) was an air-stable, red solid, mp 90–92 °C, a mixture of two isomers, 3.2:1 Et(a)/Et(e).

IR: ν(C≡C) 2100 cm^{-1}; Me_3Si, 1257 cm^{-1}; terminal CO, 2080 (s), 2042 (vs), 2007 (vs), 1998 (sh) cm^{-1}. ^1H NMR (C_6D_6, 250 MHz): δ 0.08 (s, $SiCH_3$), 0.09 (s, $SiCH_3$), 0.63 [t, *J* = 7.3 Hz, CH_3(a)], 0.75 [t, *J* = 7.4 Hz, CH_3(e)], 1.42 [q, *J* = 7.4 Hz, CH_2(a)], 1.83 [q, *J* = 7.3 Hz, CH_2(e)]. $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 Hz): δ_C −0.48 ($SiCH_3$), 17.1 [CH_3(a)], 17.5 [CH_3(e)], 20.1 [CH_2(a)], 31.9 [CH_2(e)], 97.3, 99.3 (alkynyl), 208.3 and 209.1 (CO). Anal. Calcd for $C_9H_4Fe_2O_6S_2$: C, 33.21; H, 3.00. Found: C, 33.94; H, 3.02.

Reaction between (μ-Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide,[17] and Iodomethane. A dry, 300-mL, three-necked, round-bottomed flask equipped with a magnetic stir bar, serum caps, and a gas dispersion tube was flushed with nitrogen. THF (50 mL) was added, and acetylene (Airco) was bubbled into the solvent for 10 min. While acetylene addition was continued, 1.6 mL (3.61 mmol) of a 2.26 M THF ethylmagnesium bromide solution was added by syringe. The mixture acquired a pink tint and was stirred with continuous acetylene bubbling for another 20 min. The gas dispersion tube was removed and the solution cooled to −78 °C. In 10 mL of THF, 0.5 g (1.46 mmol) of (μ-S_2)$Fe_2(CO)_6$ was then cannulated into the HC≡C-MgBr solution, resulting in a brown reaction mixture. After the mixture was stirred for 30 min at −78 °C, 0.90 mL (14.4 mmol) of CH_3I was added. Stirring was continued for 30 min at −78 °C and 2 h at room temperature during which time the solution became red. The solvent was removed, leaving a red tar which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.43 g (77% yield) of (μ-HC≡CS)(μ-MeS)$Fe_2(CO)_6$ as a slightly air-sensitive, red solid. After crystallization from pentane, mp 95–100 °C dec, it was identified as a mixture of two isomers, 3:1 CH_3(a)/CH_3(e).

IR ($CHCl_3$): 3309 (s) (≡CH) cm^{-1}; terminal CO, 2078 (s), 2040 (vs), 2002 (vs), 1997 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 1.55 [s, CH_3(a)], 2.09 [s, CH_3(e)], 2.24 and 2.33 (both s, ≡CH). ^{13}C NMR (C_6D_6, 67.9 MHz): δ_C 9.2 [q, *J* = 142 Hz, CH_3(a)], 20.0 [q, *J* = 141 Hz, CH_3(e)], 76.2 (d, *J* = 257 Hz, ≡CH), 77.0 (d, *J* = 257 Hz, ≡CH, 78.8 (s, alkynyl), 208.2 and 209.1 (both s, CO). Anal. Calcd for $C_9H_4Fe_2O_6S_2$: C, 28.15; H, 1.05. Found: C, 28.35; H, 1.19.

B. Protonation of Intermediates. 1. PhC≡CLi/(μ-S_2)$Fe_2(CO)_6$. Lithium phenylacetylide, 6.96 mmol, was generated in 20 mL of THF from 0.80 mL (7.20 mmol) of phenylacetylene and 6.96 mmol of lithium diisopropylamide. This reagent solution was cannulated into a 300-mL, three-necked flask containing 1.0 g (2.91 mmol) of (μ-S_2)$Fe_2(CO)_6$ and 50 mL of THF cooled to −78 °C, producing a green reaction mixture which was stirred for 30 min at −78 °C. Trifluoroacetic acid (Baker), 0.6 mL (8.08 mmol), was added, causing an immediate color change to red. Stirring was continued at −78 °C for 30 min and then at room temperature for 30 min prior to removal of the solvent. The remaining black solid was subjected to filtration chromatography (silicic acid/pentane), pentane eluting a red band which gave 1.17 g (2.53 mmol, 87% yield) of (μ-SCH=C(Ph)S)$Fe_2(CO)_6$ as an air-stable, dark red solid, mp 98–100 °C dec (lit.[4] mp 95–97 °C dec) after crystallization from pentane.

IR ($CHCl_3$): 3030 (m, br), 1483 (m), 1440 (m), 1175 (m), 892 (m), 613 (m), 573 (s), 550 (s) cm^{-1}; terminal carbonyl region ($CHCl_3$), 2078 (s), 2043 (vs), 2000 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 6.46 (s, 1 H, =CH), 7.30 (s, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 125.1 (d, *J* = 166 Hz, Ph), 128.5 (d, *J* = 162 Hz, Ph), 129.5 (d, *J* = 161 Hz, Ph), 133.2 (s, ipso Ph), 134.4 (d, *J* = 183 Hz, =CH), 166.7 (s, =CPh), 207.5 (s, CO). Mass spectrum: *m/z* (relative intensity) 418 (M^+ − CO, 4), 390 (M^+ − 2CO, 6), 362 (M^+ − 3CO, 4), 334 (M^+ − 4CO, 4), 306 (M^+ − 5CO, 8), 278 (M^+ − 6CO, 23), 176 (Fe_2S_2, 100), 144 (Fe_2S, 11) 112 (Fe_2, 4), 88 (FeS, 3), 56 (Fe, 17). Anal. Calcd for $C_{14}H_6Fe_2O_6S_2$: C, 37.70; H, 1.36. Found: C, 37.66; H, 1.42.

2. CH_3C≡CLi/(μ-S_2)$Fe_2(CO)_6$. The product **9** (R = CH_3) was isolated (76% yield) by extraction of the brown reaction residue with pentane, removal of solvent, and crystallization from pentane: red, air-stable solid, mp 61–62 °C.

IR: 2974 (m), 2955 (m), 2922 (s), 2860 (sh), 2849 (m), 1613 (w), 1424 (s), 1373 (m), 1160 (m), 1083 (s), 555 (m) cm^{-1}; terminal CO, 2089 (s), 2050 (vs), 2010 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.61 (d, *J* = 1.7 Hz, 3 H, CH_3), 5.77 (q, *J* = 1.7 Hz, 1 H, vinyl). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 19.6 (q, *J* = 131 Hz, CH_3), 134.2 (d, *J* = 183 Hz, =CH), 159.5 (s, =CMe), 207.7 (s, CO). Mass spectrum: *m/z* (relative intensity) 356 (M^+ − CO, 4), 328 (M^+ − 2CO, 5), 300 (M^+ − 3CO, 4), 272 (M^+ − 4CO, 5), 244 (M^+ − 5CO, 8), 216 (M^+ − 6CO, 21), 176 (Fe_2S_2, 100), 144 (Fe_2S, 25), 112 (Fe_2, 19), 88 (FeS, 10), 56 (Fe, 35). Anal. Calcd for $C_9H_4Fe_2O_6S_2$: C, 28.15; H, 1.05. Found: C, 28.46; H, 1.16.

