(Thioallyl)Iron Tricarbonyl Complexes

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The tetramethylallene episulfide 1a reacts with $Fe_2(CO)_9$ to afford (tetramethylthioallyl)iron tricarbonyl complex 2a and (μ-2,4-dimethyl-2-pentene-3,4-dithiolato-$\kappa^2 S$:$\kappa^2 S'$)diiron hexacarbonyl (3). The structure of 3 was characterized crystallographically. The reaction of 1-*tert*-butyl-3,3-diphenylallene 1-episulfide (1b) with $Fe_2(CO)_9$ resulted in the formation of (1-*tert*-butyl-3,3-diphenyl-2-thioallyl)iron tricarbonyl (2b). The (thioallyl)iron tricarbonyl complex 2b exists as an η^4-π-complex as revealed by ^1H and ^{13}C NMR spectroscopy as well as by X-ray diffraction analysis. Thermolysis of 2b in the presence of carbon monoxide gave 2-*tert*-buyl-4-(diphenylmethylidene)thietan-3-one (7). Complex 2b reacts with PPh_3 to give 7 and metalathiopentanone 8. Heating of 8 gave 7 and a corresponding allene 5b. According to the structure of 7 and 8 and chemical observations, thermolysis of 8 took place to give 7 via a metathesis-like reaction of 1,2- or 1,3-metalathietane 13 and 15.

Introduction

Trimethylenemethane (TMM)[1] and its heteroatom analogues[2] have been the subjects of theoretical and synthetic studies. Thioallyl,[3,4] sulfur analogue of TMM, is a biradical with a partial ionic character similar to TMM[1c-e] rather than to oxyallyl,[2c] according to the kinetic[4f-g] and MCSCF calculation[4e] studies. Thioallyl has been referred to as an intermediate for the tautomeric system of an allene episulfide and a cyclopropanethione. Whereas allene episulfide can be stable with alkyl or aryl substituents, thioallyl and cyclopropanethione are elusive intermediates only identified by trapping experiments.[4g] The coordination of a transition metal has been well-known to stabilize the reactive TMM intermediate. A theoretical calculation, by both Albright[5] and Trost,[6] shows that d^8-metal complexes adopt a stable (η^4-TMM)ML_3 structure (I), and [3 + 2] cycloaddition does not occur. With d^{10}-

$M = d^8$ metal
(I)

$M = d^{10}$ metal
(II)

Scheme I

* = radical or ion

$X = CH_2, O, S$
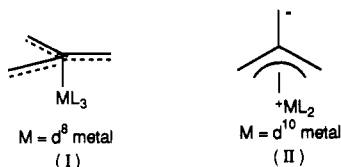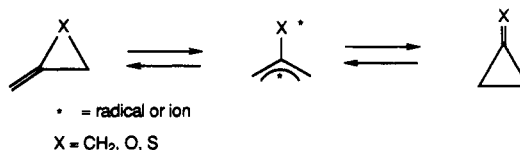
metal complexes, the TMM ligand is coordinated in an unsymmetrical geometry, i.e. (η^3-TMM)ML_2 (II), and the catalytic cycloaddition proceeds via a zwitterionic intermediate which causes a nucleophilic attack on electron-deficient alkenes and imines.[7] As with trimethylenemethane,[8] thioallyl can be isolated as its iron tricarbonyl complex. We have previously reported preliminaly experiments on the first synthesis of (thioallyl)iron tricarbonyl complexes by the reaction of allene episulfides with diiron noncarbonyl.[9] As other heteroatom analogus complexes of TMM, the isolation of the monomeric (η^4-oxyallyl)ruthenium complex and the dimeric (μ-η^3,η^1-oxyallyl)iron complex were recently reported by Bergman[10] and Jenny[11] independently. In this paper, we present the first full details and reactions of stable (η^4-thioallyl)iron tricarbonyl complexes.

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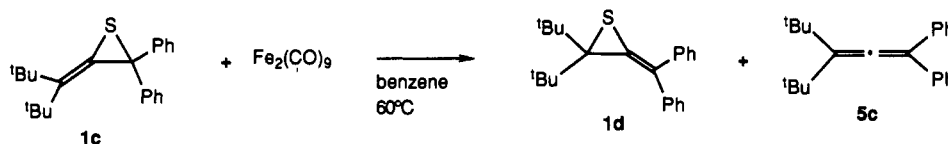(11) Frey, M.; Jenny, T. A.; Stoeckli-Evans, H. *Organometallics* 1990, 9, 1806.
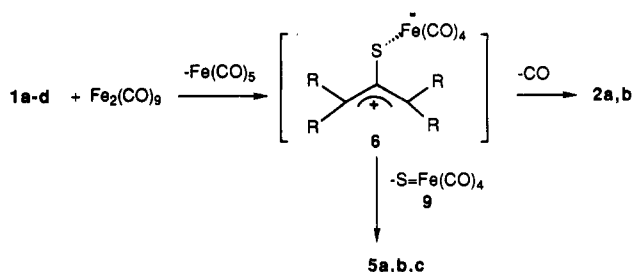
Scheme II
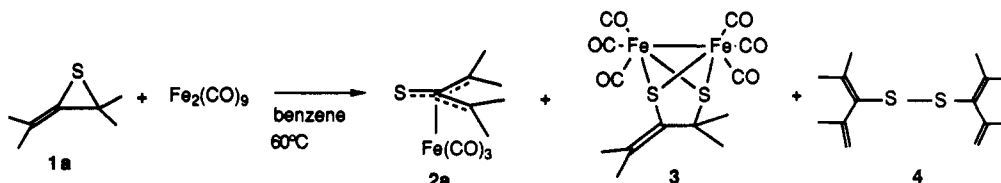
**Scheme III**
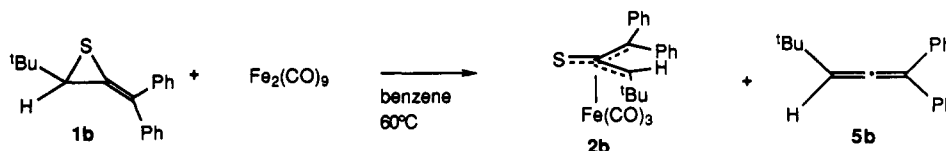
Scheme IV

Results and Discussion

Reaction of Allene Episulfides (1a-c) with Fe₂(CO)₉.
The reaction of tetramethylallene episulfide (1a) with 1.2
equiv of Fe₂(CO)₉ in benzene for 10 min at 60 °C gave
β-thioallyliron–Fe(CO)₃ (2a) as yellow crystals in 16% yield
along with 3 (Me₄C₃Fe₂(CO)₆, 11.5%) as orange crystals
and (1-isopropenyl-2-methyl-1-propenyl)disulfide 4
(13.8%) (Scheme II). 2a was not so stable against air in
solution. (1-*tert*-Butyl-3,3-diphenyl-2-thioallyl)iron tri-
carbonyl (2b) was prepared by a method similar to that
used to prepare 2a. Compound 2b was obtained in 29%
yield as orange crystals along with a corresponding allene
5b which was a desulfurized product by Fe₂(CO)₉ in 25%
yield (Scheme III). In the case of 0.5 equiv of Fe₂(CO)₉,
for 1b, a half amount of 1b was recovered together with
2b and 5b, 14% and 12%, respectively. Therefore an
equimolar amount of Fe₂(CO)₉ for allene episulfides 1 was
required for formation of thioallyl complexes 2. Replacing
a proton of 1b with a *tert*-butyl group (1c)[4h] resulted in
the isomerization of allene episulfide 1c to 1d along with
the formation of 5c in 15% and 46% yields (Scheme IV).
We thought that a monomeric coordinatively unsaturated
species, i.e. Fe(CO)₄ (generated from the breakdown of
Fe₂(CO)₉), acts as a Lewis acid to promote the ring opening
and isomerization of allene episulfides. We have already
reported that a Lewis acid such as BF₃·Et₂O[4h,k,l] or
Me₂SO₄[4k] showed the same behavior toward allene epi-
sulfides to produce thioallyl cation intermediates at low
temperature.[4m] Thus, the C–S bond cleavage of the thi-
irane ring by Fe(CO)₄ produces 6 with the positive charge
on the thioallyl ligand and the negative charge on the metal
atom, that is an allyl cation type intermediate. Recently,
Adams[12] has also reported the ring opening and oligom-
erization of thiirane and thietane by triosmium carbonyl
clusters and pointed out the strong Lewis acidic character
of the carbonyl cluster. Complex 6 loses carbon monoxide,
and subsequent coordination transfer gives the complex
2a,b. Alternatively, the thioallyl cation complex 6, on
account of the strong sulfur–iron bond, prefers to eliminate
allene 5b,c and iron-bound sulfur 9. Meanwhile, allene-
dithiolato complex 3 could be formed by following two
routes. One route is a manner similar to that of an ethe-
nedithiolato complex which was reported by Lorenz et al.[13c]

