Reactions of thioallenes with triiron dodecacarbonyl: a route to thioallyl-bridged diiron hexacarbonyl complexes

Dietmar Seyferth, Lea L. Anderson, William B. Davis, and Martin Cowie

Organometallics, **1992**, 11 (11), 3736-3744• DOI: 10.1021/om00059a042 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

determinations.

Acknowledgment. We thank the McMaster University Regional Centre for Mass Spectrometry for mass spectral determinations, D. S. Mitchell (Uniroyal Chemical, Guelph, Ontario) for combustion analyses, and the Natural Sciences and Engineering Research Council of Canada for its financial support of this work.

OM920413B

Reactions of Thioallenes with Triiron Dodecacarbonyl: A Route to Thioallyl-Bridged Diiron Hexacarbonyl Complexes

Dietmar Seyferth,* Lea L. Anderson, and William B. Davis

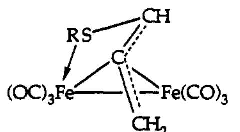
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Martin Cowie

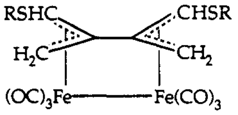
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Received April 17, 1992

Thioallenes, $RSC(X){=}C{=}CH_2$ ($R = CH_3, C_2H_5$, Ph; $X = OCH_3$, H) react with $Fe_3(CO)_{12}$ to give products of type A. An additional product, B, is obtained when the thioallene used is $PhSCH{=}C{=}CH_2$. A complex



A

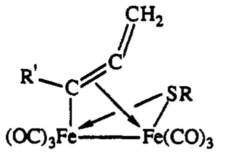


B

of this type and the isomer in which the RS groups are in trans position also are obtained in low yield in the case of $CH_3SCH{=}C{=}CH_2$, in addition to the type B major product. The formation of $(\mu\text{-}RS)_2Fe_2(CO)_6$ as by-products indicates that some C-S bond cleavage occurs as well. The structures of one example each of structural types A and B have been determined: $(\eta^1{:}\eta^3\text{-}CH_3SCHCCH_2)Fe_2(CO)_6$ (**2a**) for $R = CH_3$, $X = H$; $(\eta^3\text{-}PhSCHCCH_2)_2Fe_2(CO)_6$ (**15b**) for R = Ph. Compound **2a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.7134$ (4) Å, $b = 13.6321$ (5) Å, $c = 12.9757$ (9) Å, $\beta = 102.318$ (6)°, $V = 1333.0$ (3) Å^3, and $Z = 4$, and has refined to $R = 0.041$ and $R_w = 0.047$ based on 2192 unique observations. Compound **15b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.938$ (1) Å, $b = 12.064$ (2) Å, $c = 9.806$ (1) Å, $\alpha = 92.02$ (1)°, $\beta = 93.03$ (1)°; $\gamma = 68.15$ (1)°, $V = 1199.2$ (4) Å^3, $Z = 2$, and has refined to $R = 0.038$ and $R_w = 0.054$ based on 3360 unique observations.

Introduction

The thermal reaction of vinyl sulfides, $RSCH{=}CH_2$, with triiron dodecacarbonyl was reported to give low yields of $(\mu\text{-}\eta^1{:}\eta^2\text{-}CH_2{=}CH)(\mu\text{-}RS)Fe_2(CO)_6$ complexes.[1] A similar reaction between allenyl sulfides, $RSC(R'){=}C{=}CH_2$, might then be expected to result in formation of analogous $(\mu\text{-}\eta^1{:}\eta^2\text{-allenyl})(\mu\text{-}RS)Fe_2(CO)_6$ complexes, 1. We had



1

prepared complexes of type 1 in earlier studies by reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with propargyl halides, $RC{\equiv}CCH_2X$ ($R = H, CH_3$),[2a] and by the reaction of allenylmercuric iodide with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$.[2b] An alternate route to such complexes would be of interest, and accordingly we have studied some reactions of $Fe_3(CO)_{12}$ with various thioallenes. In part, these reactions took a different course than we had anticipated, one not involving C–S bond cleavage.

Results and Discussion

The initial reaction studied was that of 1-methoxy-1-(methylthio)allene, $(CH_3O)(CH_3S)C{=}C{=}CH_2$, with triiron dodecacarbonyl. A reflux period of 4 h under nitrogen in tetrahydrofuran (THF) solution was sufficient to cause a color change from the initial green of the $Fe_3(CO)_{12}$ to dark red. Two crystalline products could be isolated. One, a red-orange solid, was identified as a mixture of the two isomers of the known[3] $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$. Its yield was 19%, based on available CH_3S groups, and its formation indicated that some C–S bond cleavage had indeed occurred. The other product, isolated in 48% yield, a red-orange solid, was not the expected $(\mu\text{-}\eta^1{:}\eta^2\text{-}C(OCH_3){=}C{=}CH_2)(\mu\text{-}CH_3S)Fe_2(CO)_6$ since, according to its ^1H NMR spectrum, it did not contain a $\mu\text{-}CH_3S$ ligand, although its C, H analysis and EI mass spectrum suggested the presence of the $CH_2CHC(OCH_3)$ and CH_3S groups as well as $Fe_2(CO)_6$.

Similar products were obtained on reaction of $(CH_3O)(C_2H_5S)C{=}C{=}CH_2$ with $Fe_3(CO)_{12}$: $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$

---

[1] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600.

[2] (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Archer, C. M.; Ruschke, D. P.; Cowie, M.; Hilts, R. W. *Organometallics* **1991**, *10*, 3363.

[3] King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

0276-7333/92/2311-3736$03.00/0

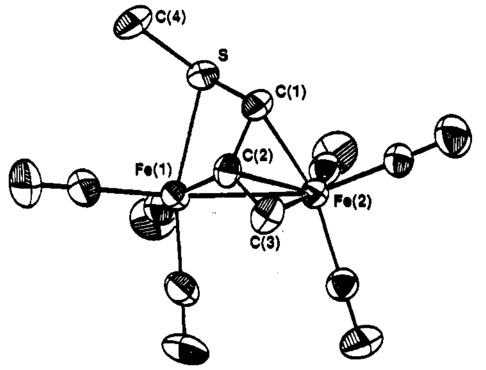


Figure 1. ORTEP plot of $[\eta^1{:}\eta^3\text{-}CH_3SCHCCH_2]Fe_2(CO)_6$, **2a**.

Table I. Important Intramolecular Bond Distances (Å) for $(\eta^1{:}\eta^3\text{-}CH_3SCHCCH_2)Fe_2(CO)_6$, 2a, Involving the Non-Hydrogen Atoms[a]

atom	atom	dist	atom	atom	dist
Fe(1)	C(11)	1.760 (5)	Fe(2)	C(21)	1.789 (5)
Fe(1)	C(13)	1.785 (6)	Fe(2)	C(2)	1.953 (4)
Fe(1)	C(12)	1.820 (5)	Fe(2)	C(1)	2.078 (4)
Fe(1)	C(2)	1.948 (4)	Fe(2)	C(3)	2.174 (5)
Fe(1)	S	2.331 (1)	S	C(1)	1.780 (4)
Fe(1)	Fe(2)	2.6177 (9)	S	C(4)	1.799 (5)
Fe(2)	C(22)	1.774 (5)	C(1)	C(2)	1.401 (6)
Fe(2)	C(23)	1.775 (5)	C(2)	C(3)	1.393 (6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

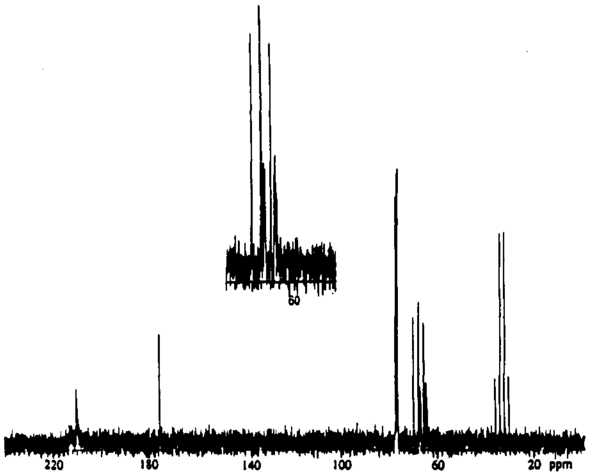


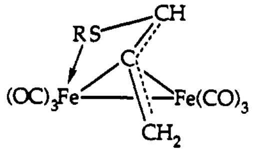
Figure 2. Proton-coupled ^{13}C NMR spectrum for $[\eta^1{:}\eta^3\text{-}CH_3SCCHCH_2]Fe_2(CO)_6$, **2a**.