3. *n*-C_4H_9C≡CLi/(μ-S_2)$Fe_2(CO)_6$. The product **9** (R = *n*-C_4H_9), a red, slightly air-sensitive oil (92% yield), was isolated by filtration chromatography (silicic acid/pentane).

IR: terminal CO, 2075 (vs), 2039 (vs), 2000 (vs), 1995 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 0.80–1.87 (m, 9 H, butyl group), 5.73 (s, 1 H, vinyl). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 13.6 (q, *J* = 125 Hz, CH_3), 21.9 (t, *J* = 126 Hz, CH_2), 28.8 (t, *J* = 125 Hz, CH_2), 33.5 (t, *J* = 128 Hz, CH_2), 133.4 (d, *J* = 183 Hz, =CH), 164.4 (s, =C(butyl)), 207.8 (s, CO). Mass spectrum: *m/z* (relative intensity) 342 (M^+ − 3CO, 2), 314 (M^+ − 4CO, 8), 386 (M^+ − 5CO, 14), 258 (M^+ − 6CO, 37), 176 (Fe_2S_2, 100), 144 (Fe_2S, 18), 112 (Fe_2, 10), 88 (FeS, 4), 56 (Fe, 18). Anal. Calcd for $C_{12}H_{10}Fe_2O_6S_2$: C, 33.83; H, 2.37. Found: C, 33.43; H, 2.32.

4. *n*-C_5H_{11}C≡CLi/(μ-S_2)$Fe_2(CO)_6$. The product, a slightly air-sensitive, red oil, **9** (R = *n*-C_5H_{11}) (77% yield) was isolated as in section B.3.

IR: terminal CO, 2080 (s), 2041 (vs), 2007 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 60MHz): δ 0.88–1.88 (m, 11 H, pentyl group), 5.77 (s, 1 H, vinyl). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 13.8 (q, *J* = 125 Hz, CH_3), 22.2 (t, *J* = 124 Hz, CH_2), 26.4 (t, *J* = 129 Hz, CH_2), 30.9 (t, *J* = 125 Hz, CH_2), 33.7 (t, *J* = 129 Hz, CH_2), 133.4 (d, *J* = 183 Hz, =CH), 164.4 (s, =C(pentyl), 207.8(s, CO). Mass spectrum: *m/z* (relative intensity) 412 (M^+ − CO, <1), 384 (M^+ − 2CO, <1), 356 (M^+ − 3CO, 1), 328 (M^+ − 4CO, 4), 300 (M^+ − 5CO, 8), 272 (M^+ − 6CO, 24), 176 (Fe_2S_2, 100), 144 (Fe_2S, 6), 112 (Fe_2, 9), 88 (FeS, 2), 56 (Fe, 18). Anal. Calcd for $C_{13}H_{12}Fe_2O_6S_2$: C, 35.48; H, 2.75. Found: C, 35.68; H, 2.78.

5. CH_2=C(CH_3)C≡CLi/(μ-S_2)$Fe_2(CO)_6$. Workup as above in section B.2 gave the product **9** (R = CH_2=C(CH_3)) as an air-stable, dark red solid, mp 65.5–67 °C (pentane), in 89% yield.

---

(17) Skatteböl, L.; Jones, E. R. H.; Whiting, M. C. *Org. Synth.* **1963**, *4*, 792.

IR: terminal CO, 2078 (s), 2043 (vs), 2000 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.70 (s, 3 H, CH_3), 5.16 (s, 1 H, vinyl), 5.41 (s, 1 H, vinyl, 6.09 (s, 1 H, vinyl). ^{13}C NMR (CD_2Cl_2, 67.0 MHz): δ_C 21.3 (q, J = 128 Hz, CH_3), 118.7 (t, J = 159 Hz, $=CH_2$), 135.7 (d, J = 183 Hz, =C(H)S), 138.5 (s, =CMe), 162.8 (s, =CS), 208.3 (s, CO). Mass spectrum: m/z (relative intensity) 382 (M^+ – CO, 6), 354 (M^+ – 2CO, 9), 326 (M^+ – 3CO, 7), 298 (M^+ – 4CO, 6), 270 (M^+ – 5CO, 10), 242 (M^+ – 6CO, 29), 176 (Fe_2S_2, 100), 144 (Fe_2S, 5), 112 (Fe_2, 3), 88 (FeS, 2), 56 (Fe, 14). Anal. Calcd for $C_{11}H_6Fe_2O_6S_2$: C, 32.23; H, 1.48. Found: C, 32.24; H, 1.59.

6. **$(CH_3)_3SiC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$.** Filtration chromatography (silicic acid, 9:1 pentane/CH_2Cl_2) was followed by column chromatography (silicic acid/pentane). Two components of the product oil were separated.

(a) **10** (R = Me_3Si): air-stable, red solid; 29% yield; mp 47–49 °C (ethanol). IR ($CHCl_3$): 2958 (m), 2800 (w), 2870 (sh), 1620 (m), 1565 (s), 1545 (s), 1398 (w), 1246 (m), 1205 (sh), 850 (s), 610 (m), 550 (s) cm^{-1}; terminal carbonyl region, 2083 (vs), 2048 (vs), 2005 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.12 (s, 9 H, $SiCH_3$), 4.86 (s, 1 H, vinyl). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ_C –0.84 (q, J = 119 Hz, $SiCH_3$), 115.4 (d, J = 142 Hz, =CH($SiMe_3$)), 157.9 (d, J = 7 Hz, $=CS_2$), 208.0 (s, CO). Mass spectrum: m/z (relative intensity) 414 (M^+ – CO, 6) 386 (M^+ – 2CO, 8), 358 (M^+ – 3CO, 8), 330 (M^+ – 4CO, 9), 302 (M^+ – 5CO, 23), 274 (M^+ – 6CO, 100), 176 (Fe_2S_2, 67), 144 (Fe_2S, 12), 112 (Fe_2, 1), 56 (Fe, 2). Anal. Calcd for $C_{11}H_{10}Fe_2O_6S_2Si$: C, 29.88; H, 2.28. Found: C, 30.00; H, 2.28.