Scheme V

Scheme VI
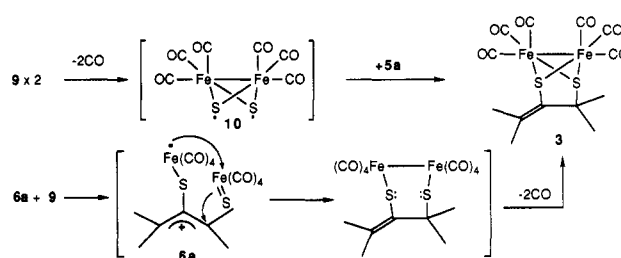
A reactive intermediate 10[13,14] reacts with tetramethyl-
allene 5a to give 3, as shown in Scheme VI. An alternative
mechanism is that a zwitterionic intermediate 6a causes
a nucleophilic attack on the Fe–S double bond of 9 and
2 equiv of carbon monoxide is eliminated to form bridged
Fe–S–Fe bonds. Then we have carried out the reaction
of the allene episulfide 1b with Fe₂(CO)₉ in the presence
of α-methylstyrene. Neither a corresponding ethenedi-
thiolato complex nor (μ-dithio)diiron complex [SFe(C-
O)₃]₂[14] was obtained besides the formation of 2b and allene
5b. These results indicated the second route via inter-
mediate 6a, taking place in the formation of 3. However,

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was prepared from iron pentacarbonyl and sodium polysulfide solution
by Hieber and Gruber. A reactive intermediate [SFe(CO)₃]₂* (10) was
generated by photolysis of [SFe(CO)₃]₂ or a reaction of C₂H₄SO (or
C₂H₄S) with Fe₃(CO)₁₂.

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Table I. Crystallographic Data for Diffraction Studies

compd	2b	3	8
empirical formula	$C_{22}H_{20}FeO_3S$	$C_{13}H_{12}Fe_2O_6S_2$	$C_{41}H_{35}FeO_4PS$
fw	420.31	440.06	710.62
cryst syst	monoclinic	monoclinic	triclinic
lattice params			
a, Å	11.437 (4)	8.346 (1)	9.805 (1)
b, Å	7.003 (3)	16.811 (1)	12.151 (1)
c, Å	25.235 (9)	12.677 (2)	16.121 (1)
α, deg			103.55 (1)
β, deg	91.37 (3)	90.24 (1)	101.25 (1)
γ, deg			98.80 (1)
V, Å^3	2020.7	1778.6	1791.1
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P1$ (No. 1)
Z value	4	4	2
D_{calc}, g/cm^3	1.38	1.64	1.32
$F(000)$	872	888	740
μ(Mo Kα), cm^{-1}	8.6	18.8	5.6
temp, °C	23	23	23
$2\theta_{max}$, deg	50	50	50
no. of observns ($I > 3\sigma(I)$)	3972	4757	3912
no. of variables	304	244	682
residuals: R; R_w	0.091; 0.107	0.031; 0.034	0.061; 0.067
goodness of fit indicator	3.59	1.11	1.85
max shift in final cycle	1.28	2.57	5.57
largest peak in final diff map, e/Å^3	2.06	0.58	0.42

the different reactivity between α-methylstyrene and allene **5a** does not permit an unambiguous conclusion and the first route cannot be rejected.

Structures of 2a, 2b, and 3. The structures of two thioallyl complexes **2a** and **2b** were identified by their characteristic infrared (IR), ^{1}H NMR, ^{13}C NMR, and mass spectra and elemental analysis. The IR absorption for the iron carbonyl in thioallyl-Fe(CO)$_3$ complexes appears as two distinct peaks in the region 2000–2080 cm^{-1}. These absorptions are similar to those of other Fe(CO)$_3$ complexes.[8b] A very weak absorption of **2a** occurs at frequencies (1960 cm^{-1}) lower than those of the broad carbonyl peak (2080 and 2000 cm^{-1}) and may be characteristic of a thioallyl-Fe(CO)$_3$ complex similar to TMM-Fe(CO)$_3$.[8b] Two (105.1 and 117.9 ppm in **2a**) or three (106.3, 118.6, and 122.6 ppm in **2b**) sets of olefin signals in ^{13}C NMR spectra suggest that **2a** and **2b** are π complexes of the η^4 type. At room temperature, the carbonyl ligands at iron are fluxional in **2a** with one broad carbonyl signal in the ^{13}C NMR spectra but not in **2b** as indicated by the three distinct carbonyl signals in the ^{13}C NMR spectra. The fragment pattern of mass spectra of **2a** and **2b** indicated an elimination of three carbon monoxides at iron. A single-crystal X-ray diffraction structure analyses was undertaken to determine the unequivocal molecular structure of **2b**. An ORTEP drawing of the molecular structure of **2b** is shown in Figure 1. Selected interatomic distances and angles are listed in Tables II and III. The iron atom is located directly beneath the central atom [C(1)] of the thioallyl residue and is π-bonded to all three carbon and one sulfur atoms of this ligand. The thioallyl ligand and the Fe(CO)$_3$ moiety adopt a mutually staggered conformation. Interatomic distances within the thioallyl residue are C(1)–C(2) = 1.41 (1), C(1)–C(3) = 1.40 (1), and C(1)–S = 1.757 (8) Å. The skeleton of the thioallyl ligand is significantly nonplanar, with the central carbon atom [C(1)] being displaced 0.258 Å (away from the iron atom) relative to the plane defined by the terminal atoms C(2), C(3), and S(1). This value is slightly shorter than that of TMM–Fe(CO)$_3$ (0.285[8c] and 0.315 Å[8d]). These results were similar to those of TMM–Fe(CO)$_3$.[8a-h]

The ^{1}H NMR spectrum of **3** showed three singlets at 1.59, 1.73, and 2.11 ppm in the ratio 2:1:1. The structure of **3** was assigned by comparison with the published data of the analogous complex [Me$_4$C$_3$SOFe$_2$(CO)$_6$],[15] and its
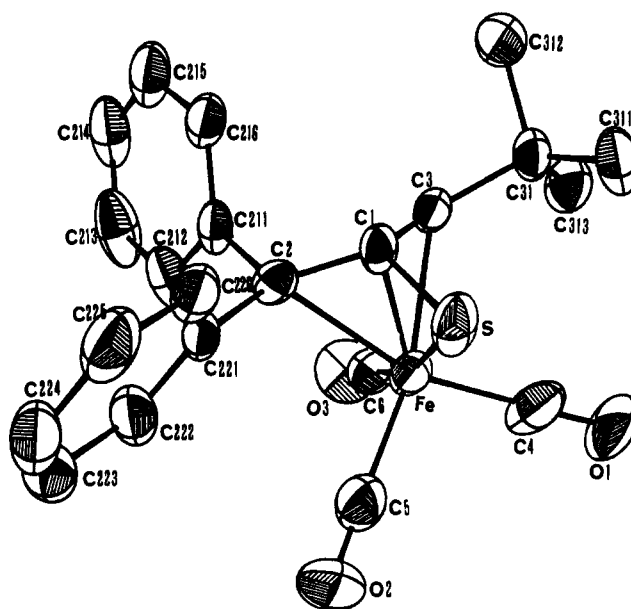
Figure 1. ORTEP drawing of (η^4-1-*tert*-butyl-3,3-diphenyl-2-thioallyl)iron tricarbonyl (**2b**).

