Organometallics 1991, *10*, 3363–3380

Reactions of Triethylammonium Salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ Anion with Alkyl-, Aryl-, and Vinylmercuric Halides. Formal C-Alkylation of the Bridging CO Ligand

Dietmar Seyferth,* Colin M. Archer, and David P. Ruschke

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

Martin Cowie and Robert W. Hilts

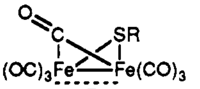
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Received February 15, 1991

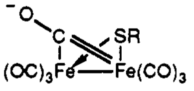
The reaction of alkyl- and arylmercuric halides with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ gives bridging acyl complexes, $(\mu\text{-R'C{=}O})(\mu\text{-RS})Fe_2(CO)_6$. In the case of vinylmercuric halides the bridging acyl complexes are less stable and, in some cases ($CH_2{=}CHHgBr$, $PhCH{=}CHHgCl$, $ClCH{=}CHHgCl$), they undergo decarbonylation to give the μ-σ,π-vinyl complexes, $(\mu\text{-CH{=}CH_2})(\mu\text{-RS})Fe_2(CO)_6$ in the case of $CH_2{=}CHHgBr$. Methyl substituents on the vinyl carbon atoms stabilize the μ-acyl complex. The reaction of $CH_3OCH_2CH_2HgCl$ with $[Et_3NH][\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ gave the bridging carboxylato complex $(\mu\text{-}CH_3CO_2)(\mu\text{-RS})Fe_2(CO)_6$. Such compounds are more readily prepared by the reaction of $Hg(O_2CR')_2$ with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$. The reaction of $Hg(SCH_3)_2$ with $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$ resulted in formation of $(\mu\text{-}CH_3S)(\mu\text{-PhS})Fe_2(CO)_6$. Possible mechanisms of these reactions are discussed. The structure of $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ has been determined by X-ray techniques. This compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.608$ (2) Å, $b = 16.945$ (1) Å, $c = 8.599$ (1) Å, $\alpha = 98.52$ (1)°, $\beta = 99.00$ (1)°, $\gamma = 113.03$ (1)°, $V = 1753.8$ Å^3, and $Z = 4$. Refinement has converged at $R = 0.055$ and $R_w = 0.093$ on the basis of 325 parameters varied and 3310 unique observations. Both independent molecules have essentially identical geometries in which the $Fe_2(CO)_6$ moiety is bridged by a 1,1-dimethylethanethiolate and an acetate ligand.

Introduction

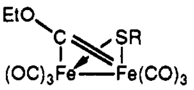
In earlier papers we have described the synthesis of triethylammonium salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions by the action of alkanethiol and arenethiol/triethylamine systems on $Fe_3(CO)_{12}$ in THF at room temperature, as well as some of their reactions.[1] Such anions are ambident reagents, as is readily understood on consideration of the resonance hybrid that serves to describe them (**1a**,**b**). The action of triethyloxonium tetrafluoroborate on such anions (Et_3NH^+ counterion) resulted in O-alkylation of the bridging CO ligand, giving a bridging carbyne complex (**2**).[1a] However, all other conversions of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions (R = Et, *t*-Bu, Ph) that we investigated could be rationalized best in terms of reactions of the anions as iron nucleophiles, i.e., in terms of **1a**. Among the diverse reactions of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions that we have investigated are those with alkyl-, aryl-, and vinylmercuric halides, and these are the subject of the present paper.



1a



1b



2

Table I. $(\mu\text{-R'C{=}O})(\mu\text{-RS})Fe_2(CO)_6$ **Complexes Prepared by the R′HgX +** $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ **Reaction**

R′	R	yield of μ-acyl complex, %
$CH_3OCH_2CH_2$	Et	65
$HOCH_2CH_2$	Et	70
$(CH_3)_3C$	Et	58
C_6H_5	Et	54
p-FC_6H_4	Et	53
p-$Me_2NC_6H_4$	Et	41
n-C_4H_9	*t*-Bu	44
$(CH_3)_3CCH_2$	*t*-Bu	66
$CH_2{=}CH(CH_2)_4$	*t*-Bu	40
c-C_6H_{11}	*t*-Bu	61
$HOCH_2CH_2$	*t*-Bu	64
c-2-$MeOC_6H_{10}$	*t*-Bu	34
C_6H_5	*t*-Bu	86
C_2H_5	Ph	74
c-C_3H_5	Ph	81
n-C_4H_9	Ph	27
sec-C_4H_9	Ph	48
$CH_3OCH_2CH_2$	Ph	44
p-ClC_6H_4	Ph	82