(b) **9** (R = Me_3Si): air-stable, dark red solid; 45% yield; mp 69–70 °C (ethanol). IR ($CHCl_3$): 2970 (m), 2905 (w), 1550 (m), 1405 (w), 1254 (m), 1115 (w), 900 (s), 845 (s), 830 (sh), 620 (m), 555 (vs) cm^{-1}; terminal carbonyl region, 2000 (vs), 2035 (vs), 2077 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.04 (s, 9 H, $SiCH_3$), 6.43 (s, 1 H, vinyl). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ_C –2.40 (q, J = 111 Hz, $SiCH_3$), 150.8 (d, J = 185 Hz, =CH), 159.7 (s, $=CSiMe_3$), 207.9 (s, CO). Mass spectrum: m/z (relative intensity) 414 (M^+ – CO, 4), 386 (M^+ – 2CO, 8), 358 (M^+ – 3CO, 13), 330 (M^+ – 4CO, 9), 302 (M^+ – 5CO, 23), 274 (M^+ – 6CO, 86), 176 (Fe_2S_2, 100), 144 (Fe_2S, 7), 112 (Fe_2, 1), 56 (Fe, 7). Anal. Calcd for $C_{11}H_{10}Fe_2O_6S_2Si$: C, 29.88; H, 2.28. Found: C, 29.84; H, 2.31.

7. **$LiC{\equiv}CCO_2CH_3/(\mu\text{-}S_2)Fe_2(CO)_6$.** The lithium reagent was generated by the action of lithium diisopropylamide in THF on an equimolar quantity of methyl propiolate (Aldrich) in THF at –78 °C.[18]

The product **10** (R = CO_2CH_3), a red, air-stable solid, mp 63–65 °C (pentane/CH_2Cl_2), was isolated in 51% yield by column chromatography (silicic acid, 4:1 pentane/CH_2Cl_2) of the initially obtained brown oil.

IR ($CHCl_3$): 2960 (m), 2850 (w), 1700 (s) (C=O), 1580 (s) (C=O), 1433 (m), 1300 (s), 1270 (sh), 1160 (s), 1008 (m), 957 (m), 830 (m), 609 (m), 550 (m) cm^{-1}; terminal carbonyl region, 2090 (s), 2055 (vs), 2015 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 3.67 (s, 3 H, CH_3), 5.34 (s, 1 H, vinyl). ^{13}C NMR (CD_2Cl_2, 22.5 MHz): δ_C 51.8 (q, J = 147 Hz, CH_3), 108.4 (d, J = 169 Hz, =CH), 165.3 (d, ^2J = 4 Hz, $=CS_2$), 166.4 (s, ester CO), 207.9 (s, CO). Mass spectrum: m/z (relative intensity) 400 (M^+ – CO, 5), 372 (M^+ – 2CO, 5), 344 (M^+ – 3CO, 5), 316 (M^+ – 4CO, 13), 288 (M^+ – 5CO, 7), 260 (M^+ – 6CO, 90), 176 (Fe_2S_2, 100), 144 (Fe_2S, 87), 112 (Fe_2, 6), 88 (FeS, 6), 56 (Fe, 24). Anal. Calcd. for $C_{10}H_4Fe_2O_8S_2$: C, 28.07; H, 0.94. Found: C, 27.63; H, 1.09.

Reaction between (μ-Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide, and Trifluoroacetic Acid. Ethynylmagnesium bromide, 28.2 mmol, was generated in 50 mL of THF from 17 mL (28.2 mmol) of a 1.66 M THF–ethylmagnesium bromide solution and acetylene (Airco). The Grignard reagent solution was cooled to –78 °C, and 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 15 mL of THF was cannulated into it, resulting in a green reaction mixture. After 1 h of stirring, 2.3 mL (31.0 mmol) of trifluoroacetic acid was added, causing an immediate color change to red. Stirring was continued for 10 min at –78 °C and then for 1 h at room temperature prior to removal of solvent. The remaining red tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.57 g (53% yield) of $(\mu\text{-}SCH{=}CHS)Fe_2(CO)_6$ as an air-stable, red solid, mp 55–56 °C (lit.[5] mp 54–55 °C), after crystallization from pentane.

IR ($CHCl_3$): 1564 (w) (C=C) cm^{-1}; terminal CO, 2087 (s), 2050 (vs), 2000 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 6.47 (s, vinyl). ^{13}C NMR (CD_3CN, 22.5 MHz): δ_C 146.3 (dd, J = 190 Hz, ^2J = 9 Hz, vinyl), 209.2 (s, CO). Anal. Calcd for $C_8H_2Fe_2O_6S_2$: C, 25.98; H, 0.54. Found: C, 25.74; H, 0.62.

C. Reaction of Intermediates with Aldehydes. 1. Pivalaldehyde. Following the standard procedure, 3.19 mmol of lithium phenylacetylide was generated in 40 mL of THF from 0.35 mL (3.19 mmol) of phenylacetylene (Aldrich) and 1.45 mL (3.19 mmol) of a 2.2 M *n*-butyllithium solution. This reagent solution was cooled to –78 °C, and 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 10 mL of THF was cannulated into it, resulting in a green reaction mixture. This was stirred for 30 min at –78 °C, and then 1.09 mL (10.0 mmol) of pivalaldehyde (Aldrich) was added by syringe. The mixture was stirred for 30 min at –78 °C and 1.5 h at room temperature. Trifluoroacetic acid, 0.3 mL (4.04 mmol), was added and the solution stirred another 30 min prior to removal of the solvent. The remaining brown oil was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band (trace amount of a red, oily solid, not identified), pentane/CH_2Cl_2 (4:1, v/v) removed a minor band (not identified), and pentane/Et_2O (4:1, v/v) eluted a red band, giving 1.28 g of a red tar. This tar was subjected to column chromatography (silicic acid/CH_2Cl_2), CH_2Cl_2 eluting a red band which gave 1.18 g (2.21 mmol, 76% yield) of an air-stable, red solid, mp 92–94 °C, after crystallization from CH_2Cl_2/pentane, identified as **11b**.

IR: ν(OH) 3597, 3470 (br) cm^{-1}; terminal CO, 2089 (s), 2051 (vs), 2002 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6, 90 MHz): δ 3.74 and 4.50 (both d, J = 5.9 Hz, 2 H, OH and CH), 0.80 (s, 9 H, $C(CH_3)_3$), 7.10 (m, 2 H, Ph), 7.32 (m, 3 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 Hz): δ_C 26.6 (q, J = 128 Hz, CH_3), 36.4 (s, *C*Me_3), 77.0 (d, J = 148 Hz, CH), 126.5 (d, J = 169 Hz, Ph), 129.0 (d, J = 161 Hz, Ph), 135.5 (s, ipso Ph), 153.7 (s, vinyl), 153.9 (s, vinyl), 207.6 and 207.9 (both s, CO). Mass spectrum: m/z (relative intensity) 476 (M^+ – 2CO, 9), 448 (M^+ – 3CO, 15), 420 (M^+ – 4CO, 7), 392 (M^+ – 5CO, 6), 364 (M^+ – 6CO, 100), 346 (M^+ – 6CO – H_2O, 74), 176 (Fe_2S_2, 76), 112 (Fe_2, 5), 88 (FeS, 16), 77 (Ph, 100), 56 (Fe, 80). Anal. Calcd for $C_{19}H_{16}Fe_2O_7S_2$: C, 42.88; H, 3.03. Found: C, 42.69; H, 3.09.