Table II. Intramolecular Distances (Å) for 2b

Fe–S	2.308 (3)	C(31)–C(311)	1.54 (1)
Fe–C(1)	1.937 (8)	C(31)–C(312)	1.56 (1)
Fe–C(2)	2.261 (8)	C(31)–C(313)	1.52 (1)
Fe–C(3)	2.180 (8)	C(211)–C(212)	1.37 (1)
Fe–C(4)	1.81 (1)	C(211)–C(216)	1.40 (1)
Fe–C(5)	1.84 (1)	C(212)–C(213)	1.41 (1)
Fe–C(6)	1.758 (9)	C(213)–C(214)	1.37 (2)
S–C(1)	1.757 (8)	C(214)–C(215)	1.40 (2)
O(1)–C(4)	1.13 (1)	C(215)–C(216)	1.41 (1)
O(2)–C(5)	1.12 (1)	C(221)–C(222)	1.35 (1)
O(3)–C(6)	1.16 (1)	C(221)–C(226)	1.38 (1)
C(1)–C(2)	1.41 (1)	C(222)–C(223)	1.43 (1)
C(1)–C(3)	1.40 (1)	C(223)–C(224)	1.40 (2)
C(2)–C(211)	1.53 (1)	C(224)–C(225)	1.38 (2)
C(2)–C(221)	1.52 (1)	C(225)–C(226)	1.41 (1)
C(3)–C(31)	1.54 (1)		

butterfly structure was finally comfirmed by X-ray analysis. An ORTEP drawing of the molecular structure of **3** is

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Table III. Intramolecular Bond Angles (deg) for 2b

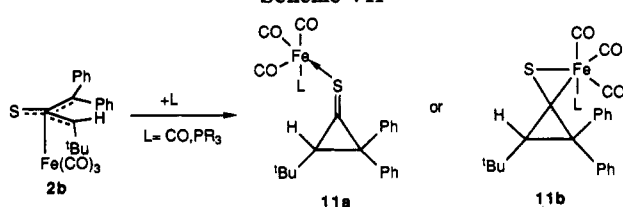|			
S–Fe–C(1)	47.9 (2)	C(1)–C(2)–C(211)	118.9 (6)
S–Fe–C(2)	71.8 (2)	C(1)–C(2)–C(221)	123.3 (7)
S–Fe–C(3)	73.9 (2)	C(211)–C(2)–C(221)	112.1 (6)
S–Fe–C(4)	93.6 (3)	Fe–C(3)–C(1)	61.0 (4)
S–Fe–C(5)	96.0 (4)	Fe–C(3)–C(31)	126.9 (5)
S–Fe–C(6)	163.3 (3)	C(1)–C(3)–C(31)	133.5 (7)
C(1)–Fe–C(2)	38.3 (2)	Fe–C(4)–O(1)	177 (1)
C(1)–Fe–C(3)	39.3 (3)	Fe–C(5)–O(2)	178.9 (8)
C(1)–Fe–C(4)	121.8 (5)	Fe–C(6)–O(3)	178.8 (9)
C(1)–Fe–C(5)	122.9 (4)	C(3)–C(31)–C(311)	116.9 (7)
C(1)–Fe–C(6)	115.5 (3)	C(3)–C(31)–C(312)	103.6 (6)
C(2)–Fe–C(3)	66.3 (2)	C(3)–C(31)–C(313)	109.9 (7)
C(2)–Fe–C(4)	160.1 (4)	C(311)–C(31)–C(312)	107.0 (8)
C(2)–Fe–C(5)	96.2 (4)	C(311)–C(31)–C(313)	111.4 (7)
C(2)–Fe–C(6)	95.5 (3)	C(312)–C(31)–C(313)	107.3 (7)
C(3)–Fe–C(4)	97.2 (4)	C(2)–C(211)–C(212)	122.3 (7)
C(3)–Fe–C(5)	161.6 (4)	C(2)–C(211)–C(216)	116.6 (7)
C(3)–Fe–C(6)	91.3 (4)	C(212)–C(211)–C(216)	120.9 (8)
C(4)–Fe–C(5)	98.8 (4)	C(211)–C(212)–C(213)	120.2 (9)
C(4)–Fe–C(6)	95.8 (4)	C(212)–C(213)–C(214)	119 (1)
C(5)–Fe–C(6)	96.1 (4)	C(213)–C(214)–C(215)	120.7 (9)
Fe–S–C(1)	54.9 (2)	C(214)–C(215)–C(216)	120 (1)
Fe–C(1)–S	77.2 (4)	C(211)–C(216)–C(215)	118.7 (9)
Fe–C(1)–C(2)	83.4 (5)	C(2)–C(221)–C(222)	120.5 (8)
Fe–C(1)–C(3)	79.7 (5)	C(2)–C(221)–C(226)	118.2 (7)
S–C(1)–C(2)	115.1 (6)	C(222)–C(221)–C(226)	121.1 (8)
S–C(1)–C(3)	116.9 (5)	C(221)–C(222)–C(223)	121 (1)
C(2)–C(1)–C(3)	119.3 (7)	C(222)–C(223)–C(224)	117.0 (9)
Fe–C(2)–C(1)	58.3 (4)	C(223)–C(224)–C(225)	121.3 (9)
Fe–C(2)–C(211)	117.5 (5)	C(224)–C(225)–C(226)	120 (1)
Fe–C(2)–C(221)	116.4 (5)	C(221)–C(226)–C(225)	119.5 (9)

Table IV. Intramolecular Distances (Å) for 3

Fe(1)–Fe(2)	2.4972 (6)	O(41)–C(41)	1.133 (4)
Fe(1)–S(1)	2.2357 (8)	O(42)–C(42)	1.133 (1)
Fe(1)–S(2)	2.2424 (8)	O(43)–C(43)	1.135 (4)
Fe(1)–C(41)	1.791 (3)	O(51)–C(51)	1.130 (4)
Fe(1)–C(42)	1.791 (3)	O(52)–C(52)	1.138 (4)
Fe(1)–C(43)	1.788 (3)	O(53)–C(53)	1.135 (4)
Fe(2)–S(1)	2.2428 (8)	C(1)–C(2)	1.519 (4)
Fe(2)–S(2)	2.2416 (8)	C(1)–C(11)	1.531 (4)
Fe(2)–C(51)	1.800 (3)	C(1)–C(12)	1.533 (4)
Fe(2)–C(52)	1.790 (3)	C(2)–C(3)	1.338 (4)
Fe(2)–C(53)	1.791 (3)	C(3)–C(31)	1.498 (5)
S(1)–C(1)	1.860 (3)	C(3)–C(32)	1.520 (4)
S(2)–C(2)	1.784 (3)		

Scheme VII

Figure 2. ORTEP drawing of (μ-2,4-dimethyl-2-pentene-3,4-di-thiolato-$\kappa^2 S{:}\kappa^2 S'$) diiron hexacarbonyl (**3**).

Table V. Intramolecular Bond Angles (deg) for 3

Fe(2)–Fe(1)–S(1)	56.24 (2)	C(51)–Fe(2)–C(52)	99.4 (1)
Fe(2)–Fe(1)–S(2)	56.14 (2)	C(51)–Fe(2)–C(53)	98.5 (2)
Fe(2)–Fe(1)–C(41)	151.8 (2)	C(52)–Fe(2)–C(53)	91.2 (1)
Fe(2)–Fe(1)–C(42)	98.2 (1)	Fe(1)–S(1)–Fe(2)	67.78 (2)
Fe(2)–Fe(1)–C(43)	103.5 (2)	Fe(1)–S(1)–C(1)	105.63 (9)
S(1)–Fe(1)–S(2)	79.24 (2)	Fe(2)–S(1)–C(1)	105.34 (9)
S(1)–Fe(1)–C(41)	106.6 (2)	Fe(1)–S(2)–Fe(2)	67.69 (2)
S(1)–Fe(1)–C(42)	154.1 (1)	Fe(1)–S(2)–C(2)	105.78 (9)
S(1)–Fe(1)–C(43)	89.1 (2)	Fe(2)–S(2)–C(2)	103.62 (9)
S(2)–Fe(1)–C(41)	101.4 (1)	S(1)–C(1)–C(2)	108.1 (2)
S(2)–Fe(1)–C(42)	90.2 (2)	S(1)–C(1)–C(11)	105.8 (2)
S(2)–Fe(1)–C(43)	159.6 (1)	S(1)–C(1)–C(12)	106.6 (2)
C(41)–Fe(1)–C(42)	98.6 (1)	C(2)–C(1)–C(11)	113.5 (2)
C(41)–Fe(1)–C(43)	97.9 (2)	C(2)–C(1)–C(12)	112.7 (2)
C(42)–Fe(1)–C(43)	93.2 (2)	C(11)–C(1)–C(12)	109.7 (2)
Fe(1)–Fe(2)–S(1)	55.98 (2)	S(2)–C(2)–C(1)	115.0 (2)
Fe(1)–Fe(2)–S(2)	56.17 (2)	S(2)–C(2)–C(3)	117.6 (2)
Fe(1)–Fe(2)–C(51)	150.7 (1)	C(1)–C(2)–C(3)	127.3 (2)
Fe(1)–Fe(2)–C(52)	100.50 (9)	C(2)–C(3)–C(31)	123.0 (3)
Fe(1)–Fe(2)–C(53)	102.4 (1)	C(2)–C(3)–C(32)	124.3 (3)
S(1)–Fe(2)–S(2)	79.11 (3)	C(31)–C(3)–C(32)	112.6 (3)
S(1)–Fe(2)–C(51)	102.1 (1)	Fe(1)–C(41)–O(41)	178.6 (3)
S(1)–Fe(2)–C(52)	91.86 (9)	Fe(1)–C(42)–O(42)	179.0 (3)
S(1)–Fe(2)–C(53)	158.3 (1)	Fe(1)–C(43)–O(43)	178.5 (3)
S(2)–Fe(2)–C(51)	104.0 (1)	Fe(2)–C(51)–O(51)	179.3 (3)
S(2)–Fe(2)–C(52)	156.2 (1)	Fe(2)–C(52)–O(52)	178.6 (3)
S(2)–Fe(2)–C(53)	89.6 (1)	Fe(2)–C(53)–O(53)	178.9 (3)

shown in Figure 2. Selected interatomic distances and angles are listed in Tables IV and V. Compound **3** contains an allenedithiolato ligand, whose two sulfur atoms bridge the same Fe–Fe bond.