Table II. Important Intramolecular Bond Angles (deg) for $[\eta^1{:}\eta^3\text{-}CH_3SCHCCH_2]Fe_2(CO)_6$, 2a, Involving the Non-Hydrogen Atoms[a]

atom	atom	atom	angle	atom	atom	atom	angle
C(11)	Fe(1)	C(2)	94.5 (2)	C(21)	Fe(2)	C(3)	90.9 (2)
C(11)	Fe(1)	S	162.4 (2)	C(21)	Fe(2)	Fe(1)	103.3 (1)
C(11)	Fe(1)	Fe(2)	85.6 (2)	C(2)	Fe(2)	C(1)	40.5 (2)
C(13)	Fe(1)	C(2)	101.1 (2)	C(2)	Fe(2)	C(3)	39.0 (2)
C(13)	Fe(1)	S	98.4 (2)	C(2)	Fe(2)	Fe(1)	47.8 (1)
C(13)	Fe(1)	Fe(2)	149.0 (2)	C(1)	Fe(2)	C(3)	69.1 (2)
C(12)	Fe(1)	C(2)	157.0 (2)	C(1)	Fe(2)	Fe(1)	65.8 (1)
C(12)	Fe(1)	S	95.7 (2)	C(3)	Fe(2)	Fe(1)	78.2 (1)
C(12)	Fe(1)	Fe(2)	110.7 (2)	C(1)	S	C(4)	103.3 (2)
C(2)	Fe(1)	S	72.8 (1)	C(1)	S	Fe(1)	76.8 (1)
C(2)	Fe(1)	Fe(2)	47.9 (1)	C(4)	S	Fe(1)	110.8 (2)
S	Fe(1)	Fe(2)	76.88 (4)	C(2)	C(1)	S	106.4 (3)
C(22)	Fe(2)	C(2)	124.0 (2)	C(2)	C(1)	Fe(2)	64.9 (2)
C(22)	Fe(2)	C(1)	99.8 (2)	S	C(1)	Fe(2)	105.9 (2)
C(22)	Fe(2)	C(3)	162.3 (2)	C(3)	C(2)	C(1)	119.4 (4)
C(22)	Fe(2)	Fe(1)	84.7 (2)	C(3)	C(2)	Fe(1)	130.4 (4)
C(23)	Fe(2)	C(2)	117.1 (2)	C(3)	C(2)	Fe(2)	79.1 (3)
C(23)	Fe(2)	C(1)	93.2 (2)	C(1)	C(2)	Fe(1)	100.0 (3)
C(23)	Fe(2)	C(3)	96.8 (2)	C(1)	C(2)	Fe(2)	74.5 (3)
C(23)	Fe(2)	Fe(1)	158.9 (1)	Fe(1)	C(2)	Fe(2)	84.3 (2)
C(21)	Fe(2)	C(2)	118.2 (2)	C(2)	C(3)	Fe(2)	61.9 (2)
C(21)	Fe(2)	C(1)	158.5 (2)				

in 42% yield and a red, crystalline solid (also in 42% yield) that analyzed correctly for $[(CH_3O)(C_2H_5S)(C_2CH_2)]Fe_2(CO)_6$. With $(CH_3O)(t\text{-}BuS)C{=}C{=}CH_2$, however, only $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ could be isolated in 74% yield.

Reactions of $Fe_3(CO)_{12}$ with allenes of type $RSCH{=}C{=}CH_2$ also were studied. With $CH_3SCH{=}C{=}CH_2$, $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ was obtained in 5% yield. A red compound of composition $(CH_3SCHCCH_2)Fe_2(CO)_6$ was the major (43%) product, but there was another minor orange-red product that, on the basis of its C, H analysis and FD mass spectrum, contained *two* units of the allene and one of $Fe_2(CO)_6$. In the case of the $PhSCH{=}C{=}CH_2/Fe_3(CO)_{12}$ reaction such a $(PhSCHCCH_2)_2Fe_2(CO)_6$ product was formed in higher (29%) yield in addition to the $(PhSCHCCH_2)Fe_2(CO)_6$ product (also in 29% yield). In marked contrast, $C_2H_5SCH{=}C{=}CH_2$ reacted with $Fe_3(CO)_{12}$ in refluxing THF to give mainly (93% yield) $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ and the $(C_2H_5SCHCCH_2)Fe_2(CO)_6$ product in only 5% yield.



2 a, R = CH_3
b, R = Ph
c, R = C_2H_5

The structure of the $(C_4H_6S)Fe_2(CO)_6$ product from the $CH_3SCH{=}C{=}CH_2/Fe_3(CO)_{12}$ reaction was determined by single-crystal X-ray diffraction and is represented in formula **2a**. Figure 1 shows an ORTEP plot of the molecule, and relevant bond lengths and angles are given in Tables I and II. Compound **2a** contains an $\eta^1{:}\eta^3$-bridging allyl ligand which is composed of the atoms C(1), C(2), and C(3), with C(2) being the central allyl carbon atom. Coordination of the methylthio group to iron closes a four-membered ring whose vertices are defined by Fe(1)–C(2)–C(1)–S. The Fe(1)–Fe(2) bond length of 2.6177 (9) Å is within the typical range for an Fe–Fe single bond. The nearly identical C(1)–C(2) and C(2)–C(3) bond distances (1.401 (6) and 1.393 (6) Å, respectively), which are within the range for a C–C allylic bond, indicate that there is complete delocalization of the allyl group. The allyl carbon atom, C(2), is positioned equidistant from each iron center, Fe(1)–C(2) = 1.948 (4) Å, Fe(2)–C(2) = 1.953 (4) Å. The allyl ligand has a bond angle of 119.4 (4)° which is in close agreement with the 120° bond angle expected for an allyl group. The bond distance Fe(2)–C(1) of 2.078 (4) Å is shorter than its counterpart, Fe(2)–C(3), which is 2.174 (5) Å. This is undoubtedly due to the strain imposed on the molecule by the sulfur atom which bridges C(1) and Fe(1).

Di- and trinuclear complexes with bridging allenyl ligands have been reported previously by others and three modes of bridging allenyl coordination are known: $\mu\text{-}\eta^2{:}\eta^2$, C, as in **3**[4] and **4**,[5] $\mu\text{-}\eta^1{:}\eta^3$, with a metal–metal bond, D, as in **5**,[6] and its ruthenium and osmium analogs,[5,7] as well as

---

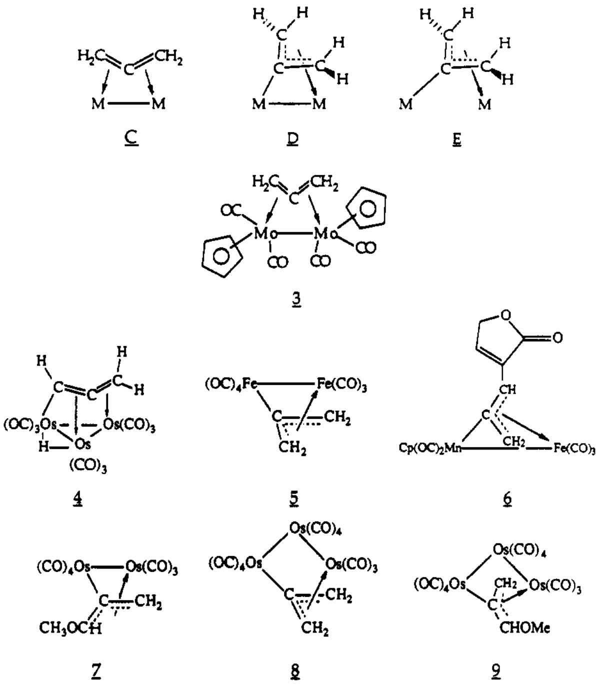
(4) Chisholm, M. H.; Rankel, L. A.; Bailey, W. I.; Cotton, F. A.; Murrillo, C. A. *J. Am. Chem. Soc.* 1977, *99*, 1261.

(5) Deeming, A. J.; Arce, A. J.; DeSantis, Y.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1987, 2935.

(6) Benn-Shoshan, R.; Pettit, R. *Chem. Commun.* 1968, 247.

(7) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* 1982, *232*, C65.

Chart I



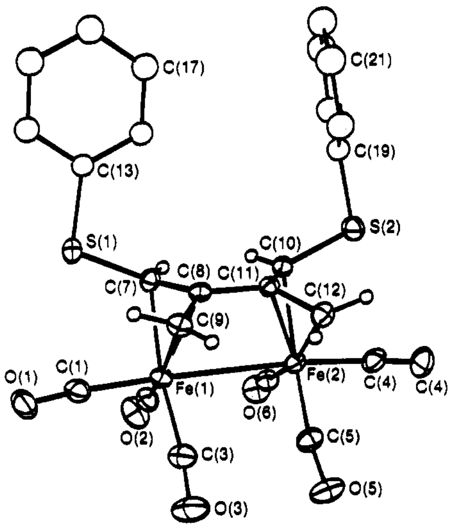
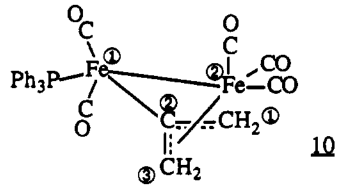


Figure 3. ORTEP plot of *cisoid*-[η^3-PhSCHCCH$_2$]$_2$Fe$_2$(CO)$_6$, **15b**.

in **6**[8] and **7**;[9] μ-η^1:η^3, without a metal–metal bond, E, as in **8**[5] and **9**[9] (Chart I).

Direct comparison of **2a** can be made to other (η^1:η^3-allyl)iron carbonyl complexes. Complex **5** is an oil, but a triphenylphosphine substitution product, **10**, could be



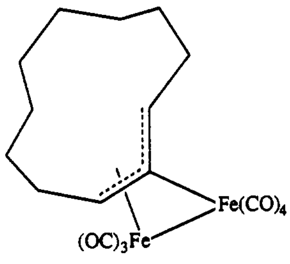
10

prepared and its molecular structure was determined by Davis.[10] The similarity of bond distances is striking. Distances equivalent to those in Figure 3 were as follows (in Å): Fe(1)–Fe(1), 2.65; C(1)–C(2), 1.45 (2); C(2)–C(3), 1.41 (2); Fe(1)–C(2), 2.03; Fe(2)–C(2), 1.93; Fe(2)–C(1), 2.18; Fe(2)–C(3), 2.19, with a C(1)–C(2)–C(3) angle of 116.0 ± 1.3°. As in **2c**, the Fe(1)–C(2) bond does not lie in the C(1)–C(2)–C(3) plane as a result of the constraint placed on the system by the presence of the short Fe–Fe bond.