2. Benzaldehyde. This product was purified by filter chromatography (silicic acid, 4:1 pentane/CH_2Cl_2) (→red tar) and subsequent column chromatography (silicic acid, CH_2Cl_2). A red, glassy solid, **11c**, was obtained in 47% yield.

IR: ν(OH) 3593, 3400 (br) cm^{-1}; terminal CO, 2087 (s), 2051 (vs), 2014 (vs) cm^{-1}. ^{1}H NMR (CD_3CN, 270 MHz): δ 3.86 and 5.05 (both d, 2 H, J = 5.2 Hz, OH and CH), 7.22 and 7.36 (both m, 10 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 Hz): δ_C 70.3 (d, J = 146 Hz, CH), 125.5 (d, J = 160 Hz, Ph), 126.4 (d, J = 160 Hz, Ph), 128.1 (d, J = 160 Hz, Ph), 128.6 (d, J = 160 Hz, Ph), 128.8 (d, J = 162 Hz, Ph), 129.4 (d, J = 162 Hz, Ph), 134.4 (s, ipso Ph), 138.9 (s, ipso Ph), 153.1, 154.0 (both s, vinyl), 207.4 and 207.6 (both s, CO). Mass spectrum: m/z (relative intensity) 524 (M^+ – CO, 4), 496 (M^+ – 2CO, 19), 468 (M^+ – 3CO, 28), 440 (M^+ – 4CO, 15), 412 (M^+ – 5CO, 11), 384 (M^+ – 6CO, 100), 176 (Fe_2S_2, 24), 144 (Fe_2S, 4), 88 (FeS, 11), 77 (Ph, 46), 56 (Fe, 10). Anal. Calcd for $C_{21}H_{12}Fe_2O_7S_2$: C, 45.68; H, 2.19. Found: C, 45.44; H, 2.23.

3. Acetaldehyde. The product, **11a**, an air-stable, red solid, mp 87–89 °C (from CH_2Cl_2/pentane), was purified by filtration chromatography (silicic acid, 4:1 pentane/Et_2O, after pentane alone had separated some **8**) and column chromatography (silicic acid, CH_2Cl_2). A 31% yield of **11a** was obtained.

IR: ν(OH) 3608, 3450 (br) cm^{-1}; terminal CO, 2088 (s), 2062 (vs), 2004 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.34 (d, J = 6.3 Hz, 3 H, CH_3), 1.55 (d, J = 5.9 Hz, 1 H, OH), 4.19 (quintet, J = 6.3 Hz, 1 H, CH), 7.34 (m, 3 H, Ph), 7.07 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 20.6 (q, J = 128 Hz, CH_3), 64.9 (d, J = 150 Hz, CH), 126.3 (d, J = 155 Hz, Ph), 128.7 (d, J = 166 Hz, Ph), 129.2 (d, J = 166 Hz, Ph), 134.4 (s, ipso Ph), 151.6 (s, vinyl), 155.8 (s, vinyl), 207.6 (s, CO). Mass spectrum: m/z (relative intensity) 434 (M^+ – 2CO, 3), 406 M^+ – 3CO, 7), 378 (M^+ – 4CO, 5), 350 (M^+ – 5CO, 15), 322 (M^+ – 6CO, 22), 304 (M^+ – 6CO – H_2O, 60), 176 (Fe_2S_2, 100), 144 (Fe_2S, 12), 88 (FeS, 6), 77 (Ph, 34), 56 (Fe, 10). Anal. Calcd for $C_{16}H_{10}Fe_2O_7S_2$: C, 39.21; H, 2.06. Found: C, 39.44; H, 2.07.

---

(18) (a) Yamada, K.; Miyaura, N.; Itoh, M.; Suzuki, A. *Synthesis* **1977**, 679. (b) Midland, M. M.; Tramontano, A.; Cable, J. R. *J. Organomet. Chem.* **1980**, *45*, 28.

D. Reactions with Group IV (14^{20}) Halides. 1. $PhC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$. a. Trimethylchlorosilane. The $PhC{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture was prepared (same scale) as described in section A.1. The resulting green reaction mixture was stirred for 30 min at −78 °C, and then 3.70 mL (29.2 mmol) of trimethylchlorosilane (Petrarch) was added by syringe. The solution was stirred for 15 min at −78 °C and 19 h at room temperature during which time a color change of green-to-red occurred. The solvent was removed on a rotary evaporator, leaving a brown oil which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which after removal of solvent yielded an oily red solid. This material was crystallized from pentane/ethanol, mp 81–82 °C, to yield 0.994 g (1.92 mmol, 66% yield) of **12c** as an air-stable, red solid.

IR: terminal CO, 2070 (s), 2033 (vs), 1998 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ −0.10 (s, 9 H, $SiCH_3$), 7.04 and 7.29 (both m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −1.4 (q, J = 120 Hz, $SiCH_3$), 126.6 (d, J = 159 Hz, Ph), 128.5 (d, J = 162 Hz, Ph), 129.3 (d, J = 160 Hz, Ph), 136.8 (s, ipso Ph), 148.6 (s, $=CSiMe_3$), 167.2 (s, $=CPh$), 208.3 (s, CO). Anal. Calcd for $C_{17}H_{14}Fe_2O_6S_2Si$: C, 39.40; H, 2.72. Found: C, 39.48; H, 2.84.

b. Trimethyltin Bromide. The red oil which was obtained was purified by filtration chromatography (silicic acid/pentane) to give **12d** in 91% yield as an air-stable, red solid, mp 117–119 °C dec (from pentane).

IR: terminal CO, 2074 (s), 2035 (vs), 2000 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ −0.01 (s, $J(^{119}Sn\text{–}H)$ = 56.9 Hz, $J(^{117}Sn\text{–}H)$ = 54.7, 9 H, $SnCH_3$), 7.08 and 7.28 (both m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −8.1 (q, J = 131 Hz, $SnCH_3$), 126.3 (d, J = 155 Hz, Ph), 128.5 (d, J = 156 Hz, Ph), 129.3 (d, J = 161 Hz, Ph), 137.0 (s, ipso Ph), 149.5 (s, $=CSnMe_3$), 156.1 (s, $=CPh$), 208.2 (s, CO). Anal. Calcd for $C_{17}H_{14}Fe_2O_6S_2Sn$: C, 33.54; H, 2.32. Found: C, 33.61; H, 2.38.

c. Triphenylgermanium Bromide. The product **12f**, an air-stable, red solid, mp 147–149 °C dec (from pentane/CH_2Cl_2), was isolated in 41% yield after filtration chromatography (silicic acid, 4:1 pentane/CH_2Cl_2). Pentane alone eluted some **8** (12% yield).