Reaction of (Thioallyl)iron Tricarbonyl 2b with CO and Phosphines. If a 2-electron-donating nucleophile (L) is accommodated into the Fe(CO)$_3$ ligand of **2b**, the thioallyl moiety might simultaneously rearrange into η^1- or η^2-cyclopropanethione **11a** or **11b** in order to achieve an 18-electron configuration (Scheme VII). So we examined the reaction of **2b** with CO and phosphines in the hope of isolating η^1- or η^2-cyclopropanethione **11a** or **11b**. However the reaction revealed unexpected facts and will be described in the following. Heating **2b** in toluene at 80 °C gave allene episulfide **1b** in 24% yield (Scheme VIII). Curiously this reaction was performed in a sealed tube to give the carbonylation product 2-*tert*-butyl-4-(diphenyl-
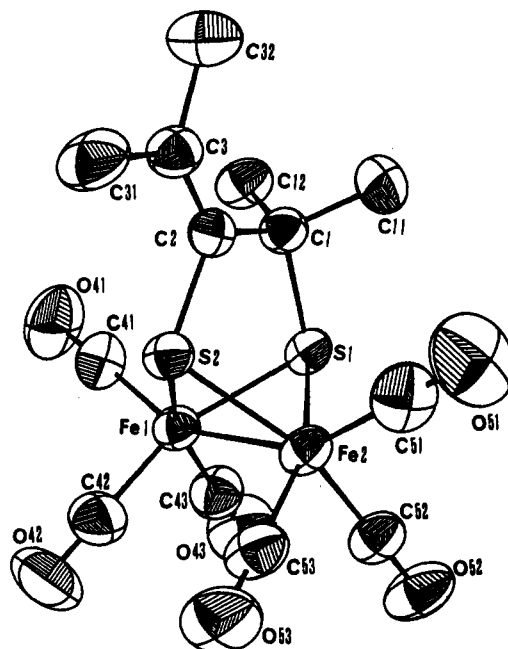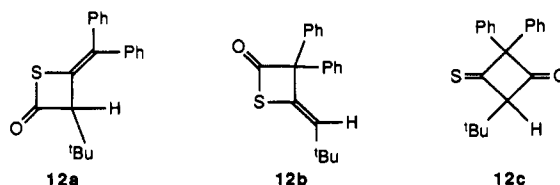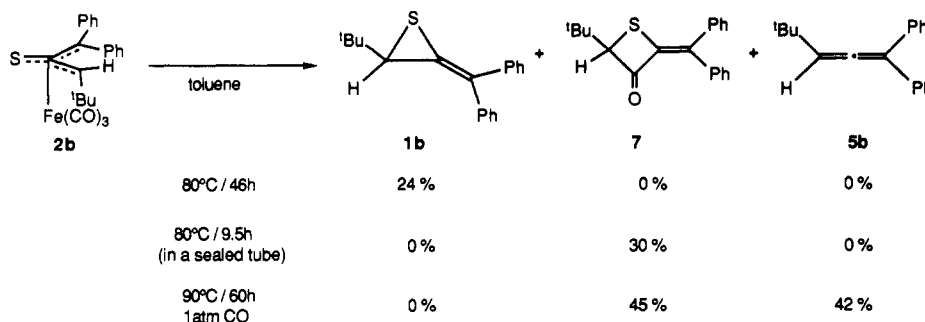
methylidene)thietan-3-one (**7**) in 30% yield. The structure of **7**, an unexpected product, was assigned by ¹H and ¹³C NMR and especially IR (ν 1780 cm⁻¹) spectroscopy. Furthermore an atomsphere of CO raised the yield of **7** accompanied by the formation of **5b** in 45% and 42% yields, respectively. The preparation of **7** was quite unexpected, because direct CO insertion products into the thioallyl ligand are assumed to be thietan-2-one (**12a** and
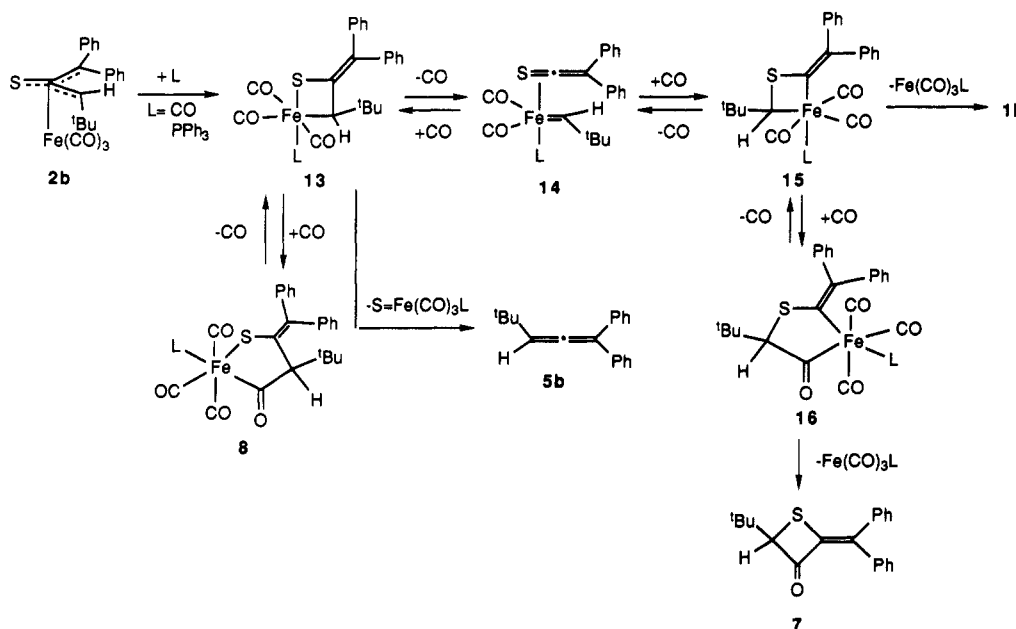

12b) or oxocyclobutane-3-thione (**12c**). Alper et al. re-

Scheme VIII

	1b	7	5b
80°C / 46h	24 %	0 %	0 %
80°C / 9.5h (in a sealed tube)	0 %	30 %	0 %
90°C / 60h 1atm CO	0 %	45 %	42 %

Scheme IX

ported the regiospecific, rhodium(I)-catalyzed insertion of carbon monoxide into an aziridine to give β-lactam[16] and the catalytic carbonylation reactions of thiirane via thietan-2-one[17] by a similar method. These catalytic carbonylation reactions of thiirane and azirizine do not occur at the position β to the heteroatom to give thietan-3-one and azetidin-3-one. Because transition metals insert to the position α to the heteroatom in thiirane and aziridine, 1b and Fe$_2$(CO)$_9$ were heated at 90 °C in toluene in the presence of carbon monoxide for the investigation of direct carbonylation of 1b to give 7. After 1b was consumed completely, 2b and 5b were recovered but 7 was not detected. Since 1b was not carbonylated to 7 under the same reaction conditions as run 3 in Scheme VIII, the metathesis-like mechanism outlined in Scheme IX should be considered. Migration of iron would give a metallathietane 13, which can rearrange to a thioketene–carbene complex 14. Next, 1,3-metallathientane 15 was produced, following a metathesis-like reaction.