Results and Discussion

Reaction Chemistry. Nucleophilic displacement of halide ions from organomercuric halides is a facile process,[2] and we found that alkyl- and arylmercuric halides react readily with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ complexes

---

[1] (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Womack, G, B.; Archer, C. M.; Fackler, J. P., Jr.; Marler, D. O. *Organometallics* **1989**, *8*, 443. (c) Seyferth, D.; Hoke, J. B. *Organometallics* **1988**, *7*, 714. (d) Wisian-Neilson, P.; Onan, K. D.; Seyferth, D. *Organometallics* **1988**, *7*, 917. (e) Seyferth, D.; Hoke, J. B.; Womack, G. B. *Organometallics* **1990**, *9*, 2662.

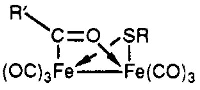
[2] (a) Zeller, K.-P.; Straub, H.; Leditschke, H., In *Houben/Weyl Methoden der Organischen Chemie*; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, FRG, 1974; Vol. XIII/2b. (b) Makarova, L. G.; Nesmeyanov, A. N. *The Organic Compounds of Mercury*; North-Holland: Amsterdam, 1967. (c) See especially A. J. Bloodworth (Part 3) in: McAuliffe, C. A., Ed. *The Chemistry of Mercury*; Macmillan: London, 1977.

0276-7333/91/2310-3363$02.50/0

Table II. ν(C═O) IR Stretching Frequencies and δ_C(R′*C*═O) in the ^{13}C NMR Spectra of (μ-R′C═O)(μ-RS)$Fe_2(CO)_6$ (A) and (μ-R′C═O)(μ-RS)$Fe_2(CO)_5PPh_3$ (B)

		ν(C═O), cm^{-1}		δ_C(R′*C*═O), ppm	
R′	R	A	B	A	B
$CH_3OCH_2CH_2$	Et	1510	1507 1483	300.3 300.9	298.8
$HOCH_2CH_2$	Et	1501			301.8 304.1
$(CH_3)_3C$	Et	1490	1485	307.4	307.0
C_6H_5	Et	1470		289.0 291.6	
p-FC_6H_4	Et	1501	1503	289.6	286.6
p-$Me_2NC_6H_4$	Et	1520	1510	275.0	277.9
n-C_4H_9	*t*-Bu	1522	1508	300.7	299.8
$(CH_3)_3CCH_2$	*t*-Bu	1510	1509	302.7	301.3
CH_2═$CH(CH_2)_4$	*t*-Bu	1510	1510	300.4	299.7 301.1
c-C_6H_{11}	*t*-Bu	1502	1495	304.1	304.0
c-2-$MeOC_6H_{10}$	*t*-Bu	1502	1499	305.1	304.1
$HOCH_2CH_2$	*t*-Bu	1505		300.9 301.7	300.9 301.7
C_6H_5	*t*-Bu	1470		287.9 288.8	
C_2H_5	Ph	1518		302.2 302.5	
n-C_4H_9	Ph	1510		302.3 302.9	
sec-C_4H_9	Ph	1506	1442	302.3 302.9	301.8 302.4
c-C_3H_5	Ph	1497		297.0	
$CH_3OCH_2CH_2$	Ph	1512 1507	1505 1480	301.9	
p-ClC_6H_4	Ph	1472		290.7	

(R = Et, *t*-Bu, Ph) in THF at room temperature. Brisk gas evolution was observed, and a white to white-gray precipitate and droplets of elemental mercury were formed. The color of the solution changed from red-brown to red. Evaporation of the solvent and filtration chromatography of the residue in most cases served well in the isolation of the products as red oils or red crystalline solids. They were identified by standard spectroscopic techniques as μ-acyl complexes, (μ-R′C═O)(μ-RS)$Fe_2(CO)_6$ (**3**). Such μ-acyl



3

complexes are readily available by reactions of the [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ anions with acid chlorides, RC(O)Cl.[1a] IR and ^{13}C NMR spectroscopy were the most useful techniques for their identification. In the IR spectra the C═O stretching vibration of the μ-acyl ligand was observed as a strong band between 1465 and 1525 cm^{-1}. The chemical shift of the μ-acyl carbon atom in the ^{13}C NMR spectra of the products was observed far downfield, in the region between 280 and 310 ppm. The μ-acyl complexes prepared in this manner are listed in Table I. As can be seen, only a few were obtained in yields greater than 80%, and yields of 40–65% were more usual. In those cases, a byproduct usually was obtained as well, (μ-RS)$_2Fe_2(CO)_6$. Thus, most such reactions can be described by eq 1.