IR: terminal CO, 2082 (s), 2051 (vs), 2001 (vs) cm^{-1}. ^1H NMR (acetone-d_6 90 MHz): δ 6.90 (s, 5 H, Ph), 7.35 (s, 15 H, $GePh_3$). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 126.5 (d, J = 160 Hz, Ph), 127.8 (d, J = 161 Hz, Ph), 128.3 (d, J = 160 Hz, Ph), 129.2 (d, J = 161 Hz, Ph), 129.3 (d, J = 160 Hz, Ph), 134.0 (s, ipso Ph), 134.9 (d, J = 160 Hz, Ph), 135.3 (s, ipso Ph), 144.5 (s, $=CGePh_3$), 169.1 (s, $=CPh$), 208.1 (s, CO). Anal. Calcd for $C_{32}H_{20}GeFe_2O_6S_2$: C, 51.32; H, 2.69. Found: C, 51.30; H, 2.73.

d. Triphenyltin Chloride. The product **12e**, an air-stable, red solid, mp 127–128 °C (dec) (from pentane/CH_2Cl_2), was isolated in 86% yield by filtration chromatography (silicic acid, 4:1 pentane/CH_2Cl_2) after pentane had eluted a 9% yield of **8**.

IR: terminal CO, 2086 (s), 2051 (vs), 2005 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 6.92 (s, 5 H, Ph), 7.31 (s, 15 H, $SnPh_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz): δ_C 126.2, 128.1, 128.6, 128.7, 129.1, 129.3, 129.4 (all Ph), 136.6 (s, $J_{C\text{–}Sn}$ = 39 Hz, ipso, SnPh), 146.1 (s, $=CSnPh_3$), 170.7 (s, $=CPh$), 208.0 (s, CO). Anal. Calcd for $C_{32}H_{20}Fe_2S_2Sn$: C, 48.35; H, 2.54. Found: C, 48.44; H, 2.56.

e. Triphenyllead Bromide. The product **12g**, an air-stable, red solid, mp 128–130 °C dec (from pentane/CH_2Cl_2), was isolated in 70% yield after filtration chromatography and subsequent column chromatography (silicic acid, 4:1 pentane/CH_2Cl_2) Pentane eluted a 7% yield of **8**.

IR: terminal CO, 2070 (s), 2036 (vs), 2000 (vs) cm^{-1}. ^1H NMR (acetone-d_6, 90 MHz): δ 7.39, 7.02 (both s, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz): δ_C 126.2, 128.1, 128.8 ($J_{Pb\text{–}C}$ = 23 Hz), 129.2, 129.6 ($J_{Pb\text{–}C}$ = 91 Hz), 135.8, 136.9 ($J_{Pb\text{–}C}$ = 73 Hz), 150.2 ($J_{Pb\text{–}C}$ = 545 Hz) (all Ph), 157.4 ($J_{Pb\text{–}C}$ = 63 Hz, $=CPbPh_3$), 167.8 ($=CPh$), 208.1 (s, CO). Anal. Calcd for $C_{32}H_{20}Fe_2O_6PhS_2$: C, 43.50; H, 2.28. Found: C, 43.19; H, 2.25.

2. $n\text{-}C_4H_9C{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$. a. Trimethylchlorosilane. The brown oil obtained was purified by filtration chromatography (silicic acid/pentane) to give **12h**, a red, air-stable solid, mp 54–55 °C (from pentane/EtOH), in 82% yield.

IR: terminal CO, 2065 (s), 2029 (vs), 1996 (vs), 1985 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 0.14 (s, 9 H, $SiCH_3$), 0.80–2.24 (m, 9 H, butyl). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −1.1 (q, J = 120 Hz, $SiCH_3$), 13.7 (q, J = 125 Hz, CH_3), 22.3 (t, J = 125 Hz, CH_2), 29.2 (t, J = 133 Hz, CH_2), 34.1 (t, J = 130 Hz, CH_2), 143.7 (s, $=CSiMe_3$), 170.3 (s, $=CCH_2$), 208.2 (s, CO). Anal. Calcd for $C_{15}H_{18}Fe_2O_6S_2Si$: C, 36.16; H, 3.64. Found: C, 36.23; H, 3.65.

b. Trimethyltin Chloride. The product **12i** was isolated from the initially obtained brown oil by filtration chromatography (silicic acid/pentane), 86% yield. Recrystallization from pentane/ethanol gave a red, air-stable solid, mp 48–49 °C.

IR: terminal CO, 2069 (s), 2031 (vs), 1998 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 0.21 (s, $J(^{119}Sn\text{–}H)$ = 55.9 Hz, $J(^{117}Sn\text{–}H)$ = 54.6 Hz, $SnCH_3$), 0.8–2.1 (m, butyl). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −8.3 (q, J = 130 Hz, $SnCH_3$), 13.8 (q, J = 124 Hz, CH_3), 22.2 (t, J = 126 Hz, CH_2), 29.6 (t, J = 130 Hz, CH_2), 34.9 (t, J = 130 Hz, CH_2), 143.8 (s, $=CSnMe_3$), 169.2 (s, $=CCH_2$), 208.3 (s, CO). Anal. Calcd for $C_{15}H_{18}Fe_2O_6S_2Sn$: C, 30.60; H, 3.08. Found: C, 30.71; H, 3.13.

3. $CH_3C{\equiv}CLi/(\mu\text{-}S_2)Fe_2(CO)_6$. Trimethyltin Bromide. The product **12b** was purified by filtration chromatography to give a red, air-stable solid, mp 74–75 °C (from pentane/EtOH), in 75% yield.

IR: terminal CO, 2068 (s), 2030 (vs), 1998 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 0.22 (s, 9 H, $J(^{119}Sn\text{–}H)$ = 57.0 Hz, $J(^{117}Sn\text{–}H)$ = 54.0 Hz, $SnCH_3$), 1.72 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −8.5 (q, J = 130 Hz, $SnCH_3$), 21.1 (q, J = 129 Hz, CH_3), 143.7 (s, $=CSnMe_3$), 163.8 (s, $=CMe$), 208.2 (s, CO). Anal. Calcd for $C_{12}H_{12}Fe_2O_6S_2Sn$: C, 26.36; H, 2.21. Found: C, 26.54; H, 2.29.

4. $LiC{\equiv}CCO_2CH_3/(\mu\text{-}S_2)Fe_2(CO)_6$. a. Trimethylchlorosilane. The lithium reagent was generated as described in section B.6, and the reaction with $(\mu\text{-}S_2)Fe_2(CO)_6$ was carried out at −78 °C.

The red tar that was obtained was purified by filtration chromatography (silicic acid, 4:1 pentane/CH_2Cl_2); **13** (M = Si), an air-stable, red solid, mp 46–47 °C (from pentane), was isolated in 69% yield.