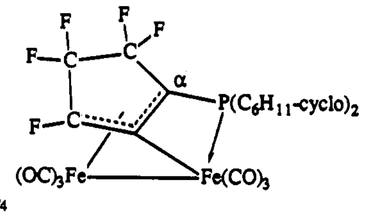
Table III. ^{1}H NMR Spectrum (ppm) of 2a

2.48 (s, 3 H, CH_3S)	4.08 (s, 1 H, =CH_2)
3.32 (s, 1 H, CH$_3$SCH)	4.20 (s, 1 H, =CH_2)

Further examples are known of complexes in which a Fe$_2$(CO)$_6$ unit is bridged by an η^1,η^3-allyl ligand. Complex **11** is nearly identical to **5** except for the large polymethylene chain joining the two ends of the allyl group.[11] The bond distances and the internal angle of the allyl unit compare very closely with those reported for **10**. More closely related to **2a** is complex **12**.[12] As with **11**, the allyl unit of **12** is part of a ring. However, here the ring is much smaller, only five-membered, and is substituted with fluorine atoms. The feature which bears a striking resemblance to **2a** is the phosphine ligand which bridges C$_\alpha$ and the σ-bonded Fe(CO)$_3$ center to close a four-membered chelate ring. The σ-Fe–allyl carbon bond [Fe(2)–C(2) = 1.938 (5) Å] more closely resembles that of **2a** [1.948 (4) Å] than that of either **10** (2.03 Å) or **11** (2.02 Å). This suggests that the iron-coordinated thio or phosphino group has some effect on the shortening of this bond. The C(2)–C(3) bond distance of 1.393 (7) Å is significantly shorter than C(1)–C(2) at 1.447 (7) Å, which implies that C(2)–C(3) has more double bond character and that there is not complete delocalization of the allyl functionality. The C(1)–C(2)–C(3) bond angle [103.2 (4)°] is much smaller than in any of the other cases due to ring strain of the five-membered ring of which it is part. This also results in a C(2)–C(1)–P bond angle of 98.1 (3)° which is smaller than the C(2)–C(1)–S bond angle of **2a** of 106.4 (3)°.



11



12

The ^{1}H NMR spectrum of **2a** is summarized in Table III, together with the assignments of the observed resonances. In the ^{1}H NMR spectrum of **2a**, two methylene proton resonances are observed as sharp singlets at 4.08 and 4.20 ppm, each integrating for one proton. This indicates that these protons are inequivalent. Their upfield shifts confirm that the organic fragment has lost its allenic character. The SCH_3 resonance at 2.48 ppm is further downfield than those usually observed for equatorial or axial bridging SCH_3 groups in Fe$_2$(CO)$_6$ complexes (~ 1.6–2.3 ppm), in agreement for a different mode of bonding of the SCH$_3$ group of **2a**. The ^{13}C NMR resonances due to the terminal carbon atoms of the π-allyl portion of the organic ligand in **2a** are somewhat upfield from the range of terminal allene carbon atom shifts (~75–95 ppm), which provides further confirmation that the organic fragment is not allenic.

The ^{13}C NMR spectrum of **2a** is shown in Figure 2. The triplet at 66.1 ppm corresponding to the methylene carbon

---

(8) Kolobova, N. E.; Derunov, V. V.; Batsanov, A. S.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1191 (Engl. transl. p 1104).

(9) Arce, A. J.; DeSantis, Y.; Deeming, A. J.; Hardcastle, K. I.; Lee, R. *J. Organomet. Chem.* **1991**, *406*, 209.

(10) Davis, R. E. *Chem. Commun.* **1968**, 248.

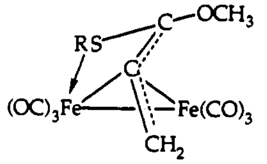
(11) Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1970**, 38.

(12) Cullen, W. R.; Williams, M.; Einstein, F. W. B.; Willis, A. C. *J. Organomet. Chem.* **1978**, *155*, 259.

atom of **2a** does not appear in the normal 1:2:1 peak intensity ratio for a triplet. Rather, the center peak is only slightly more intense than the outer peaks. This is a result of the inequivalence of the methylene protons. These protons give rise to two separate resonances in the ^{1}H NMR spectrum, and it might be expected that this would lead to a doublet of doublets in the proton-coupled ^{13}C NMR spectrum. In fact, it can be seen upon close inspection of the spectrum that the center peak of the triplet actually is slightly broadened in comparison with the two outer peaks. Thus, it can be deduced that the J_{CH} coupling constants are not sufficiently inequivalent to cause splitting into a true doublet of doublets, but enough so that distortion of the triplet is observed.

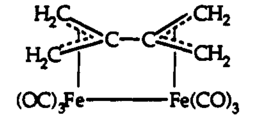
A comparison of the ^{1}H NMR spectrum of **2a** with that of **6**, a complex that also contains a monosubstituted η^1:η^3-allyl ligand is of interest. As reported,[8] the ^{1}H NMR spectrum of **6** shows three signals at δ 3.56, 3.73, and 4.33 ppm that were attributed to the allyl protons; the similarity to the 3.32, 4.08, and 4.20 ppm singlet resonances in the ^{1}H NMR spectrum of **2a** is striking.

Complexes **2b** and **2c** have the same structure as **2a** according to their ^{1}H and ^{13}C NMR spectra. The $CH_2{=}C{=}C(OCH_3)SCH_3$ and $CH_2{=}C{=}C(OCH_3)SC_2H_5$-derived complexes most likely have the structure shown in **13**.

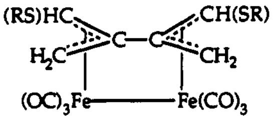


13 a, R = CH_3
b, R = C_2H_5

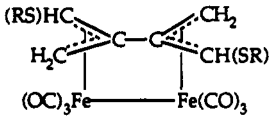
As noted above, in the reactions of $PhSCH{=}C{=}CH_2$ and $CH_3SCH{=}C{=}CH_2$ with $Fe_2(CO)_6$ products of type $(RSCHCCH_2)_2Fe_2(CO)_6$ also were formed. The formation of such products has a precedent in the reaction of allene itself with $Fe_2(CO)_9$ in which **14** is produced in addition to **5**.[13] Should our $(RSCHCCH_2)_2Fe_2(CO)_6$ products be of this type, then two isomers would be possible: the cisoid **15** and the transoid **15′**. In the case of $PhSCH{=}C{=}CH_2$ only one $(RSCHCCH_2)_2Fe_2(CO)_6$ product was detected, but with $CH_3SCH{=}C{=}CH_2$ two such products, whose ^{1}H and ^{13}C NMR spectra showed them to be very similar, could be isolated.



14



15, a = CH_3
b = Ph



15′, a = CH_3
b = Ph

An X-ray crystal structure of the $PhSCH{=}C{=}CH_2$/$Fe_3(CO)_{12}$ deep red, crystalline 2:1 product, **15b**, was obtained. The molecular structure is shown in the ORTEP plot in Figure 3. Relevant bond lengths and angles are given in Tables IV and V. It can be seen to be similar to that of **14** in that it contains two equivalent η^3 allyl groups which are σ-bonded to each other at the central carbon atoms of the allyl groups. The PhS groups remain bonded to carbon atoms as substituents on the allyl groups, in cisoid orientation as in **15**. They are not coordinated to iron atoms. The iron atoms in **15** and **15′** are coordinatively saturated since the η^3 allyl moieties are three-electron donors, so the PhS groups remain free.

Table IV. Important Intramolecular Bond Distances (Å) for (η^3-PhSCHCCH$_2$)$_2$Fe$_2$(CO)$_6$, 15b, Involving the Non-Hydrogen Atoms[a]

atom	atom	dist	atom	atom	dist
Fe(1)	Fe(2)	2.9767 (5)	Fe(2)	C(11)	2.030 (2)
Fe(1)	C(1)	1.797 (3)	Fe(2)	C(12)	2.122 (3)
Fe(1)	C(2)	1.803 (3)	S(1)	C(7)	1.788 (2)
Fe(1)	C(3)	1.802 (3)	S(1)	C(13)	1.765 (2)
Fe(1)	C(7)	2.106 (2)	S(2)	C(10)	1.785 (2)
Fe(1)	C(8)	2.043 (2)	S(2)	C(19)	1.775 (3)
Fe(1)	C(9)	2.123 (3)	C(7)	C(8)	1.423 (3)
Fe(2)	C(4)	1.799 (3)	C(8)	C(9)	1.415 (3)
Fe(2)	C(5)	1.801 (3)	C(8)	C(11)	1.483 (3)
Fe(2)	C(6)	1.804 (3)	C(10)	C(11)	1.423 (3)
Fe(2)	C(10)	2.108 (2)	C(11)	C(12)	1.410 (3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