In the absence of carbon monoxide, 15 gave 1b by reductive elimination. In the presence of carbon monoxide successive CO migration and addition of CO would form the metallathiopentanone 16. Reductive elimination in 16 would generate alkylidenethietanone 7. Allene 5b would be formed by a metathesis-like reaction from 13. Aumann et al. have already reported that TMM–iron tricarbonyl can be synthesized by the carbene–iron complex and allene via metallacyclobutane.[18] That corresponds to the reverse

reaction of 2b → 13 → 14. Meanwhile Huttner[19] reported the carbonylation reaction of a metallathiopentadiene complex, in which mechanisms analogous to 15 → 7 were found. Day and Powell[20] reported the photolysis of TMM–Fe(CO)$_3$ in several solvents. Contrary to our results, the photolysis of TMM–Fe(CO)$_3$ in cyclopentene afforded the three cyclobutane derivatives, which were probably formed by carbonylation of TMM to a primary product believed to be 3-methylenecyclobutanone. In the case of TMM–Fe(CO)$_3$, the cyclobutane derivatives via 2-methylenecyclobutanone were not recovered. Thus a metathesis-like reaction did not occur in thermolysis[18] or photolysis of TMM–Fe(CO)$_3$, but a metathesis-like reaction could be observed in thermolysis of thioallyl–Fe(CO)$_3$. We have also recovered thietan-3-one 7 from photolysis of 2b by our preliminary experiments.[21]

Compound 2b was allowed to react with triphenylphosphine at room temperature to yield adduct 8, metallathiopentanone, in 11% yield along with 5b (11%) and 7 (19%). The yield of 8 increased to 24% by the introduction of carbon monoxide during thermolysis (Scheme X). In the case of trimethylphosphine, thietanone 7 and allene 5b were recovered in 31% and 18% yields, respectively. A structure for 8 was assigned by ^{1}H NMR, ^{13}C NMR, and IR analysis. The IR absorptions for three carbonyls were observed at 1655 (m), 2010 (s), and 2075

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(17) Calet, S.; Alper, H. *Tetrahedron Lett.* **1986**, *27*, 3573.

(18) Aumann, R.; Helchers, H.-D. *J. Organomet. Chem.* **1980**, *355*, 351.
(19) Fassler, Th.; Huttner, G. *J. Organomet. Chem.* **1990**, *381*, 391.
(20) Day, A. C.; Powell, J. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1241.
(21) Photolysis of 2b in benzene gave 5b (18%) and 7 (12%).

Scheme X

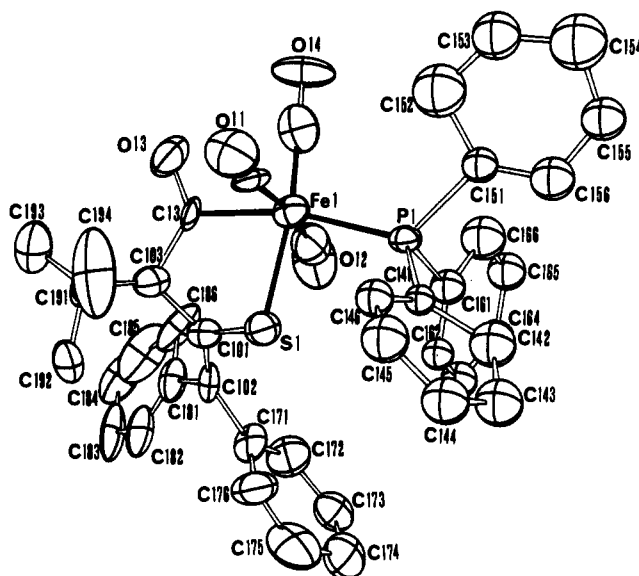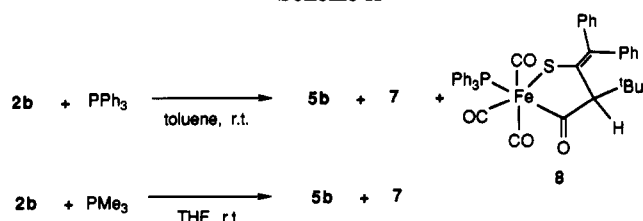**Figure 3.** ORTEP drawing of [FeCOCHC(CH₃)₃C=C-(C₆H₅)₂S](CO)₃(PPh₃) (8).

Figure 3. ORTEP drawing of $[\overline{FeCOCHC(CH_3)_3C=C-(C_6H_5)_2S}](CO)_3(PPh_3)$ (8).

Table VI. Intramolecular Distances (Å) for 8 (Molecule 1)

Fe(1)–S(1)	2.356 (3)	C(151)–C(156)	1.29 (2)
Fe(1)–P(1)	2.296 (4)	C(152)–C(153)	1.39 (3)
Fe(1)–C(11)	1.80 (1)	C(153)–C(154)	1.41 (3)
Fe(1)–C(12)	1.86 (2)	C(154)–C(155)	1.44 (3)
Fe(1)–C(13)	2.11 (1)	C(155)–C(156)	1.36 (2)
Fe(1)–C(14)	1.69 (2)	C(161)–C(162)	1.33 (2)
S(1)–C(101)	1.72 (1)	C(161)–C(166)	1.51 (2)
P(1)–C(141)	1.85 (1)	C(162)–C(163)	1.40 (2)
P(1)–C(151)	1.93 (1)	C(163)–C(164)	1.43 (2)
P(1)–C(161)	1.86 (1)	C(164)–C(165)	1.45 (2)
O(11)–C(11)	1.18 (2)	C(165)–C(166)	1.41 (2)
O(12)–C(12)	1.11 (2)	C(171)–C(172)	1.48 (2)
O(13)–C(13)	1.27 (2)	C(171)–C(176)	1.43 (2)
O(14)–C(14)	1.22 (2)	C(172)–C(173)	1.47 (3)
C(13)–C(103)	1.58 (2)	C(173)–C(174)	1.47 (3)
C(101)–C(102)	1.39 (2)	C(174)–C(175)	1.71 (2)
C(101)–C(103)	1.50 (2)	C(175)–C(176)	1.32 (2)
C(102)–C(171)	1.49 (2)	C(181)–C(182)	1.36 (2)
C(102)–C(181)	1.56 (2)	C(181)–C(186)	1.43 (2)
C(103)–C(191)	1.61 (2)	C(182)–C(183)	1.38 (2)
C(141)–C(142)	1.47 (2)	C(183)–C(184)	1.56 (3)
C(141)–C(146)	1.35 (1)	C(184)–C(185)	0.92 (3)
C(142)–C(143)	1.52 (2)	C(185)–C(186)	1.52 (3)
C(143)–C(144)	1.44 (2)	C(191)–C(192)	1.50 (2)
C(144)–C(145)	1.38 (2)	C(191)–C(193)	1.56 (3)
C(145)–C(146)	1.32 (2)	C(191)–C(194)	1.41 (3)
C(151)–C(152)	1.55 (3)		

(m) cm⁻¹. ¹³C NMR spectra showed three terminal carbonyl peaks (203.5, 204.0, and 206.0 ppm) and one characteristic carbonyl resonance at 252.1 ppm, which is similar to chemical shifts of bridging ligands [Fe(μ-CO)(CO)Cp]₂²² (273.2 ppm) and Fe₂(CNEt)₉²³ (255.7 ppm). The un-

(m) cm^{-1}. ^{13}C NMR spectra showed three terminal carbonyl peaks (203.5, 204.0, and 206.0 ppm) and one characteristic carbonyl resonance at 252.1 ppm, which is similar to chemical shifts of bridging ligands [Fe(μ-CO)(CO)Cp]$_2$[22] (273.2 ppm) and Fe$_2$(CNEt)$_9$[23] (255.7 ppm). The un-

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Table VII. Intramolecular Distances (Å) for 8 (Molecule 2)