IR: ν(C=O) 1700 cm^{-1}; ν(C=C) 1525 cm^{-1}; terminal CO, 2076 (s), 2039 (vs), 2002 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 0.18 (s, 9 H, $SiCH_3$), 3.67 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −0.64 (q, J = 120 Hz, $SiCH_3$), 51.4 (q, J = 147 Hz, CH_3), 121.8 (s, $=CSiMe_3$), 165.4 (s, $=CS_2$), 167.1 (s, ester CO), 207.4 (s, CO). Anal. Calcd for $C_{13}H_{12}Fe_2O_8S_2Si$: C, 31.22; H, 2.42. Found: C, 31.37; H, 2.47.

b. Trimethyltin Bromide. The brown oil obtained was purified by filtration chromatography and recrystallization from pentane to give **13** (M = Sn), an air-stable, red solid, mp 71–72 °C.

IR: ν(CO) 1685 cm^{-1}; ν(C=C) 1525 cm^{-1}; terminal CO, 2079 (s), 2043 (vs), 2006 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ 0.29 (s, $J(^{119}Sn\text{–}H)$ = 57.6 Hz, $J(^{117}Sn\text{–}H)$ = 54.7 Hz, 9 H, $SnCH_3$), 3.65 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C −6.9 (q, J = 130 Hz, $SnCH_3$), 51.4 (q, J = 147 Hz, CH_3), 121.7 (s, $=CSnMe_3$), 165.6 (s, $=CS_2$), 167.7 (s, ester CO), 207.4 (s, CO). Anal. Calcd for $C_{13}H_{12}Fe_2O_8S_2Si$: C, 26.43; H, 2.05. Found: C, 26.69; H, 2.08.

Reaction between (μ-Dithio)bis(tricarbonyliron), Ethynylmagnesium Bromide, and Trimethylchlorosilane. Ethynylmagnesium bromide (18.0 mmol) was prepared as above by using 50 mL of THF and 10 mL (18.0 mmol) of a 1.80 M THF solution of EtMgBr. The Grignard reagent solution was cooled to −78 °C, and 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 10 mL of THF was cannulated into it, resulting in a green reaction mixture. After the mixture was stirred for 1.5 h at −78 °C, 2.30 mL (18.4 mmol) of Me_3SiCl was added. Stirring was continued for 30 min at −78 °C and 1.5 h at room temperature during which time the solution became red. The solvent was removed, leaving a black solid which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.517 g (40% yield) of $[\mu\text{-}SCH{=}C(SiMe_3)S]Fe_2(CO)_6$ as an air-stable, red solid. After crystallization from ethanol, mp 69–70 °C, it was identified by comparison of its ^1H NMR spectrum with that of an authentic sample (see above).

E. Reactions with Methylmercuric Chloride. 1. Use of the "Standard" Procedure. Following the procedure in section A.1, 3.19 mmol of lithium phenylacetylide was generated in 40 mL of THF from 0.35 mL of phenylacetylene (Aldrich) and 1.45 mL (3.19 mmol) of a 2.2 M n-butyllithium solution. This solution was cooled to −78 °C, and 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 10 mL of THF was cannulated into it, resulting in a green reaction mixture. This was stirred for 30 min at −78 °C, and then 0.83

g (3.30 mmol) of methylmercuric chloride (Organometallics, Inc.) in 10 mL of THF was cannulated in, causing a color change to red. The mixture was stirred for 30 min at −78 °C and 30 min at room temperature prior to removal of the solvent. The remaining red oil was taken up in pentane/CH_2Cl_2 (4:1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red solid which was applied to filtration chromatography (silicic acid/pentane). Pentane eluted two red bands which gave respectively 0.23 g (0.51 mmol, 18% yield) of **8**, identified by comparison to an authentic sample, and 0.30 g (0.45 mmol, 16% yield) of **17** as an air-stable, red solid, mp 123–130 °C dec, after crystallization from pentane/CH_2Cl_2.

IR ($CHCl_3$): 2915 (m), 1594 (m), 1550 (m, br), 1487 (m), 1447 (m), 1078 (m), 907 (m), 617 (s), 555 (s) cm^{-1}; terminal carbonyl region, 2079 (s), 2045 (vs), 2004 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 270 MHz): δ 0.53 (s, J_{Hg-H} = 135.2 Hz, 3 H, CH_3), 7.30 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 11.2 (q, J = 133 Hz, CH_3), 125.2 (d, J = 158 Hz, Ph), 128.6 (d, J = 162 Hz, Ph), 129.4 (d, J = 162 Hz, Ph), 136.4 (s, ipso Ph), 167.3 (s, vinyl), 189.1 (s, vinyl), 208.2 (s, CO). Anal. Calcd for $C_{15}H_8Fe_2O_6S_2Hg$: C, 27.27; H, 1.22. Found: C, 27.35; H, 1.46.

Pentane/CH_2Cl_2 (4:1, v/v) eluted a third red band which yielded 1.0 g (1.52 mmol, 52% yield) of **16** as a dark red, air-stable solid, mp 125–130 °C dec, after crystallization from pentane/CH_2Cl_2.

IR ($CHCl_3$): 2925 (w), 2174 (w) (C≡C), 1597 (m), 1489 (m), 1443 (m), 1267 (m), 912 (w), 861 (w), 614 (s), 560 (s) cm^{-1}; terminal carbonyl region, 2080 (s), 2047 (vs), 2004 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 270 MHz): δ 0.91 (s, J_{Hg-H} = 165.6 Hz, 3 H, CH_3), 7.38 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 17.5 (q, J = 138 Hz, CH_3), 84.9 (s, alkynyl), 85.1 (s, alkynyl), 122.0 (s, ipso Ph), 128.4 (d, J = 162 Hz, Ph), 129.1 (d, J = 162 Hz, Ph), 132.2 (d, J = 164 Hz, Ph), 208.8 (s, CO). Anal. Calcd for $C_{15}H_8Fe_2O_6S_2Hg$: C, 27.27; H, 1.22. Found: C, 27.32; H, 1.29.

2. Rapid Workup after Reaction at −78 °C. Following the procedure outlined above, 3.19 mmol of lithium phenylacetylide was reacted with 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ at −78 °C, resulting in a green reaction mixture. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 mL of THF, was cannulated into the reaction mixture, producing a red solution which was stirred for 4.5 h at −78 °C. It was then taken from the cold bath and the solvent removed rapidly on a rotary evaporator. The remaining red oil was taken up in pentane/CH_2Cl_2 (4:1, v/v) and filtered through a pad of silicic acid. Removal of the solvent left a red solid which was extracted with two 30-mL portions of pentane, leaving much of the solid but giving a red filtrate. This pentane solution was subjected to filtration chromatography (silicic acid/pentane), giving two red bands which yielded respectively 0.044 g (0.099 mmol, 3% yield) of **8** and 0.11 g (0.16 mmol, 6% yield) of **17**, both identified by comparison of their ^1H NMR spectra to those of the authentic samples. Pentane/CH_2Cl_2 (4:1, v/v) eluted a third red band which was combined with the extracted red solid to give 1.52 g (2.30 mmol, 79% yield) of **16**, identified by comparison of its ^{13}C NMR spectrum with that of an authentic sample.