Table V. Important Intramolecular Bond Angles (deg) for (η^3-PhSCHCCH$_2$)$_2$Fe$_2$(CO)$_6$, 15b, Involving the Non-Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Fe(2)	Fe(1)	C(1)	177.6 (1)	C(5)	Fe(2)	C(11)	123.2 (1)
Fe(2)	Fe(1)	C(2)	86.68 (8)	C(5)	Fe(2)	C(12)	93.3 (1)
Fe(2)	Fe(1)	C(3)	88.2 (1)	C(6)	Fe(2)	C(10)	96.0 (1)
Fe(2)	Fe(1)	C(7)	87.86 (7)	C(6)	Fe(2)	C(11)	126.5 (1)
Fe(2)	Fe(1)	C(8)	67.75 (6)	C(6)	Fe(2)	C(12)	165.0 (1)
Fe(2)	Fe(1)	C(9)	90.29 (8)	C(10)	Fe(2)	C(11)	40.16 (9)
C(1)	Fe(1)	C(2)	93.5 (1)	C(10)	Fe(2)	C(12)	69.2 (1)
C(1)	Fe(1)	C(3)	89.4 (1)	C(11)	Fe(2)	C(12)	39.7 (1)
C(1)	Fe(1)	C(7)	94.5 (1)	C(7)	S(1)	C(13)	104.3 (1)
C(1)	Fe(1)	C(8)	113.9 (1)	C(10)	S(2)	C(19)	102.1 (1)
C(1)	Fe(1)	C(9)	90.2 (1)	Fe(1)	C(7)	S(1)	111.7 (1)
C(2)	Fe(1)	C(3)	99.4 (1)	Fe(1)	C(7)	C(8)	67.6 (1)
C(2)	Fe(1)	C(7)	96.8 (1)	S(1)	C(7)	C(8)	121.8 (2)
C(2)	Fe(1)	C(8)	127.2 (1)	Fe(1)	C(8)	C(7)	72.3 (1)
C(2)	Fe(1)	C(9)	165.8 (1)	Fe(1)	C(8)	C(9)	73.2 (1)
C(3)	Fe(1)	C(7)	163.1 (1)	Fe(1)	C(8)	C(11)	112.5 (1)
C(3)	Fe(1)	C(8)	123.8 (1)	C(7)	C(8)	C(9)	115.7 (2)
C(3)	Fe(1)	C(9)	94.3 (1)	C(7)	C(8)	C(11)	121.2 (2)
C(7)	Fe(1)	C(8)	40.08 (9)	C(9)	C(8)	C(11)	121.7 (2)
C(7)	Fe(1)	C(9)	69.2 (1)	Fe(1)	C(9)	C(8)	67.1 (1)
C(8)	Fe(1)	C(9)	39.67 (9)	Fe(2)	C(10)	S(2)	112.3 (1)
Fe(1)	Fe(2)	C(4)	175.3 (1)	Fe(2)	C(10)	C(11)	67.0 (1)
Fe(1)	Fe(2)	C(5)	85.6 (1)	S(2)	C(10)	C(11)	122.7 (2)
Fe(1)	Fe(2)	C(6)	88.07 (9)	Fe(2)	C(11)	C(8)	110.6 (1)
Fe(1)	Fe(2)	C(10)	91.03 (7)	Fe(2)	C(11)	C(10)	72.9 (1)
Fe(1)	Fe(2)	C(11)	69.19 (6)	Fe(2)	C(11)	C(12)	73.7 (1)
Fe(1)	Fe(2)	C(12)	89.69 (8)	C(8)	C(11)	C(10)	120.2 (2)
C(4)	Fe(2)	C(5)	89.7 (1)	C(8)	C(11)	C(12)	122.2 (2)
C(4)	Fe(2)	C(6)	92.3 (1)	C(10)	C(11)	C(12)	116.0 (2)
C(4)	Fe(2)	C(10)	93.6 (1)	Fe(2)	C(12)	C(11)	66.7 (1)
C(4)	Fe(2)	C(11)	114.1 (1)	S(1)	C(13)	C(14)	116.1 (2)
C(4)	Fe(2)	C(12)	91.2 (1)	S(1)	C(13)	C(18)	125.3 (2)
C(5)	Fe(2)	C(6)	101.3 (1)	S(2)	C(19)	C(20)	120.2 (2)
C(5)	Fe(2)	C(10)	162.2 (1)	S(2)	C(19)	C(24)	120.6 (2)

Complex **15b** has a saw-horse structure, typical of complexes containing the $Fe_2(CO)_6$ moiety, which is capped by the diallyl fragment. This complex is highly symmetrical, having an approximate mirror plane bisecting the Fe–Fe bond and the diallyl fragment, as seen by a comparison of the parameters in the two halves of the molecule (see Tables IV and V). This symmetry is also seen in the torsion angles about the Fe–Fe bond, ranging from only 1.6 (1)° to 3.7 (2)°, indicating that the substituents on the

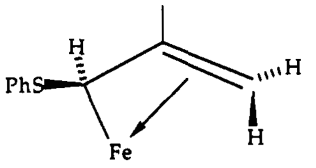
---

[13] (a) Nakamura had earlier reported **16** to be the only product of the allene/$Fe_3(CO)_{12}$ reaction: Nakamura, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 543. (b) Benn-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1968**, *89*, 2231.

Table VI. ^{1}H and ^{13}C NMR Spectral Data (ppm) for Complexes 15a, 15′a, and 15b

	15a	**15′a**	**15b**
^{1}H NMR	2.18 (t, J = 2.24 Hz, 1 H, CH_3SCH)	2.65 (t, J = 1.87 Hz, 1 H, CH_3SCH)	2.23 (t, J = 2.50 Hz, 1 H, PhSCH)
	2.78 (d, J = 1.95 Hz, 1 H, $=CH_2$)	2.84 (d, J = 2.69 Hz, 1 H, $=CH_2$)	2.89 (d, J = 2.29 Hz, 1 H, $=CH_2$)
	3.59 (d, J = 2.57 Hz, 1 H, $=CH_2$)	3.24 (d, J = 1.70 Hz, 1 H, $=CH_2$)	3.70 (d, J = 2.72 Hz, 1 H, $=CH_2$)
^{13}C NMR	40.26 (t, J_{CH} = 162.1 Hz, $=CH_2$)	44.64 (t, J_{CH} = 164.2 Hz, $=CH_2$)	40.16 (t, J_{CH} = 163.4 Hz, $=CH_2$)
	63.51 (d, J_{CH} = 170.6 Hz, CH_3SCH)	58.67 (d, J_{CH} = 168.7, SCH_3CH)	55.81 (d, J_{CH} = 171.2 Hz, PhSCH)
	85.80 (s, allyl C)	87.38 (s, allyl C)	87.19 (s, allyl C)

two Fe centers are essentially eclipsed. The lack of exact mirror symmetry results from the orientations of the phenyl substituents, which are twisted by 72.0 (1)° to each other. Within the diallyl fragment the parameters are typical of η^3-allyl groups;[14] the C–C distances within each allyl fragment (range: 1.410 (3)–1.423 (3) Å) are essentially as expected, and the C(8)–C(11) bond between the two alkyl moieties (1.483 (3) Å) represents a normal single bond between sp^2 carbons. In addition, all angles within the diallyl group itself are close to the expected 120°. As is also typically the case,[14] the central carbon of each allyl group is closer to the metals (2.043 (2), 2.030 (2) Å) than are the outer carbons (range 2.106 (2)–2.123 (3) Å), even though each allyl plane is inclined slightly such that the central carbon is tipped *away* from the metal. This tipping of the allyl planes is clearly seen in a least-squares plane calculation[15] involving the six carbons of the diallyl group, which shows that C(8) and C(11) lie 0.100 (3) Å and 0.105 (3) Å, respectively, above this plane, whereas the others lie below this plane, toward the Fe atoms, by between 0.021 (3) and 0.082 (3) Å. Such tipping has been explained in terms of overlap between the metal and allyl orbitals.[16] The present diallyl unit is unusual in the positioning of the substituents on the terminal carbons of the allyl groups. Usually the anti substituents (to the C(8)–C(11) bond in this case) are displaced toward the metal whereas the syn substituents are displaced away from the metal;[14] in compound **15b** the opposite is found. The sulfur atoms (0.612 (1) and 0.640 (1) Å) and the anti protons on C(9) and C(12) (0.29 (3), 0.19 (3) Å) are displaced *away from* the Fe atoms, whereas all syn hydrogen are displaced, by between 0.05 (3) and 0.19 (3) Å, *toward* the Fe atoms. It appears that this anomaly results from steric repulsions between the axial carbonyls (C(1)O(1) and C(4)O(4)) and the anti substituents, since the contacts between these groups (C(1)–H(2C9) = 2.53 (2) Å, C(4)–H(1C12) = 2.52 (2) Å; S(1)–C(1) = 2.915 (3), S(2)–C(4) = 2.910 (3) Å) are less than the normal van der Waals contacts of ca. 3.0 and 3.7 Å, respectively.[17] Surprisingly, C(7) and C(10), having the large SPh substituents, are actually slightly closer to the Fe atoms (2.106 (2), 2.108 (2) Å) than are the other ends of the allyl groups (2.123 (3), 2.122 (3) Å) which have only hydrogen substituents, in spite of potentially more severe van der Waals repulsions involving the former. It is also noteworthy that the C(7)–C(8) and C(10)–C(11) bonds within the allyl groups are longer (1.423 (3) Å) than those involving C(9) and C(12) (1.415 (3), 1.410 (3) Å). Taken together these observations suggest that the σ,π resonance formulation (F) may make a significant contribution to the bonding.



(F)

All sulfur–carbon distances are normal, although those involving the phenyl groups are somewhat shorter than those to the allyl moieties. This difference is consistent with the expected rehybridization of the allyl carbons toward sp^3 upon coordination to the metals. It is significant however that this difference in S–C distances is also consistent with the involvement of a σ,π bonding model as suggested.

An interesting feature of the structure of this complex is the long Fe–Fe bond: 2.9767 (5) Å (compared with 2.6177 (9) for the Fe–Fe bond distance of **2a**). This elongation is presumably due to the large size of the organic ligand that bridges the two iron atoms. The difference between these two Fe–Fe distances is a good example of the flexibility of the $Fe_2(CO)_6$ unit in its accommodation to the ligands which bridge the iron atoms.

The two $(CH_3SCHCCH_2)_2Fe_2(CO)_6$ products were obtained only in low yield. They were difficult to separate from one another, but very slow medium-pressure column chromatography (pentane eluant) was successful. Their EI mass spectra gave identical patterns of fragmentation. Both gave acceptable C, H analyses for the $(CH_3SCHCCH_2)_2Fe_2(CO)_6$ composition. Thus it was very probable that they were isomeric species, most likely the cisoid and transoid forms, **15a** and **15′a** (R = CH_3), respectively.

In Table VI are compared the ^{1}H and ^{13}C NMR spectra of the two $(CH_3SCHCCH_2)_2Fe_2(CO)_6$ isomers and $(PhSCHCCH_2)_2Fe_2(CO)_6$, **15b**. The ^{1}H NMR spectrum of one of the isomers more nearly matches that of **15b** than does that of isomer **15′a**. The methylene proton resonances of **15b** at 2.89 and 3.70 ppm are separated by 0.81 ppm as are those of isomer **15a**. In contrast, those of isomer **15′a** are separated by 0.40 ppm, suggesting that the CH_2 environments of **15b** and isomer **15a** are similar. The chemical shifts of the central carbon atoms of the diallyl ligands in the ^{13}C NMR of all three compounds in Table VI are within 1.5 ppm of one another, whch indicates that the allyl groups of isomers **15a** and **15′a** are bonded to iron in a manner analogous to the bonding in **15b**. If isomer **15a** is assigned the cisoid structure, then isomer **15′a** must be the transoid species.