Fe(2)–S(2)	2.287 (4)	C(251)–C(256)	1.53 (2)
Fe(2)–P(2)	2.387 (5)	C(252)–C(253)	1.36 (2)
Fe(2)–C(21)	1.82 (1)	C(253)–C(254)	1.34 (2)
Fe(2)–C(22)	1.80 (2)	C(254)–C(255)	1.39 (2)
Fe(2)–C(23)	1.93 (2)	C(255)–C(256)	1.52 (3)
Fe(2)–C(24)	1.88 (1)	C(261)–C(262)	1.29 (2)
S(2)–C(201)	1.83 (1)	C(261)–C(266)	1.51 (2)
P(2)–C(241)	1.81 (1)	C(262)–C(263)	1.48 (2)
P(2)–C(251)	1.81 (2)	C(263)–C(264)	1.31 (2)
P(2)–C(261)	1.74 (1)	C(264)–C(265)	1.40 (3)
O(21)–C(21)	1.11 (2)	C(265)–C(266)	1.53 (3)
O(22)–C(22)	1.13 (2)	C(271)–C(272)	1.33 (2)
O(23)–C(23)	1.18 (2)	C(271)–C(276)	1.40 (2)
O(24)–C(24)	1.07 (2)	C(272)–C(273)	1.39 (2)
C(23)–C(203)	1.55 (2)	C(273)–C(274)	1.27 (2)
C(201)–C(202)	1.32 (2)	C(274)–C(275)	1.14 (2)
C(201)–C(203)	1.56 (2)	C(275)–C(276)	1.50 (2)
C(202)–C(271)	1.53 (2)	C(281)–C(282)	1.40 (2)
C(202)–C(281)	1.41 (2)	C(281)–C(286)	1.47 (2)
C(203)–C(291)	1.59 (1)	C(282)–C(283)	1.50 (3)
C(241)–C(242)	1.47 (2)	C(283)–C(284)	1.85 (2)
C(241)–C(246)	1.33 (1)	C(284)–C(285)	1.31 (3)
C(242)–C(243)	1.45 (3)	C(285)–C(286)	1.49 (3)
C(243)–C(244)	1.37 (2)	C(291)–C(292)	1.53 (3)
C(244)–C(245)	1.30 (2)	C(291)–C(293)	1.63 (2)
C(245)–C(246)	1.48 (2)	C(291)–C(294)	1.57 (3)
C(251)–C(252)	1.29 (2)		

Table VIII. Intramolecular Bond Angles (deg) for 8 (Molecule 1)

S(1)–Fe(1)–P(1)	84.9 (1)	C(143)–C(144)–C(145)	117 (1)
S(1)–Fe(1)–C(11)	89.9 (3)	C(144)–C(145)–C(146)	119 (1)
S(1)–Fe(1)–C(12)	86.1 (5)	C(141)–C(146)–C(145)	128 (1)
S(1)–Fe(1)–C(13)	81.8 (3)	P(1)–C(151)–C(152)	109 (1)
S(1)–Fe(1)–C(14)	171.9 (6)	P(1)–C(151)–C(156)	123 (1)
P(1)–Fe(1)–C(11)	100.6 (5)	C(152)–C(151)–C(156)	128 (1)
P(1)–Fe(1)–C(12)	90.0 (6)	C(151)–C(152)–C(153)	107 (2)
P(1)–Fe(1)–C(13)	165.7 (4)	C(152)–C(153)–C(154)	128 (2)
P(1)–Fe(1)–C(14)	103.2 (7)	C(153)–C(154)–C(155)	115 (2)
C(11)–Fe(1)–C(12)	168.4 (6)	C(154)–C(155)–C(156)	122 (1)
C(11)–Fe(1)–C(13)	84.8 (5)	C(151)–C(156)–C(155)	118 (2)
C(11)–Fe(1)–C(14)	88.1 (6)	P(1)–C(161)–C(162)	121.2 (9)
C(12)–Fe(1)–C(13)	83.8 (7)	P(1)–C(161)–C(166)	111 (1)
C(12)–Fe(1)–C(14)	94.3 (7)	C(162)–C(161)–C(166)	128 (1)
C(13)–Fe(1)–C(14)	90.2 (6)	C(161)–C(162)–C(163)	118 (1)
Fe(1)–S(1)–C(101)	94.9 (4)	C(162)–C(163)–C(164)	120 (1)
Fe(1)–P(1)–C(141)	117.4 (3)	C(163)–C(164)–C(165)	120 (1)
Fe(1)–P(1)–C(151)	122.2 (5)	C(164)–C(165)–C(166)	123 (1)
Fe(1)–P(1)–C(161)	110.6 (5)	C(161)–C(166)–C(165)	111 (1)
C(141)–P(1)–C(151)	97.8 (5)	C(102)–C(171)–C(172)	112 (1)
C(141)–P(1)–C(161)	104.1 (6)	C(102)–C(171)–C(176)	127 (1)
C(151)–P(1)–C(161)	102.3 (5)	C(172)–C(171)–C(176)	121 (2)
Fe(1)–C(11)–O(11)	170 (1)	C(171)–C(172)–C(173)	121 (2)
Fe(1)–C(12)–O(12)	171 (2)	C(172)–C(173)–C(174)	118 (1)
Fe(1)–C(13)–O(13)	113.1 (8)	C(173)–C(174)–C(175)	120 (2)
Fe(1)–C(13)–C(103)	120.9 (9)	C(174)–C(175)–C(176)	113 (2)
O(13)–C(13)–C(103)	126 (1)	C(171)–C(176)–O(175)	128 (2)
Fe(1)–C(14)–O(14)	176 (2)	C(102)–C(181)–O(182)	116 (1)
S(1)–C(101)–C(102)	122 (1)	C(102)–C(181)–O(186)	120 (1)
S(1)–C(101)–C(103)	120 (1)	C(182)–C(181)–C(186)	124 (1)
C(102)–C(101)–C(103)	119 (1)	C(182)–C(182)–C(183)	120 (2)
C(101)–C(102)–C(171)	121 (1)	C(182)–C(183)–C(184)	118 (2)
C(101)–C(102)–C(181)	124 (1)	C(183)–C(184)–C(185)	101 (2)
C(171)–C(102)–C(181)	115 (1)	C(184)–C(185)–C(186)	161 (2)
C(13)–C(103)–C(101)	103 (1)	C(181)–C(186)–C(185)	97 (1)
C(13)–C(103)–C(191)	111 (1)	C(103)–C(191)–C(192)	104 (1)
C(101)–C(103)–C(191)	116 (1)	C(103)–C(191)–C(193)	103 (1)
P(1)–C(141)–C(142)	115.2 (8)	C(103)–C(191)–C(194)	116 (1)
P(1)–C(141)–C(146)	123 (1)	C(192)–C(191)–C(193)	111 (1)
C(142)–C(141)–C(146)	121 (1)	C(192)–C(191)–C(194)	100 (2)
C(141)–C(142)–C(143)	109 (1)	C(193)–C(191)–C(194)	122 (2)
C(142)–C(143)–C(144)	124 (2)		

equivocal molecular structure of 8 was determined by single-crystal X-ray diffraction analyses. Compound 8 crystallized with two independent molecules in a crystal unit. An ORTEP drawing of 8 (molecule 1) is shown in Figure 3. Interatomic distances for molecule 1 with the corresponding values for molecule 2 are listed in Tables

Table IX. Intramolecular Bond Angles (deg) for 8 (Molecule 2)