3. Reaction for 1 h at −78 °C and 4.5 h at Room Temperature. The PhC≡CLi/$(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture was prepared as described above. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 mL of THF, was cannulated into the reaction mixture, producing a red solution which was stirred for 1 h at −78 °C and then was removed from the cold bath and stirred at room temperature for 4.5 h prior to removal of solvent. The remaining red tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.32 g (0.71 mmol, 25% yield) of **16**, and pentane/CH_2Cl_2 (4:1, v/v) eluted a red band which gave 1.02 g (1.54 mmol, 53% yield) of **17**.

In another experiment, the PhC≡CLi/$(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture was removed from the cold bath and stirred for 35 min, at which point it looked brown. Methylmercuric chloride, 0.83 g (3.30 mmol), dissolved in 10 mL of THF, was cannulated into the reaction mixture, producing a red solution which was stirred for 5 h. The solvent was removed on a rotary evaporator, leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band which gave 0.117 g (0.262 mmol, 9% yield) of **8**. Pentane/CH_2Cl_2 (4:1, v/v) eluted a red band which yielded 1.28 g (1.94 mmol, 67% yield) of **17**.

4. Isomerization of 16 in the Presence of Lithium Chloride. A dry, 100-mL, round-bottomed flask equipped with a stir bar and a serum cap was charged with 0.83 g (1.26 mmol) of **16** and 0.05 g (1.26 mmol) of anhydrous lithium chloride in a glovebox. After removal from the glovebox, 40 mL of THF was added and the solution stirred for 3 h. The solvent was removed on a rotary evaporator, leaving a red tar which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor red band which yielded 0.096 g (0.22 mmol, 17% yield) of **8**. Further elution with pentane/CH_2Cl_2 (9:1, v/v) moved a red band which gave 0.65 g (0.98 mmol, 78% yield) of **17**. Both were identified by comparison of their ^1H NMR spectra to those of the authentic samples.

Reaction between $[\mu\text{-}SC(SnPh_3){=}C(Ph)S]Fe_2(CO)_6$ (12e), Phenyllithium and Iodomethane. A dry, 300-mL, round-bottomed flask equipped with a magnetic stir bar and a serum cap was charged with 0.38 g (0.48 mmol) of $[\mu\text{-}SC(SnPh_3){=}C(Ph)S]Fe_2(CO)_6$ and flushed with nitrogen. Diethyl ether (30 mL) was added and the red solution cooled to −78 °C. By syringe, 0.84 mL (0.72 mmol) of a 0.86 M phenyllithium solution in Et_2O was added the reaction mixture stirred for 1 h. The solution became red-brown, and a white precipitate (Ph_4Sn) was observed. Subsequently, 1 mL of iodomethane was added, and the solution was stirred for 0.5 h at −78 °C and 2 h at room temperature. The reaction mixture was filtered and the white solid obtained washed with water and Et_2O. After being dried, this solid was identified as Ph_4Sn [mp 229–231 °C (lit.[19] 228–230 °C)], 0.103 g (50% yield). The solvent was removed from the red filtrate, leaving a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.14 g (63% yield) of $(\mu\text{-}CH_3S)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$, identified by comparison of its IR, ^1H NMR, and ^{13}C NMR spectra to those of an authentic sample. It was found to be a 1.4:1 CH_3(a)/CH_3(e) mixture of both isomers.

Reaction between (μ-Dithio)bis(tricarbonyliron), Lithium Phenylacetylide, and Triphenyltin Chloride in Diethyl Ether. Following the standard procedure, 3.19 mmol of lithium phenylacetylide was generated in 30 mL of Et_2O. This reagent solution was cooled to −78 °C, and 1.0 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ in 20 mL of Et_2O was cannulated into it, resulting in a brown solution. This was stirred for 30 min at −78 °C, and then 1.16 g (3.0 mmol) of solid Ph_3SnCl was added against a counterflow of nitrogen. The solution was stirred for 30 min at −78 °C during which time it became red and a white precipitate (LiCl) formed. It was then removed from the cold bath and stirred another 45 min. The solution then was filtered and the diethyl ether removed, leaving a red oil which was taken up in pentane and filtered. Removal of the solvent left a red tar which was dried under vacuum. This was dissolved in pentane, and the solution was concentrated to about 5 mL. A red solid, 0.61 g (0.77 mmol, 26% yield), was deposited overnight at room temperature. The material, mp 105–107 °C dec, was identified as $(\mu\text{-}Ph_3SnS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$.

IR ($CHCl_3$): ν(C≡C) 2172 cm^{-1}; terminal CO, 2079 (s), 2043 (vs), 2005 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 7.25–7.8 (complex m, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz): δ_C 86.6, 86.9 (alkyne), 122.8 (ipso Ph), 129–139.6 (Ph), 208.7 (s, CO). Anal. Calcd for $C_{32}H_{20}Fe_2O_6SnS_2$: C, 48.34; H, 2.54. Found: C, 48.16; H, 2.60%.

Reaction between (μ-Dithio)bis(tricarbonyliron), Lithium Phenylacetylide, and Triphenyllead Chloride in Diethyl Ether. Following the standard reaction procedure, 1.50 mmol of lithium phenylacetylide was generated in 30 mL of Et_2O and treated with 0.5 g (1.46 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ as before. The resulting brown solution was stirred for 30 min at −78 °C. Then, against a counterflow of nitrogen, 0.78 g (1.50 mmol) of solid

---

(19) Gielen, M.; Nasielski, J. *Organotin Compounds*; Sawyer, A. K.; Ed.; Marcel Dekker: New York, 1972; Vol. 3, p 671.

(20) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Ph_3PbBr was added. The solution was stirred for 30 min at −78 °C during which time it became red and a white precipitate formed (LiBr). It then was removed from the cold bath and stirred another 3 h at room temperature. After the solution was filtered, the diethyl ether was removed, leaving a red tar. This tar was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Pentane/CH_2Cl_2 (9:1, v/v) eluted a red band which gave 0.91 g (71% yield of $(\mu\text{-}Ph_3PbS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$ as a glassy, red solid.

IR ($CHCl_3$): $\nu(C{\equiv}C)$ 2175; terminal CO, 2079 (s), 2044 (vs), 2007 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 90 MHz): δ 7.1–7.8 (complex m, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 67.9 MHz): δ_C 86.1, 87.0 (alkyne), 122.7 (ipso Ph), 129–132.5 (Ph), 155.5 ($J_{C\text{-}Pb}$ = 438 Hz, ipso PbPh), 209.1 (CO). Anal. Calcd for $C_{32}H_{20}Fe_2O_6PbS$: C, 43.50; H, 2.28. Found: C, 43.73; H, 2.44.