$$[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6] + R'HgX \rightarrow (\mu\text{-}R'C{=}O)(\mu\text{-}RS)Fe_2(CO)_6 + (\mu\text{-}RS)_2Fe_2(CO)_6 + Hg + [Et_3NH]X + CO \quad (1)$$

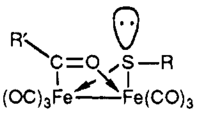
Obviously, a redox process has occurred. It is noteworthy that the action of $HgCl_2$ on [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$] gave (μ-Me_3CS)$_2Fe_2(CO)_6$ as the only product in 100% yield, based on available RS. This also was the case with CH_3O_2CHgCl.

Table III. Reactions of Vinylic Mercuric Halides with [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$] Complexes

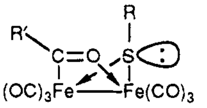
		product yield, %		ν(C═O) of 7, cm^{-1}
R′ in R′HgX	R	7	8	
CH_2═CH	Et	0	64	1462[a]
CH_2═CH	Ph	0	35	
trans-ClCH═CH	Et	0	21	
trans-PhCH═CH	Et	0	47	1448[a]
CH_2═$C(CH_3)$	Et	34	20	1467
trans-CH_3CH═CH	Et	50	25	1460
CH_3CH═$C(CH_3)$	Et	46	13	1481 1451
$(CH_3)_2C$═CH	Et	59	0	1475

[a] Complex 7 prepared by reaction of R′C(O)Cl with [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$].[1e]

In many such reactions the (μ-R′C═O)(μ-RS)$Fe_2(CO)_6$ product was present as two isomers, **3a,b**, the separation of which was not attempted. The μ-acyl complexes that

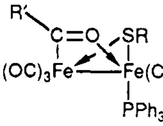


3a, equatorial (e) isomer



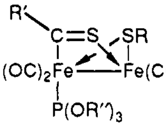
3b, axial (a) isomer

were oils did not appear to be sufficiently stable to permit overseas C, H analysis. Therefore, they were converted to the solid (and more stable) triphenylphosphine monosubstitution products (**4**). The substitution of one CO

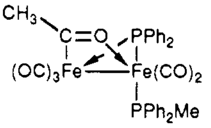


4

ligand by Ph_3P changed the pertinent IR and ^{13}C NMR characteristics only slightly, as shown in Table II. The ^{31}P NMR spectrum of the monosubstituted acyl complexes contained either a singlet in the δ_P 45–55 ppm range or two singlets in this region if two isomers were present. The structure as written is based on the fact that in the ^{13}C NMR spectra of the complexes the μ-acyl carbon signal is a singlet; no coupling to ^{31}P was observed. Such coupling would be expected if the Ph_3P ligand were bonded to the Fe atom to which the R′*C*═O carbon atom is attached. It may be noted that in the case of complexes of type **5**



5



6

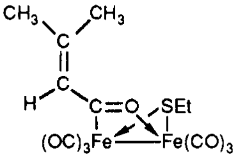
carbon-to-phosphorus coupling of 4.6–6.1 Hz was observed in their ^{13}C NMR spectra.[3] However, no carbon-to-phosphorus coupling involving the Ph_2MeP ligand was observed in the ^{13}C NMR spectrum of **6**.[4]

The reactions of vinylmercuric halides with [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$] salts in THF were more complicated (Table III). In the case of $(CH_3)_2C$═CHHgBr, the μ-acyl complex **7** was obtained in 59% yield as the only

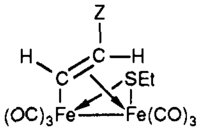
---

[3] (a) Patin, H.; Mignani, G.; Benoit, A.; McGlinchey, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1278. (b) Patin, H.; Mignani, G.; Benoit, A.; LeMarouille, J.-Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.