S(2)–Fe(2)–P(2)	86.4 (1)	C(243)–C(244)–C(245)	123 (2)
S(2)–Fe(2)–C(21)	90.6 (5)	C(244)–C(245)–C(246)	119 (1)
S(2)–Fe(2)–C(22)	90.0 (5)	C(241)–C(246)–C(245)	123 (1)
S(2)–Fe(2)–C(23)	86.7 (4)	P(2)–C(251)–C(252)	128 (1)
S(2)–Fe(2)–C(24)	177.5 (4)	P(2)–C(251)–C(256)	112 (1)
P(2)–Fe(2)–C(21)	95.3 (5)	C(252)–C(251)–C(256)	119 (1)
P(2)–Fe(2)–C(22)	93.3 (4)	C(251)–C(252)–C(253)	130 (1)
P(2)–Fe(2)–C(23)	172.6 (5)	C(252)–C(253)–C(254)	115 (1)
P(2)–Fe(2)–C(24)	94.3 (4)	C(253)–C(254)–C(255)	122 (2)
C(21)–Fe(2)–C(22)	171.4 (7)	C(254)–C(255)–C(256)	124 (1)
C(21)–Fe(2)–C(23)	87.4 (7)	C(251)–C(256)–C(255)	108 (1)
C(21)–Fe(2)–C(24)	91.8 (6)	P(2)–C(261)–C(262)	131 (1)
C(22)–Fe(2)–C(23)	84.1 (6)	P(2)–C(261)–C(266)	116 (1)
C(22)–Fe(2)–C(24)	87.5 (6)	C(262)–C(261)–C(266)	113 (1)
C(23)–Fe(2)–C(24)	92.6 (6)	C(261)–C(262)–C(263)	127 (1)
Fe(2)–S(2)–C(201)	96.3 (4)	C(262)–C(263)–C(264)	117 (2)
Fe(2)–P(2)–C(241)	107.0 (5)	C(263)–C(264)–C(265)	127 (2)
Fe(2)–P(2)–C(251)	118.7 (5)	C(264)–C(265)–C(266)	112 (2)
Fe(2)–P(2)–C(261)	117.8 (6)	C(261)–C(266)–C(265)	122 (2)
C(241)–P(2)–C(251)	103.8 (7)	C(202)–C(271)–C(272)	124 (1)
C(241)–P(2)–C(261)	105.1 (6)	C(202)–C(271)–C(276)	114 (1)
C(251)–P(2)–C(261)	102.8 (7)	C(272)–C(271)–C(276)	122 (1)
Fe(2)–C(21)–O(21)	171 (2)	C(271)–C(272)–C(273)	115 (1)
Fe(2)–C(22)–O(22)	179 (1)	C(272)–C(273)–C(274)	126 (1)
Fe(2)–C(23)–O(23)	123 (1)	C(273)–C(274)–C(275)	119 (2)
Fe(2)–C(23)–C(203)	118 (1)	C(274)–C(275)–C(276)	126 (1)
O(23)–C(23)–C(203)	108 (2)	C(271)–C(276)–O(275)	112 (1)
Fe(2)–C(24)–O(24)	171 (1)	C(202)–C(281)–O(282)	120 (1)
S(2)–C(201)–C(202)	124 (1)	C(202)–C(281)–O(286)	119 (1)
S(2)–C(201)–C(202)	106.9 (9)	C(282)–C(281)–C(286)	119 (1)
C(202)–C(201)–C(203)	129 (1)	C(281)–C(282)–C(283)	135 (1)
C(201)–C(202)–C(271)	122 (1)	C(282)–C(283)–O(284)	96 (1)
C(201)–C(202)–C(281)	125 (1)	C(283)–C(284)–C(285)	133 (2)
C(271)–C(202)–C(281)	112 (1)	C(284)–C(285)–C(286)	115 (2)
C(23)–C(203)–C(201)	112 (1)	C(281)–C(286)–C(285)	122 (2)
C(23)–C(203)–C(291)	116 (1)	C(203)–C(291)–C(292)	110 (1)
C(201)–C(203)–C(291)	112 (1)	C(203)–C(291)–C(293)	110 (1)
P(2)–C(241)–C(242)	116.9 (9)	C(203)–C(291)–C(294)	114 (1)
P(2)–C(241)–C(246)	126 (1)	C(292)–C(291)–C(293)	97 (1)
C(242)–C(241)–C(246)	117 (1)	C(292)–C(291)–C(294)	106 (1)
C(241)–C(242)–C(243)	119 (1)	C(293)–C(291)–C(294)	118 (1)
C(242)–C(243)–C(244)	118 (2)		

VI and VII. Interatomic angles for molecule 1 and for molecule 2 are listed in Tables VIII and IX. Both independent molecules of **8** are essentially identical structurally. The compound consists of a Fe(CO)₃PPh₃ fragment that may be viewed as a derivative of metallathiopentanone. This five-membered ring, metallathiopentanone unit, has a half-chair form. The bond distances and angles in the metallaselenopentenone[24] core resemble those in the metallathiopentanone core. Notable however is that the conjugated S(1)–C(101) linkage has an unusually short distance of 1.72 (1) Å [S(2)–C(201) = 1.83 (1) Å] relative to common C–S single bonds (1.80–1.86 Å).[25]

A concievable mechanism in the reaction of **2b** with phosphines was also illustrated in Scheme IX. Thioallyl complex **2b** is stable till 80 °C in benzene, but the addition of phosphine to **2b** at room temperature gave thietanone **7**, a corresponding allene **5b**, and **8**, two of which were also obtained in thermolysis of **2b**. This reaction was initiated by a nucleophilic attack of phosphine on an iron center to produce metallathietane **13**. Successive CO migration and addition of CO would form **8**. In other words, the proposed metallathietane **13** was directly evidenced by isolation of **8**. The thermolysis of **8** at 65 °C also gave **7** and allene **5b** in 27% and 18% yields (eq 1). This process involves the interconversion between the 2-(diphenyl-

$$8 \xrightarrow[\text{65°C / 3.5h}]{\text{benzene}} 5b + 7 \qquad (1)$$
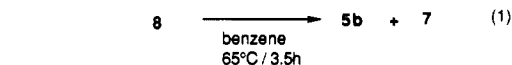
methylidene)thietan-4-one moiety in **8** and the 2-(diphenylmethylidene)thietan-3-one framework (**7**). The assumption of metathesis-like reaction is also extended in this process and strongly verified, as shown in Scheme IX.

Experimental Section

General Data. Reagent-grade solvents were distilled from sodium benzophenone ketyl prior to use. The compounds tetramethylallene episulfide[4a] (**1a**) and *tert*-butyldiphenylallene episulfide[26] (**1b**) were prepared by the published procedures. All reactions were performed under an argon atmosphere unless specified otherwise. Infrared spectra were recorded on a Hitachi 260-50 infrared spectrometer. NMR spectra were run on either a Bruker AM500 or a JEOL EX-90 spectrometer operating at 500 and 90 MHz, respectively. Elemental analyses were carried out by the Chemical Analytical Center of University of Tsukuba. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer.

Reaction of Tetramethylallene Episulfide (1a, TMAE) with Fe₂(CO)₉. A mixture of TMAE (128 mg, 1 mmol) (**1a**) and Fe₂(CO)₉ (436 mg, 1.2 mmol) in freshly distilled benzene (12 mL) were stirred for 10 min at 60 °C. The dark red solution was filtered through Celite, and the solvent was removed in vacuo. The reddish oil was separated by HPLC to yield (η⁴-1,1,3,3-tetramethyl-2-thioallyl)iron tricarbonyl (**2a**) (43 mg, 16%), (μ-2,4-dimethyl-2-pentene-3,4-dithiolato-κ²S:κ²S′)diiron hexacarbonyl (**3**) (50 mg, 11.5%) and (1-isopropenyl-2-methyl-1-propenyl) disulfide (**4**) (17.5 mg, 13.8%). Compounds **2a** and **3** were recrystallized from hexane–CH₂Cl₂.

For **2a**: yellow crystals; mp 59–60 °C; ¹H NMR (500 MHz, C₆D₆) δ 1.49 (6 H, s), 1.89 (6 H, s) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 27.5 (q), 30.4 (q), 105.1 (s), 117.9 (s), 210.1 (br s) ppm; IR (hexane) ν 2080 (s), 2000 (s), 1960 (w) cm⁻¹; MS m/z 268 (M⁺, 9%), 240 (63), 212 (42.5), 184 (70), 81 (100). Exact mass calcd for C₁₀H₁₂FeO₃S: m/z 267.9855. Found: m/z 267.9828.

For **3**: orange crystals; mp 106.5–107.0 °C; ¹H NMR (500 MHz, C₆D₆) δ 1.59 (6 H, s), 1.73 (3 H, s), 2.11 (3 H, s) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 21.98 (q), 26.97 (q), 30.50 (q), 56.16 (s), 136.23 (s), 137.36 (s), 208.81 (br s) ppm; IR (hexane) ν 2060 (s), 2030 (s), 2000 (sh), 1995 (s), 1985 (sh), 1950 (w) cm⁻¹; MS m/z 440 (M⁺, 21%), 412 (26.5), 384 (41), 356 (26.5), 328 (14.3), 300 (69.6), 272 (100). Anal. Calcd for C₁₃H₁₂Fe₂O₆S₂: C, 35.47; H, 2.74. Found: C, 35.65; H, 2.71.

For **4**: colorless oil; ¹H NMR (C₆D₆) δ 1.68 (3 H, s), 1.91 (6 H, br s), 4.82 (1 H, br s), 5.07 (1 H, br s) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 22.19 (q), 22.49 (q), 23.03 (q), 116.92 (t), 134.2 (s), 135.96 (s), 142.7 (s) ppm; MS m/z 254 (M⁺, 52%), 127 (100).

Reaction of *tert*-Butyldiphenylallene Episulfide (1b, BDPAE) with Fe₂(CO)₉. (a) BDPAE (**1b**) (248 mg, 0.88 mmol) was allowed to react with Fe₂(CO)₉ (386 mg, 1.06 mmol) in 30 mL of benzene at 60 °C for 1.5 h. After filtration through Celite and evaporation in vacuo, the residue was purified by silica-gel column chromatography using hexane–CH₂Cl₂ as eluant to give (η⁴-1-*tert*-butyl-3,3-diphenyl-2-thioallyl)iron tricarbonyl (**2b**) (110 mg, 29.5%), 1-*tert*-butyl-3,3-diphenylallene (**5b**) (64 mg, 25%), and unreacted **1b** (28.8 mg, 11%).