Addition of $(\mu\text{-}Ph_3PbS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$ to a THF Solution of Lithium Bromide. A 100-mL, round-bottomed flask was charged with 0.05 g (0.57 mmol) of anhydrous lithium bromide and 10 mL of THF. After this solution was cooled to −78 °C, 0.50 g (0.57 mmol) of $(\mu\text{-}Ph_3PbS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$ in 10 mL of THF was cannulated into it. The mixture became brown. It was stirred at −78 °C for 2 h, then removed from the cold bath, and stirred for another 3 h prior to removal of the solvent. The black tar remaining was extracted with pentane, yielding a red solution which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.065 g (26% yield) of **8** as a red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

Addition of $(\mu\text{-}Ph_3SnS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$ to a THF Solution of Lithium Chloride. A 100-mL, round-bottomed flask was charged with 0.02 g (0.46 mmol) of anhydrous lithium chloride and 10 mL of THF. After this solution was cooled to −78 °C, 0.368 g (0.46 mmol) of $(\mu\text{-}Ph_3SnS)(\mu\text{-}PhC{\equiv}CS)Fe_2(CO)_6$ in 10 mL of THF was cannulated into it. The mixture became brown. It was stirred at −78 °C for 30 min, then removed from the cold bath, and stirred for 4 h at room temperature. Removal of the solvent left a black tar which was extracted with pentane, giving a red solution. This was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which yielded 0.031 g (0.069 mmol, 15% yield) of **8** as a red solid identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

Acknowledgment. We are grateful to the National Science Foundation for support of this work. D.S. acknowledges, with thanks, an Alexander von Humboldt Prize, awarded by the Alexander von Humboldt Foundation, Bad Godesberg, during the tenure of which this paper was written.

Registry No. **2**, 14243-23-3; **6** (R = Ph, R′ = Et), 85552-98-3; **6** (R = Ph, R′ = Et) (equatorial/axial isomer), 104011-59-8; **6** (R = Ph, R′ = Et) (equatorial/equatorial isomer), 104011-60-1; **6** (R = Ph, R′ = $PhCH_2$), 103934-15-2; **6** (R = Ph, R′ = $CH_3C(O)CH_2$), 103934-16-3; **6** (R = *n*-C_4H_9, R′ = Me), 103934-18-5; **6** (R = *n*-C_5H_{11}, R′ = Me), 103934-19-6; **6** (R = *n*-C_5H_{11}, R′ = $CH_3C(O)CH_2$), 103934-20-9; **6** (R = *n*-C_5H_{11}, R′ = $CH_3C(O)CH_2$) (equatorial/axial isomer), 104011-61-2; **6** (R = *n*-C_5H_{11}, R′ = $CH_3C(O)CH_2$) (equatorial/equatorial isomer), 103934-20-9; **6** (R = $CH_2{=}C(CH_3)$, R′ = Me), 103934-21-0; **6** (R = Me_3Si, R′ = Me), 103934-22-1; **6** (R = Me_3Si, R′ = Et), 103934-23-2; **6** (R = H, R′ = Me), 103934-24-3; **6** (R = Ph, R′ = Ph_3Sn), 103934-25-4; **6** (R = Ph, R′ = Ph_3Pb), 103958-92-5; **7** (R = Ph, R′ = Me), 85553-00-0; **7** (R = Ph, R′ = Me_3C), 103934-17-4; **8**, 85553-01-1; **9** (R = Me), 85553-20-4; **9** (R = *n*-C_4H_9), 85553-21-5; **9** (R = *n*-C_5H_{11}), 85553-22-6; **9** (R = $CH_2{=}C(CH_3)$, 85553-23-7; **9** (R = H), 12079-70-8; **10** (R = Me_3Si), 85553-04-4; **10** (R = CO_2CH_3), 85553-03-3; **11a**, 85553-18-0; **11b**, 85553-19-1; **11c**, 85553-17-9; **12a**, 85553-02-2; **12b**, 85553-08-8; **12c**, 85553-05-5; **12d**, 85553-09-9; **12e**, 85553-10-2; **12f**, 85553-07-7; **12g**, 85553-12-4; **12h**, 85553-06-6; **12i**, 85553-11-3; **13** (M = Si), 85553-13-5; **13** (M = Sn), 85553-14-6; **16**, 85553-15-7; **17**, 85553-16-8; **24**, 104011-58-7; $PhC{\equiv}CLi$, 4440-01-1; *n*-$C_4H_9C{\equiv}CLi$, 17689-03-1; *n*-$C_5H_{11}C{\equiv}CLi$, 42017-07-2; $CH_2{=}C(CH_3)C{\equiv}CLi$, 38341-85-4; $(CH_3)_3SiC{\equiv}CLi$, 54655-07-1; $HC{\equiv}CMgBr$, 4301-14-8; MeI, 74-88-4; EtI, 75-03-6; $PhCH_2Cl$, 100-44-7; $CH_3C(O)CH_2Br$, 598-31-2; $CH_3C(O)Cl$, 75-36-5; $Me_3CC(O)Cl$, 3282-30-2; Me_3CCHO, 630-19-3; PhCHO, 100-52-7; CH_3CHO, 75-07-0; Me_3SiCl, 75-77-4; Me_3SnBr, 1066-44-0; Ph_3GeBr, 3005-32-1; Ph_3SnCl, 639-58-7; Ph_3PbBr, 894-06-4; MeHgCl, 115-09-3; PhLi, 591-51-5; S_2, 23550-45-0.

(3-Sulfinylpropyl)tins and (3-Sulfonylpropyl)tins: Studies on Intramolecular Coordination

Kamal Swami, Brigitte Nebout, Dan Farah, Ramesh Krishnamurti, and Henry G. Kuivila*

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

Received February 6, 1986

A series of sulfoxides of the structures $Me_nX_{3-n}Sn(CH_2)_3SOC_2H_5$ and $Me_nX_{3-n}Sn(CH_2)_3SOC_6H_5$ (X = Cl or Br; *n* = 1–3) and sulfones $Me_nX_{3-n}Sn(CH_2)_3SO_2C_2H_5$ (X = Cl or Br; *n* = 1–3) have been prepared and characterized. ^1H, ^{13}C, and ^{119}Sn NMR and IR studies were carried out. These showed that the sulfoxides with *n* = 1 or 2 are cyclic species with S–O → Sn coordination. The sulfones in chloroform showed evidence of intramolecularly coordinated species in equilibrium with acyclic species. Only the acyclic species were present in acetonitrile which presumably coordinates more strongly to the tin than does the sulfonyl group.

The synthesis of molecules bearing functional groups of opposite polarities so disposed that they can undergo intramolecular interaction with each other is of general interest because such interaction may lead to formation of cyclic compounds. The result may be the formation of a new functional group at one extreme or, at the other, a weak donor–acceptor interaction which is quite labile but will nonetheless modify the chemical and physical properties of each group. Compounds bearing Lewis acidic tin atoms and donor organofunctional groups are well-suited for studies of the nature of such donor–acceptor interactions.[1] Donors which have been studied in varying degrees

---

(1) For reviews of early work see: (a) Omae, I. *Rev. Silicon, Germanium, Tin Lead Compd.* **1972** *1*, 59. (b) Tzschach, A.; Eichmann, W.; Jurkschat, K. *Organomet. Chem. Rev.* **1981**, *12*, 293.