It is of interest to consider the route by which the products of types **2** and **15** are formed in reactions of thioallenes with $Fe_3(CO)_{12}$. The $(RSCHCCH_2)Fe_2(CO)_6$ complexes, **2**, might be formed as suggested in Scheme I. The first step is η^2 (π) coordination of the allene to Fe_3-

---

(14) (a) Jolly, P. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. A., Eds.; Pergamon: New York, 1982; Vol. 6, Section 37.6. (b) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Ibid.* Section 38.7. (c) Hartley, F. R. *Ibid.* Section 39.9.

(15) Least-squares plane through atoms C(7), C(8), C(9), C(10), C(11), and C(12): Equation of plane: $0.2478x - 0.9683y - 0.0315z = 0.37456$; $\chi^2 = 4441$. Distanes (Å) of atoms from plane: C(7), –0.080 (3); C(8), 0.100 (3); C(9), –0.021 (3); C(10), –0.021 (3); C(11), 0.105 (3); C(12), –0.082 (3). Distances (Å) of other atoms from plane: Fe(1), –1.790; Fe(2), –1.792; S(1), 0.612 (1); S(2), 0.640 (1); H(7), –0.19 (3); H(1C9), –0.05 (3); H(2C9), 0.29 (3); H(10), –0.06 (3); H(1C12), 0.19(3); H(2C12), –0.19 (3).

(16) Kettle, S. F. A; Mason, R. *J. Organometal. Chem.* **1966**, *5*, 573.

(17) The estimates used are based on the values for the C and S atoms from: Bardi, A. *J. Phys. Chem.* 1964, *68*, 441.

Scheme I. Proposed Mechanism for the Formation of [η^1,η^3-$CH_2CC(Z)(SR)$]$Fe_2(CO)_6$

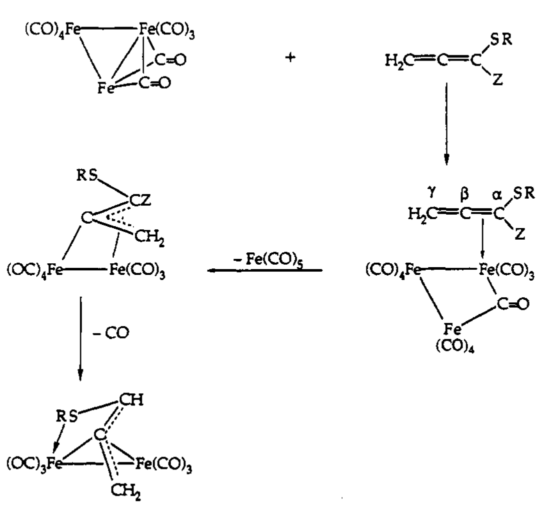
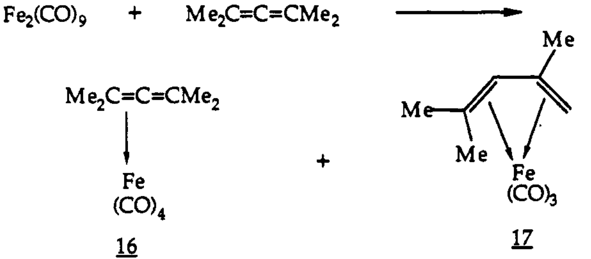


Table VII. Comparison of Yields of the Products Obtained from the Reaction of $Fe_3(CO)_{12}$ with 1 or 2 equiv of Thioallene, RSCH=C=CH₂

equiv of thioallene	R	$(\mu\text{-RS})_2Fe_2(CO)_6$ (%)	2 (%)	15, 15′ (%)
1	Me	5	43	5, 4
2	Me	5	43	3, 2
1	Ph	0	29	29
2	Ph	0	33	30

$(CO)_{12}$. In support of this suggestion, we note that Ben-Shoshan and Pettit found that tetramethylallene reacts with $Fe_2(CO)_9$ to give the π-complex 16 as well as the η^4-diene complex 17 (eq 1).[13b] Loss of $Fe(CO)_5$, π-complexation of the entire allene and σ-bond formation between the uncomplexed iron atom and the central carbon atom of the η^3-allyl ligand then follow. The final step is substitution of a CO ligand by the RS group, a process facilitated by the close (intramolecular) proximity of the sulfur donor atom to the iron atom.



(1)

16

17

It seemed reasonable to suppose that the use of an excess of the thioallene with respect to $Fe_3(CO)_{12}$ would result in formation of the $(RSCHCH_2)_2Fe_2(CO)_6$ products, 15 and 15′, in higher yield. Such, however, was not the case, as the results in Table VII show. Reactions of two equivalents of RSCH=C=CH₂ (R = CH_3 and Ph) with $Fe_3(CO)_{12}$ resulted in nearly the same yields. Another possibility that was considered by carrying out appropriate experiments was that the type 2 complex is an intermediate in the formation of 15 and 15′. Several attempts to effect a reaction of 2a and 2b with an excess of the respective thioallene in refluxing THF solution resulted only in recovery of the respective $(\mu\text{-}\eta^1\text{:}\eta^2\text{-RSCHCCH}_2)Fe_2(CO)_6$ complex. No 15 or 15′ type product was formed. This suggests that 15 and 15′ are formed by a separate, independent process in which two molecules of the thioallene become π-coordinated to a single molecule of $Fe_3(CO)_{12}$ with loss of one CO ligand. Loss of $Fe(CO)_5$ would leave no site available for σ bonding to either thioallene molecule so that C–C bond formation at C_β to link the two allene molecules results instead. This would leave each as an allyl moiety which bonds to iron in the η^3 manner. However, in the absence of stronger experimental support, these suggestions concerning the course of these reactions remain only speculation.

As noted above, the formation of $(\mu\text{-RS})_2Fe_2(CO)_6$ in these RSCH=C=CH₂/$Fe_3(CO)_{12}$ reactions is an indication of the occurrence of C–S bond cleavage. The allenyl group that would result from such cleavage may end up as a ligand on iron to give a $(\mu\text{-}\eta^1\text{:}\eta^2$-allenyl)iron carbonyl complex, but we have not been able to isolate a stable product of this kind. The possibility of the formation of wholly organic products derived from the allenyl group was not examined.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triiron dodecacarbonyl was prepared according to a literature procedure.[18] 1-Methoxy-1-methylthioallene,[19a] 1-methoxy-1-ethylthioallene,[19a] 1-methoxy-1-(*tert*-butylthio)allene,[19a] (methylthio)allene,[19b] (phenylthio)allene,[19c] and (ethylthio)allene[19b] were prepared by literature procedures and were purged with nitrogen before use. Dimethyl disulfide, diethyl disulfide, di-*tert*-butyl disulfide, thiophenol, methyl propargyl ether, 1-(dimethylamino)-2-propyne, and propargyl chloride (all purchased from Aldrich) were purged with nitrogen and used without further purification. Ammonia was passed through a column of KOH pellets before use to remove water.

The progress of all reactions was monitored by thin layer chromatography (Baker Flex, Silica Gel 1B-F). Purification was achieved by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh silicic acid (ca. 150 mL) in a 350-mL glass fritted filter funnel. Further purification was accomplished by thin-layer chromatography on preparative TLC plates (EM Science 60 F_{254}, silica gel, 20 × 20 × 0.025 cm). In addition, column chromatography was used as needed and was accomplished with a 450 × 25 mm medium-pressure column using Sigma S-0507 230–400 mesh silica gel. All chromatography was carried out without exclusion of atmopheric moisture or oxygen. Solid products were recrystallized at −20 °C. All yields are based on Fe unless otherwise indicated.

Solution or thin film infrared spectra (NaCl windows) were obtained using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer or a Perkin-Elmer 1600 Series FTIR instrument. Proton NMR spectra were recorded on either a Bruker WM-250, a Varian Gem-300, or a Varian XL-300 spectrometer operating at 250, 300, or 300 MHz, respectively. Carbon-13 NMR spectra were recorded on either a Varian Gem-300, or a Varian XL-300 spectrometer, operating at 75.5 and 75.4 MHz. Electron-impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. The FD mass spectrum was obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isotopes: ^1H, ^{12}C, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting-point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Crystallography. Structure of $(\eta^1\text{:}\eta^3\text{-CH}_3SCHCCH_2)Fe_2(CO)_6$, 2a. A suitable quality, red block crystal of $(\eta^1,\eta^3\text{-CH}_3SCHCCH_2)Fe_2(CO)_6$ (which had been grown in pentane at −20 °C) was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with

---

(18) McFarlane W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(19) (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981; p 42. (b) *Ibid.*, p 106. (c) *Ibid.*, p 110.

Table VIII. Crystal Data and Collection Details for Compounds 2a and 15b

	2a	**15b**
compound	$(\eta^1{:}\eta^3\text{-CH}_2\text{CCHSCH}_3)\text{-Fe}_2(\text{CO})_6$	$(\eta^3\text{-PhSCHCCH}_2)_2\text{-Fe}_2(\text{CO})_6$
empirical formula	$C_{10}H_8Fe_2O_6S$	$C_{24}H_{16}Fe_2O_6S_2$
formula wt	365.91	576.21
crystal color, habit	red-orange, block	red, block
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
temp, °C	23	22
radiation (λ), Å	Mo Kα (0.710 69) graphite monochromated	
lattice params		
a, Å	7.7134 (4)	10.938 (1)
b, Å	13.6321 (5)	12.064 (2)
c, Å	12.9757 (9)	9.806 (1)
α, deg		92.02 (1)
β, deg	102.318 (6)	93.03 (1)
γ, deg		68.15 (1)
V, Å^3	1333.0 (3)	1199.2 (4)
Z	4	2
D_{calc}, g/cm^3	1.823	1.596
μ(Mo Kα), cm^{-1}	23.4	14.13
range of trans factors	0.80–1.21	0.783–1.118
$2\theta_{max}$	54.9	50.0
total unique data	3185 ($h,k,\pm l$)	3948 ($h,\pm k,\pm l$)
no. of obsns	2192	3360
no. of params varied	172	271
R	0.041	0.038
R_w	0.047	0.054
GOF[22]	1.57	1.869

graphite monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $30.00 < 2\theta < 40.00°$ corresponding to a monoclinic cell with dimensions given in Table VIII. For $Z = 4$ and FW = 365.91, the calculated density is 1.823 g/cm^3. On the basis of systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 54.9°. Moving-crystal moving-counter background measurements were made by scanning an additional 25% above and below the scan range.