For **2b**: orange crystals; mp 111.5–112.5 °C; ¹H NMR (500 MHz, C₆D₆) δ 1.16 (9 H, s), 4.33 (1 H, s), 6.73–7.53 (10 H, m) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 32.26 (q), 36.22 (s), 106.34 (d), 118.56 (d), 122.60 (s), 126.88 (d), 127.15 (s), 127.24 (d), 128.32 (d), 130.57 (d), 131.97 (d), 142.68 (s), 144.30 (s), 209.06 (s), 209.48 (s), 210.12 (s) ppm; IR (hexane) ν 2080 (s), 2020 (s) cm⁻¹; MS m/z 420 (M⁺, 4%), 364 (56), 336 (100), 301 (83), 244 (27), 192 (41.6). Anal. Calcd for C₂₂H₂₀FeO₃S: C, 62.86; H, 4.79. Found: C, 62.90; H, 4.74.

For **5b**: colorless oil; ¹H NMR (CDCl₃) δ 1.15 (9 H, s), 5.66 (1 H, s), 7.13–7.46 (10 H, m) ppm; ¹³C NMR (CDCl₃) δ 30.3 (q), 33.3 (s), 106.1 (d), 111.0 (s), 126.7 (d), 128.2 (d), 128.3 (d), 137.4 (s), 202.6 (s) ppm; IR (CCl₄) ν 1950 cm⁻¹. Exact mass calcd for C₁₉H₂₀: m/z 248.1564. Found: m/z 248.1553.

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(b) In the case of using 0.57 equiv of $Fe_2(CO)_9$ (0.16 mmol) for **1b** (0.28 mmol), **2b** (14%), **5b** (12%), and unreacted **1b** (51%) were recovered.

Reaction of 1,1-Di-*tert*-butyl-3,3-diphenylallene 2-Episulfide (DBDPAE) (1c) with Diiron Nonacarbonyl. DBDPAE (**1c**) (59 mg, 0.17 mmol) was allowed to react with $Fe_2(CO)_9$ (65 mg, 0.17 mmol) in 5 mL of benzene at 60 °C for 1 h. After a common workup, the residue was separated by preparative thin-layer chromatography (TLC) (eluant, hexane) to yield **1d** (9 mg, 15%), **5c** (24 mg, 46%), and unreacted **1c** (9 mg, 15%).

Thermolysis of 2b. (a) A toluene (5 mL) solution of **2b** (30 mg) was heated at 80 °C for 46 h. Separation of the reaction mixture by preparative TLC (eluant, hexane) gave **1b** in 24% yield.

(b) A benzene-d_6 (300 μL) solution of **2b** (30 mg) was heated at 80 °C for 9.5 h in a sealed tube. The reaction was monitored by ^{1}H NMR spectroscopy. After evaporation under reduced pressure, the residue was purified by preparative TLC (eluant, hexane) yielding **7** in 30% yield.

For **7**: colorless crystals; mp 107.5–108.0 °C; ^{1}H NMR (C_6D_6) δ 0.86 (9 H, s), 4.79 (1 H, s), 7.21–7.32 (10 H, m) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 27.7 (q), 36.1 (s), 84.5 (d), 124.6 (s), 127.76 (d), 127.8 (d), 128.4 (d), 128.47 (d), 128.97 (d), 130.06 (d), 140.64 (s), 141.67 (s), 192.46 (s) ppm; IR (CCl_4) ν 1780 cm^{-1}. Anal. Calcd for $C_{20}H_{20}OS$: C, 77.92; H, 6.49. Found: C, 78.00; H, 6.54.

(c) A solution of **2b** (30 mg) in 10 mL of toluene was bubbling with carbon monoxide at 90 °C for 60 h. After removal of the solvent in vacuo, the resulting residue was chromatographed by preparative TLC. Elution with hexane yielded **5b** (7.4 mg, 42%), **7** (10 mg, 45%), and unreacted **2b** (4.9 mg, 16%).

Reaction of 2b with Triphenylphosphine. A compound **2b** (95 mg, 0.22 mmol) was allowed to react with PPh_3 (69 mg, 0.26 mmol) in 3 mL of toluene at room temperature for 20 h. After evaporation of the solvent under vacuum, the residue was separated by preparative HPLC and gave **5b** (6.2 mg, 11%), **7** (13 mg, 19%), and [$FeCOCH(CH_3)_3C{=}C(C_6H_5)_2S$]$(CO)_3PPh_3$ (**8**) (18.3 mg, 11%). **8** was recrystallized by hexane.

For **8**: yellow crystals; mp 118–123 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.30 (9 H, s), 4.26 (1 H, s), 6.92–7.9 (25 H, br, s); ^{13}C NMR (125 MHz, C_6D_6) δ 203.5 (s), 204.0 (s), 206.0 (s), 252.1 (s) ppm; IR (hexane) ν 1655 (m), 2010 (s), 2075 (m) cm^{-1}.

Reaction of 2b with Trimethylphosphine. 2b (70 mg, 0.16 mmol) was allowed to react with PMe_3 (8 mL of 0.08 mol/L solution in THF, 0.64 mmol) in 10 mL of THF at room temperature for 3 days. The resulting reaction mixture was concentrated in vacuo and separated by preparative HPLC to give **5b** (18%) and **7** (31%).

Reaction of 2b with Triphenylphosphine in the Presence of Carbon Monoxide. A toluene (10 mL) solution of **2b** (65 mg, 0.15 mmol) was allowed to react with PPh_3 (48 mg, 0.18 mmol) in the presence of 1 atm of carbon monoxide. After removal of the solvent in vacuo, the residue was separated by preparative HPLC to give **7** (11%), **5b** (13%), **8** (24%), and unreacted **2b** (15%).

Thermolysis of 8. A benzene-d_6 (300 μL) solution of **8** (18 mg, 0.025 mmol) was heated at 65 °C for 3.5 h. The reaction was monitored by ^{1}H NMR spectroscopy. The resulting reaction mixture was concentrated and separated by preparative TLC (eluant, CH_2Cl_2–hexane = 1/4) to give **5b** (18%) and **7** (27%).

Crystallographic Analysis. Orange crystals of dimensions 0.2 × 0.2 × 0.4 mm for **2b**, 0.3 × 0.2 × 0.3 mm for **3**, and 0.2 × 0.2 × 0.5 mm for **8**, obtained from slow evaporation of a hexane solution at 25 °C, were used for X-ray analyses. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled Kappa axis diffractometer by using graphite-

monochromatized Mo Kα radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table I. All data processing was performed on a Micro VAX 3100 computer by using the SDP structure-solving program obtained from Enraf-Nonius Corp., Delft, Netherlands. The ω–2θ scan technique was adopted by varying the ω scan width as a function of θ (ω scan width = 0.7 + 0.350 tan θ). All intensities were corrected for Lorentz and polarization factors as well as decay. An empirical absorption correction based on a series of ψ-scans was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[27a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[27b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, $w = 1$.

Compound **2b** crystallized in the monoclinic crystal system. From the systematic absences of $h0l$, $l = 2n$, $0k0$, $k = 2n$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$. The coordination of metal atoms was obtained by direct methods (MULTAN). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions were refined by least squares; their isotropic thermal parameters were held fixed at 4.0 Å^2.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h0l$, $h + l = 2n$, $0k0$, $k = 2n$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were located, and their positions were refined by least squares; their isotropic thermal parameters were held fixed at 4.0 Å^2.

Compound **8** crystallized in the triclinic crystal system. There were no systematic absences; the space group was determined to be $P1$. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The molecular structures with atomic labeling schemes, and the bond lengths and angles are given in Figure 1 and Tables II and III for **2b**, Figure 2 and Tables IV and V for **3**, and Figure 3 and Tables VI–IX for **8**.

Supplementary Material Available: Textual details of experimental procedures, an ORTEP figure, and tables of experimental data, positional and thermal parameters, B and U values, root-mean-square amplitudes, bond distances, bond angles, and torsion angles for **8** (28 pages). Ordering information is given on any current masthead page.

(27) (a) *International Tables for X-Ray Crystallography*; The Kynoch Press; Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *International Tables for X-Ray Crystallography*; The Kynoch Press; Birmingham, England, 1975; Vol. IV, Table 2.3.1, pp 149–150.