Of the 3415 reflections which were collected, 3185 were unique ($R_{int} = 0.029$); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

An empirical absorption correction, using the program DIFABS,[20] was applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of the Patterson method and direct methods.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{C-H} = 0.95$ Å), and were assigned isotropic thermal parameters which were 20% greater than the $B_{equivalent}$ value of the atom to which they were bonded.

Table IX. Final Positional Parameters of Non-Hydrogen Atoms for $(\eta^1{:}\eta^3\text{-CH}_2\text{CCHSCH}_3)\text{Fe}_2(\text{CO})_6$, 2a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Fe(1)	0.35361 (8)	0.00122 (4)	0.22937 (5)	3.02 (2)
Fe(2)	0.07758 (8)	0.11459 (4)	0.22285 (4)	2.92 (2)
S	0.1930 (2)	−0.08139 (8)	0.33566 (9)	3.32 (4)
O(11)	0.4710 (5)	0.1478 (3)	0.0966 (3)	6.6 (2)
O(12)	0.2830 (6)	−0.1409 (3)	0.525 (3)	6.0 (2)
O(13)	0.7130 (5)	−0.0548 (3)	0.3389 (3)	6.8 (2)
O(22)	−0.1278 (5)	−0.0436 (3)	0.1009 (3)	6.0 (2)
O(23)	−0.2225 (5)	0.2034 (3)	0.2922 (3)	5.9 (2)
O(51)	0.0826 (5)	0.2485 (3)	0.0467 (3)	5.7 (2)
C(1)	0.1657 (6)	0.0441 (3)	0.3665 (3)	3.3 (2)
C(2)	0.2962 (6)	0.0963 (3)	0.3291 (3)	3.1 (2)
C(3)	0.2870 (6)	0.1983 (3)	0.3238 (4)	4.0 (2)
C(4)	0.3385 (8)	−0.1277 (4)	0.4527 (4)	4.7 (2)
C(11)	0.4232 (7)	0.0902 (4)	0.1485 (4)	4.2 (2)
C(12)	0.3109 (7)	−0.0874 (3)	0.1220 (4)	4.0 (2)
C(13)	0.5713 (7)	−0.0355 (4)	0.2951 (4)	4.3 (2)
C(21)	0.0828 (6)	0.1945 (3)	0.1142 (4)	3.7 (2)
C(22)	−0.0434 (7)	0.0175 (4)	0.1497 (3)	3.8 (2)
C(23)	−0.1029 (6)	0.1713 (3)	0.2645 (4)	3.7 (2)

Table X. Final Positional Parameters of Non-Hydrogen Atoms (Except for Phenyl Carbons) for $(\eta^3\text{-PhSCHCCH}_2)_2\text{Fe}_2(\text{CO})_6$, 15b

atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	0.32524 (4)	0.30295 (4)	0.36069 (5)	3.45 (1)
Fe(2)	0.08919 (4)	0.23715 (4)	0.37008 (5)	3.40 (1)
S(1)	0.57355 (8)	0.12994 (8)	0.1954 (1)	4.65 (2)
S(2)	0.08533 (8)	−0.01007 (8)	0.2336 (1)	4.99 (2)
O(1)	0.5471 (3)	0.3834 (2)	0.3652 (4)	6.88 (8)
O(2)	0.1865 (3)	0.4747 (2)	0.1472 (3)	6.83 (7)
O(3)	0.2455 (3)	0.4569 (3)	0.6043 (3)	7.47 (9)
O(4)	−0.1548 (3)	0.1945 (3)	0.3989 (4)	7.82 (9)
O(5)	0.0078 (3)	0.3970 (3)	0.6081 (3)	6.57 (8)
O(6)	−0.0385 (3)	0.3952 (2)	0.1418 (3)	6.27 (7)
C(1)	0.4649 (3)	0.3472 (3)	0.3608 (4)	4.64 (8)
C(2)	0.2352 (3)	0.4067 (3)	0.2298 (4)	4.47 (8)
C(3)	0.2687 (4)	0.3967 (3)	0.5095 (4)	5.07 (9)
C(4)	−0.0583 (4)	0.2067 (3)	0.3865 (4)	5.05 (9)
C(5)	0.0455 (3)	0.3387 (3)	0.5144 (4)	4.61 (9)
C(6)	0.0165 (3)	0.3371 (3)	0.2302 (4)	4.22 (8)
C(7)	0.4077 (3)	0.1539 (3)	0.2303 (3)	3.52 (7)
C(8)	0.3735 (3)	0.1222 (2)	0.3572 (3)	3.02 (6)
C(9)	0.4386 (3)	0.1495 (3)	0.4747 (3)	3.75 (7)
C(10)	0.1791 (3)	0.0836 (3)	0.2479 (3)	3.45 (7)
C(11)	0.2568 (3)	0.0889 (2)	0.3672 (3)	3.03 (6)
C(12)	0.1999 (3)	0.0888 (3)	0.4928 (3)	3.96 (7)

The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plot of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indexes showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and −0.54 e$^-$/Å, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were included in F_{calc};[25] the values for Δ*f*′ and Δ*f*″ were those of Cromer.[26] All calculations were performed using the TEXSAN[27] crystallographic software package of Molecular Structure Corp.

Structure of $[\eta^3\text{-PhSCHCCH}_2]_2\text{Fe}_2(\text{CO})_6$, 15b. Deep red crystals of $(\eta^3\text{-PhSCHCCH}_2)_2\text{Fe}_2(\text{CO})_6$ were grown from pentane/CH$_2$Cl$_2$ at −20 °C. A suitable single crystal was mounted in air on a glass fiber. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 22 °C using graphite monochromated Mo Kα radiation. A summary of data collection details and crystal data appears in Table VIII. Data collection and structure solution and refinement proceeded as described for compound **2a**. Allyl hydrogen atoms were refined, having isotropic thermal parameters, whereas those on the phenyl rings were input as fixed contributions as described for compound **2a**.

---

(20) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

(21) Structure solution methods: PHASE: PHASE: Patterson Heavy Atom Solution Extractor. Calabrese, J. C. Ph.D. Dissertation, University of Wisconsin at Madison, 1972. DIRDIF: DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Beurskens, P. T. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(22) Least-squares: function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$

(23) Standard deviation of an observation of unit weight: $[w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.

(24) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a.

(25) Ibers, J. A.; Hamilton W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(26) Reference 24, Table 2.3.1.

(27) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

Reaction of $Fe_3(CO)_{12}$ with 1-Methoxy-1-(methylthio)allene at Reflux. A 100-mL three-necked, round-bottomed flask equipped with a stir bar, a reflux condenser with a gas inlet adapter, a glass stopper, and a rubber septum (standard apparatus) was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and 1-methoxy-1-(methylthio)allene (0.46 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 4 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. A color change from dark green to deep red was observed during the reaction time. TLC indicated that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (4:1 v/v) and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.11 g (0.29 mmol, 19% based on S, a/e:e/e = 2.3) of $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum ($CDCl_3$, 250 MHz) to that of an authentic sample.[28] Further elution with pentane/CH_2Cl_2 (5:1 v/v) gave a second orange band which yielded 0.57 g (1.43 mmol, 48%) of $(\eta^1,\eta^3\text{-}CH_3S(CH_3O)CCCH_2)Fe_2(CO)_6$, **13a**, as an air-stable, dark red-orange, crystalline solid after purification on preparative TLC plates (pentane eluant) and recrystallization from pentane/CH_2Cl_2 (3:1 v/v), mp 84.0–85.0 °C.

Anal. Calcd for $C_{11}H_8Fe_2O_7S$: C, 33.36; H, 2.04. Found: C, 33.59; H, 2.14%. IR (CCl_4, cm^{-1}): 3000 (vw), 2933 (vw), 2841 (vw), 1548 (w), 1468 (w), 1440 (w), 1424 (w), 1308 (w), 1216 (m), 1188 (w), 1085 (s), 1013 (m), 972 (w), 944 (w), 748 (s), 711 (m), 671 (w), 624 (s), 596 (s), 580 (s). Terminal carbonyl region: 2067 (vs), 2025 (vs), 1994 (vs), 1969 (vs). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.41 (s, 3 H, SCH_3), 3.24 (s, 3 H, OCH_3), 3.95 (s, 1 H, $=CH_2$), 4.13 (s, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 29.23 (q, J_{CH} = 142.3 Hz, SCH_3), 54.20 (q, J_{CH} = 145.4 Hz, OCH_3), 68.57 (t, J_{CH} = 162.6 Hz, $=CH_2$), 112.89 (s, $=C(OCH_3)(SCH_3)$), 162.00 (s, allyl C), 210.45 (s, terminal CO's). Mass spectrum (EI) *m/z* (rel intensity): 396 (M^+, 24), 368 (M^+ – CO, 58), 340 (M^+ – 2CO, 58), 312 (M^+ – 3CO, 100), 284 (M^+ – 4CO, 57), 256 (M^+ – 5CO, 74), 228 (M^+ – 6CO, 89), 198 ($Fe_2(MeS)C{=}C{=}CH_2^+$ + 1 H, 74), 183 ($Fe_2HSC{=}C{=}CH_2^+$, 14), 170 ($Fe(MeO)(MeS)C{=}C{=}C^+$, 27), 144 (Fe_2S^+, 27).

Methylene choride eluted a third orange band which appeared to be a mixture of very minor products by TLC and was discarded.

Reaction of $Fe_3(CO)_{12}$ with 1-Methoxy-1-(ethylthio)allene. The standard apparatus was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and 1-methoxy-1-(ethylthio)allene (0.52 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 4 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (4:1 v/v) and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.25 g (0.63 mmol, 42% based on S, a/e:e/e = 2.2) of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$,[28] identified by comparison of its ^1H NMR spectrum ($CDCl_3$, 250 MHz) to that of an authentic sample. Further elution with pentane/CH_2Cl_2 (3:1 v/v) gave a second orange band which yielded 0.52 g (1.26 mmol, 42%) of $(\eta^1{:}\eta^3\text{-}C_2H_5S(CH_3O)CCCH_2)Fe_2(CO)_6$, **13b**, as an air-stable, red, crystalline solid after purification on preparative TLC plates (pentane eluant) and recrystallization from pentane/CH_2Cl_2 (3:1 v/v), mp 136.0–138.0 °C.

Anal. Calcd for $C_{12}H_{10}Fe_2O_7S$: C, 35.15; H, 2.46. Found: C, 35.27; H, 2.52%. IR (CCl_4, cm^{-1}): 2934 (vw), 1456 (w), 1440 (w), 1382 (m), 1214 (m), 1085 (s), 1013 (m), 960 (w), 710 (m), 670 (w), 624 (s), 597 (s), 581 (m). Terminal carbonyl region (CCl_4, cm^{-1}): 2066 (vs), 2024 (vs), 1996 (vs), 1984 (vs), 1968 (s). ^1H NMR ($CDCl_3$, 250 MHz): δ 1.37 (t, *J* = 7.50 Hz, 3 H, SCH_2CH_3), 2.66 (m, *J* = 6.85 Hz, 1 H, SCH_2CH_3), 2.95 (m, *J* = 6.80 Hz, 1 H, SCH_2CH_3), 3.26 (s, 3 H, OCH_3), 3.93 (s, 1 H, $=CH_2$), 4.11 (s, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 12.89 (q, J_{CH} = 129.4 Hz, SCH_2CH_3), 42.12 (t, J_{CH} = 142.6 Hz, SCH_2CH_3), 54.52 (q, J_{CH} = 144.9 Hz, OCH_3), 68.18 (t, J_{CH} = 162.3 Hz, $=CH_2$), 113.56 (s, $CH_3CH_2SCOCH_3$), 162.48 (s, allyl C), 210.62 (s, terminal CO's). Mass spectrum (EI) *m/z* (rel intensity): 410 (M^+, 17), 382 (M^+ – CO, 36), 354 (M^+ – 2CO, 34), 326 (M^+ – 3CO, 55), 298 (M^+ – 4CO, 36), 270 (M^+ – 5CO, 63), 242 (M^+ – 6 CO, 91), 214 ($Fe_2HSC(OMe){=}C{=}CH_2^+$, 46), 184 ($Fe_2HSCH{=}C{=}CH_2^+$, 100), 182 ($Fe_2SC{=}C{=}CH_2^+$, 33), 170 ($Fe_2HSCH{=}C^+$, 7), 144 ($Fe_2S^+$, 53), 112 ($Fe_2^+$, 6), 56 ($Fe^+$, 18), 40 ($CH_2{=}C{=}CH_2$, 11).

Reaction of $Fe_3(CO)_{12}$ with 1-Methoxy-1-(*tert*-butylthio)allene. The standard apparatus was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and 1-methoxy-1-(*tert*-butylthio)allene (0.63 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 4 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (5:1 v/v) and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.51 g (1.11 mmol, 74% based on S, a/e:e/e = 3.1) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum ($CDCl_3$, 250 MHz) to that of an authentic sample.[29] Further elution with pentane/CH_2Cl_2 (3:1 v/v) gave a very minor orange band which was not collected.

Reaction of $Fe_3(CO)_{12}$ with (Methylthio)allene. The standard apparatus was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and (methylthio)allene (0.34 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 5 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (4:1 v/v) and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.03 g (0.08 mmol, 5% based on S, a/e:e/e = 2.1) of $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum to that of an authentic sample. Further elution with pentane/CH_2Cl_2 (5:1 v/v) gave a second orange band which yielded 0.47 g (1.29 mmol, 43%) of $(\eta^1,\eta^3\text{-}CH_3SCHCCH_2)Fe_2(CO)_6$, **2a**, as an air-stable, deep red, crystalline solid after purification on preparative TLC plates (pentane eluant) and recrystallization from pentane, mp 53.0–55.0 °C.

Anal. Calcd for $C_{10}H_6Fe_2O_6S$: C, 32.82; H, 1.66. Found: C, 33.11; H, 1.75%. IR (CCl_4, cm^{-1}): 2965 (w), 2930 (w), 2860 (w), 1465 (w), 1425 (w), 1310 (w), 1190 (w), 955 (w), 925 (w), 700 (m), 620 (m), 605 (w), 575 (m). Terminal carbonyl region (CCl_4, cm^{-1}): 2070 (s), 2030 (vs), 2010 (sh), 1990 (vs), 1950 (vs). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.48 (s, 3 H, SCH_3), 3.32 (s, 1 H, CH_3SCH), 4.08 (s, 1 H, $=CH_2$), 4.20 (s, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 75.5 Mhz): δ 33.21 (q, J_{CH} = 141.7 Hz, SCH_3), 66.00 (d, J_{CH} = 188.0 Hz, CH_3SCH), 67.88 (t, J_{CH} = 161.6 Hz, $=CH_2$), 175.46 (s, allyl C), 209.04, 212.20 (both s, terminal CO's). Mass spectrum (EI) *m/z* (rel intensity): 366 (M^+, 15), 338 (M^+ – CO, 29), 310 (M^+ – 2CO, 56), 282 (M^+ – 3CO, 20), 254 (M^+ – 4CO, 35), 226 (M^+ – 5CO, 24), 198 (M^+ – 6CO, 100), 183 ($Fe_2SCH{=}C{=}CH_2^+$, 36), 170 ($Fe_2SCH{=}CH^+$, 27), 144 (Fe_2S^+, 31).

Methylene chloride eluted a third orange band which, after slow medium pressure column chromatography with pentane as the eluant gave two orange-red bands. The first band to elute gave 0.07 g (0.16 mmol, 5%) of *transoid*-$(\eta^3\text{-}CH_3SCHCCH_2)_2Fe_2(CO)_6$, **15′a** as an air-stable, orange-red, crystalline solid after recrystallization from pentane, mp 99.0–100.0 °C.

Anal. Calcd for $C_{14}H_{12}Fe_2O_6S_2$: C, 37.19; H, 2.68. Found: C, 36.80; H, 2.95%. IR (CCl_4, cm^{-1}): 2917 (w), 1555 (w), 1540 (w), 1456 (m), 1130 (w), 659 (w), 593 (m), 569 (m), 544 (s), 525 (w), 508 (w). Terminal carbonyl region (CCl_4, cm^{-1}): 2064 (vs), 2060 (vs), 2027 (vs), 1995 (vs). ^1H NMR (CDCL$_3$, 300 MHz): δ 2.12 (s, 3 H, SCH_3), 2.65 (t, *J* = 1.87 Hz, 1 H, CH_3SCH), 2.84 (d, *J* = 2.69 Hz, 1 H, $=CH_2$), 3.24 (d, *J* = 1.70 Hz, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 20.48 (q, J_{CH} = 140.0 Hz, SCH_3), 44.64 (t, J_{CH} = 164.2 Hz, $=CH_2$), 58.67 (d, J_{CH} = 168.7 Hz, CH_3SCH), 87.38 (s, allyl C), 208.65, 211.20, 216.36 (both s, terminal CO's). Mass spectrum (EI) *m/z* (rel intensity): 424 (M^+ – CO, 9), 396 (M^+ – 2CO, 51), 368 (M^+ – 3CO, 14), 340 (M^+ – 4CO, 28), 312 (M^+ – 5CO, 29), 284 (M^+ – 6CO, 71), 269 ($Fe_2(MeSCH{=}C{=}CH_2)(SCH{=}C{=}CH_2^+$, 30), 254 ($Fe_2(SCH{=}C{=}CH_2)_2^+$, 20), 235 ($Fe_2(MeSC{=}C{=}CH_2)(C{=}C{=}CH_2)^+$, 15), 191 ($Fe_2(CH_2{=}C{=}CH)_2^+$ + 1H, 64), 177 ($Fe_2(CH_2{=}C{=}CH)(CH_2{=}C)^+$, 31), 176 ($Fe_2(CH_2{=}C{=}C)(CH_2{=}C)^+$, 100), 144 ($(HSCH{=}C{=}CH_2)_2^+$, 34),

---

[28] Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

[29] DeBeer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757.

142 $(SCH=C=CH_2)_2^+$, 16), 97 $((CH_2=C=CH)(HSCH=C)^+$, 20), 83 $(CH_2=C)(SCH=C)^+$, 17), 56 (Fe^+, 17).

The second band to elute yielded 0.06 g (0.13 mmol, 4%) of *cisoid*-$[\eta^3\text{-}CH_3SCHCCH_2]_2Fe_2(CO)_6$, **15a**, as an air-stable, orange-red, crystalline solid after recrystallization from pentane, mp 96.0–98.0 °C.

Anal. Calcd for $C_{14}H_{12}Fe_2O_6S_2$: C 37.19; H, 2.68. Found: C, 37.60; H, 2.85%. IR (CCl_4, cm^{-1}): 2916 (w), 2854 (m), 2848 (w), 1456 (m), 1433 (m), 1261 (w), 655 (m), 593 (s), 564 (vs), 520 (w). Terminal carbonyl region (CCl_4, cm^{-1}): 2064 (vs), 2027 (vs), 1995 (vs). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.18 (t, J = 2.24 Hz, 1 H, $CH_3SC\mathit{H}$), 2.24 (s, 3 H, SCH_3), 2.78 (d, J = 1.95 Hz, 1 H, $=CH_2$), 3.59 (d, J = 2.57 Hz, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 20.88 (q, J_{CH} = 140.1 Hz, $S\mathit{C}H_3$), 40.26 (t, J_{CH} = 162.1 Hz, $=\mathit{C}H_2$), 63.51 (d, J_{CH} = 170.6 Hz, $CH_3S\mathit{C}H$), 85.80 (s, allyl C), 208.05, 212.73, 213.99 (all s, terminal CO's). Mass spectrum (EI) m/z (rel intensity): 452 (M^+, 4), 424 ($M^+ - CO$, 9), 396 ($M^+ - 2CO$, 51), 368 ($M^+ - 3CO$, 14), 340 ($M^+ - 4CO$, 16), 312 ($M^+ - 5CO$, 28), 284 ($M^+ - 6CO$, 74), 269 $(Fe_2(MeSCH=C=CH_2)(SCH=C=CH_2)^+$, 25), 256 $(Fe_2(HSCH=C=CH_2)(HSCH=C=CH_2)^+$, 31), 254 $(Fe_2(SCH=C=CH_2)_2^+$, 20), 235 $(Fe_2(MeSC=C=CH_2)(C=C=CH_2)^+$, 25), 228 $(Fe(MeSC=C=CH_2)(SC=C=CH_2)^+$, 26), 212 $(Fe(MeSCH=C=CH_2)(SC=C=CH_2)^+$, 28), 191 $(Fe_2(CH_2=C=CH)(CH_2=C=CH_2)^+$, 60), 176 $(Fe_2(CH_2=C=C)(CH_2=C)^+$, 100), 157 $((MeSCH=C=CH_2)(SCH=C=CH_2),^+$ 30), 144 $((HSCH=C=CH_2)_2^+$ or Fe_2S^+, 35), 125 $((MeSCH=C=CH_2)(HC=C=CH_2)^+$, 25), 111 $((HSCH=C=CH_2)(HC=C=CH_2)^+$, 35), 102 ($FeHSCH^+$, 24), 97 $((CH_2=C=CH)\text{-}(HSCH=C)^+$, 47), 81 $((CH=C)(SC=C)^+$, 30), 71 $(SCH=C=CH_2^+$, 46), 56 (Fe^+, 57), 45 (SCH^+, 27).

Reaction of $Fe_3(CO)_{12}$ with (Phenylthio)allene. The standard apparatus was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and (phenylthio)allene (0.59 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 1.5 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (1:4 v/v) and filtered through a thin pad of silicic acid. Elution with pentane/CH_2Cl_2 (5:1 v/v) gave an orange band which yielded 0.37 g (0.85 mmol, 29%) of $(\eta^1{:}\eta^3\text{-}PhSCHCCH_2)Fe_2(CO)_6$, **2b**, as an air-stable, orange-red, crystalline solid after purification on preparative TLC plates (pentane/CH_2Cl_2 1:1 v/v eluant) and recrystallization from pentane/CH_2Cl_2 (2:1 v/v), mp 107.0–109.0 °C.

Anal. Calcd for $C_{15}H_8Fe_2O_6S$: C, 42.09; H, 1.89. Found: C, 42.17; H, 1.93%. IR (thin film, cm^{-1}): 2359 (w), 1644 (w), 1441 (w), 1068 (w), 740 (m), 702 (m), 622 (m). Terminal carbonyl region (CCl_4, cm^{-1}): 2070 (s), 2028 (vs), 1997 (vs), 1975 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.52 (s, 1 H, $PhSC\mathit{H}$), 4.12 (s, 1 H, $=CH_2$), 4.34 (s, 1H, $C\mathit{H}_2$), 7.39–7.67 (m, Ph). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 62.23 (d, J_{CH} = 181.3 Hz, $PhS\mathit{C}H$), 67.76 (t, J_{CH} = 161.3 Hz, $=\mathit{C}H_2$), 126.88 (d, J_{CH} = 162.6 Hz, Ph), 129.12 (d, J_{CH} = 165.9 Hz, Ph), 129.54 (d, J_{CH} = 163.4 Hz, Ph), 139.70 (s, ipso Ph), 174.30 (s, allyl CO), 209.20, 211.86 (both s, terminal CO's). Mass spectrum (EI) m/z (rel intensity): 428 (M^+, 6), 400 ($M^+ - CO$, 6), 372 ($M^+ - 2CO$, 22), 344 ($M^+ - 3CO$, 8), 316 ($M^+ - 4CO$, 18), 288 ($M^+ - 5CO$, 15), 260 ($M^+ - 6CO$, 100), 245 $(Fe_2(PhSC=C)^+$, 14), 221 (Fe_2SPh^+, 12), 169 ($Fe_2SCH=C^+$, 21), 165 ($FeSPh^+$, 8), 144 (Fe_2S^+, 35), 112 (Fe_2^+, 5), 56 (Fe^+, 12).

Further elution with pentane/CH_2Cl_2 (2:1 v/v) gave a minor red band which was discarded. Continued elution with CH_2Cl_2 gave a red band which afforded 0.50 g (0.87 mmol, 29%) of *cisoid*-$(\eta^3\text{-}PhSCHCCH_2)_2Fe_2(CO)_6$, **15b**, as an air-stable, deep red, crystalline solid after purification on preparative TLC plates (pentane/CH_2Cl_2 1:1 v/v eluant) and recrystallization from pentane/CH_2Cl_2 (1:1 v/v), mp 136.0–138.0 °C.

Anal. Calcd for $C_{24}H_{16}Fe_2O_6S_2$: C, 50.02; H, 2.80. Found: C, 50.31; H, 3.14%. IR (thin film, cm^{-1}): 3019 (m), 2400 (m), 1522 (w), 1218 (s), 928 (w), 770 (s), 669 (s), 566 (w), 488 (w). Terminal carbonyl region (CCl_4, cm^{-1}): 2068 (vs), 2033 (vs), 2003 (s), 1990 (sh). ^1H NMR ($CDCl_3$, 75.4 MHz): δ 2.23 (t, J = 2.50 Hz, 1 H, $PhSC\mathit{H}$), 2.89 (d, J = 2.29 Hz, 1 H, $=C\mathit{H}_2$), 3.70 (d, J = 2.72 Hz, 1 H, $=C\mathit{H}_2$), 7.24–7.33 (m, 3 H, Ph), 7.35–7.38 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 40.16 (t, J_{CH} = 163.4 Hz, $=\mathit{C}H_2$), 55.81 (d, J_{CH} = 171.2 Hz, $PhS\mathit{C}H$), 87.19 (s, allyl C), 126.87 (d, J_{CH} = 162.0 Hz, Ph), 128.38 (d, J_{CH} = 162.4 Hz, Ph), 129.41 (d, J_{CH} = 163.8 Hz), 140.05 (s, ipso Ph), 208.18, 212.76, 213.67 (all s, terminal CO's). Mass spectrum (FD): 576 (M^+). Mass spectrum (EI) m/z (rel intensity): 548 ($M^+ - CO$, 5), 520 ($M^+ - 2CO$, 32), 492 ($M^+ - 3CO$, 9), 464 ($M^+ - 4CO$, 13), 436 ($M^+ - 5CO$, 11), 408 ($M^+ - 6CO$, 51), 352 $(Fe_2(PhSCH=C=CH_2)_2^+$, 14), 330 $(Fe_2\text{-}(SC=C=CH_2)(PhSC=C=CH_2)^+$, 100), 274 $(Fe_2(PhSCH=C)\text{-}(C=CH_2)^+ + 2H$, 17), 186 $(Fe(HSCH=C=CH_2)(HSCH=C)^+$, 34), 176 $(Fe_2(CH_2=C=C)(CH_2=C)^+$, 34), 154 $(Fe(HSCH=C=CH_2)(CH_2=C)^+$, 33), 110 ($PhSH^+$, 19), 78 ($PhH^+$, 11), 77 ($Ph^+$, 8).

Reaction of $Fe_3(CO)_{12}$ with (Ethylthio)allene. The standard apparatus was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. THF (30 mL) and (ethylthio)allene (0.40 g, 4.00 mmol) then were added. The reaction mixture was stirred at gentle reflux for 1 h until TLC showed that all of the $Fe_3(CO)_{12}$ had been consumed. The solvent was removed in vacuo to leave an oily, red residue which was dissolved in pentane/CH_2Cl_2 (1:1 v/v) and filtered through a thin pad of silicic acid. Elution with pentane gave an orange band which yielded 0.55 g (1.38 mmol, 93%, a/e:e/e = 2.3) of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum to that of an authentic sample. Further elution with pentane/CH_2Cl_2 (4:1 v/v) gave 0.06 g (0.15 mmol, 5%) of $(\eta^1{:}\eta^3\text{-}C_2H_5SCHCCH_2)Fe_2(CO)_6$, **2c**, as a red-orange, oil, which was identified by comparison of its ^1H NMR spectrum to that of $(\eta^1,\eta^3\text{-}CH_3SCHCCH_2)Fe_2(CO)_6$, **2a**. However, this product could not be obtained in a pure form, even after repeated chromatography and further characterization was not completed.

^1H NMR ($CDCl_3$, 250 MHz): δ 1.32 (t, J = 7.32 Hz, 3 H, $SCH_2C\mathit{H}_3$), 2.72 (m, J = 7.41 Hz, 1 H, $SC\mathit{H}_2CH_3$), 2.81 (m, J = 7.48 Hz, 1 H, $SC\mathit{H}_2CH_3$), 3.31 (s, 1 H, $EtSC\mathit{H}$), 4.07 (s, 1 H, $=CH_2$), 4.27 (s, 1 H, $=CH_2$).

Acknowledgment. The MIT authors are grateful to the National Science Foundation for support of this research. M.C. thanks the University of Alberta and the Natural Sciences and Research Council (Canada) for financial support.

Supplementary Material Available: Tables of anisotropic temperature factors and hydrogen parameters for compound **15b** and tables of complete final positional parameters and complete bond distances and angles for compounds **2a** and **15b** (15 pages). Ordering information is given on any current masthead page.

OM920210N