[4] Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

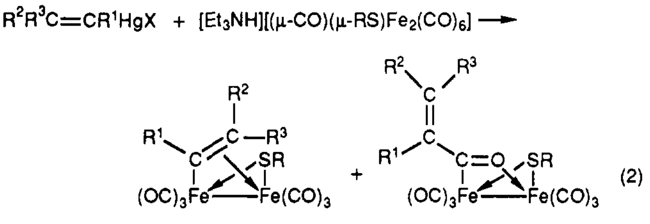


7



8a, Z = H (64%)
b, Z = Cl (21%)
c, Z = Ph (47%)

product in addition to the ubiquitous $(\mu\text{-EtS})_2Fe_2(CO)_6$ (22% yield). In contrast, in the cases of $CH_2{=}CHHgBr$, *trans*-$ClCH{=}CHHgCl$, and *trans*-$PhCH{=}CHHgCl$ the only product (in addition to $(\mu\text{-EtS})_2Fe_2(CO)_6$) was the σ,π-bridging vinyl complex **8**. In the case of methyl-substituted vinylmercuric halides ($CH_2{=}C(CH_3)HgBr$, $CH_3CH{=}C(CH_3)HgBr$, and *trans*-$CH_3CH{=}CHHgBr$) the product was a mixture of the μ-acyl and the σ,π-bridging vinyl complexes (and $(\mu\text{-EtS})_2Fe_2(CO)_6$) (eq 2 and Table III).



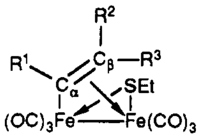
(2)

An examination of the product yields in Table III provides some insight into the nature of complexes **7** and **8** and into the reasons for their formation or absence. In every case where there were electron-donating alkyl substituents on the vinylmercuric bromide electrophile, formation of the vinylacyl complexes **7** was observed, which suggested that the stability of these complexes was related to the electron-donating ability of the substituted vinyl group attached to the bridging acyl carbon atom. This was further supported by the fact that when two rather than one alkyl substituents were present on the C=C bond, the amount of vinylacyl product obtained was significantly increased. The necessity of electron-donating groups on the vinyl ligand of μ-acyl complexes of type **7** explains the results with vinylmercuric bromide, *trans*-(β-chlorovinyl)mercuric chloride, and *trans*-β-styrylmercuric chloride, where only the μ-σ,π-vinyl complexes **8** were formed. With no electron-donating alkyl substituents on the vinylmercuric halide electrophile, no vinyl acyl products were observed. However, this does not necessarily exclude the possibility of vinylacyl formation at some point during the reaction and subsequent decomposition to the corresponding μ-σ,π-vinyl species. We will return to this point later.

A second point to be noticed from the data in Table III is that the μ-σ,π-vinyl complexes **8** were only obtained when the substituent cis to Fe was hydrogen. This may be explained by observing that the substituent cis to Fe in the μ-σ,π-vinyl complexes points directly at the bridging alkanethiolate ligand. When this substituent is anything but hydrogen, as in the isobutenylmercuric bromide case, the nonbonded steric interactions with the thiolate ligand cannot be overcome and, thus, only the vinylacyl product was observed to form.

It also should be noted that the undesirable $(\mu\text{-EtS})_2Fe_2(CO)_6$ side product was consistently obtained in very reaction in 20–23% yield (based on S), except in the case of vinylmercuric bromide, where it does not form at all. This was rather surprising, since our experience with organomercuric halides showed that with these formation of $(\mu\text{-RS})_2Fe_2(CO)_6$ was favored. Apparently, the reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]$ with vinylmercuric bromide to form $(\mu\text{-}\sigma,\pi\text{-}CH{=}CH_2)(\mu\text{-EtS})Fe_2(CO)_6$ occurred so quickly that the competing reaction to form $(\mu\text{-EtS})_2Fe_2(CO)_6$ was avoided.

Table IV. ^1H NMR Spectral Data for the μ-σ,π-Vinyl Complexes **8a–d**



8

complex	R¹	R²	R³	δ(R¹)	δ(R²)	δ(R³)
8a	H	H	H	8.17 (dd) J_{HH} = 9.2 Hz J_{HH} = 13.8 Hz	3.79 (dd) J_{HH} = 13.8 Hz J_{HH} = 2.1 Hz	2.84 (dd) J_{HH} = 9.2 Hz J_{HH} = 2.1 Hz
8b	CH_3	H	H	2.61 (s)	3.48 (d) $^2J_{HH}$ = 2.22 Hz	2.42 (d) $^2J_{HH}$ = 2.34 Hz
8c	H	CH_3	H	7.56 (d) J_{HH} = 13.06 Hz	1.72 (d) J_{HH} = 5.82 Hz	3.57 (m)
8d	CH_3	CH_3	H	2.57 (s)	1.66 (d) $^3J_{HH}$ = 6.09 Hz	3.05 (q) $^3J_{HH}$ = 6.09 Hz

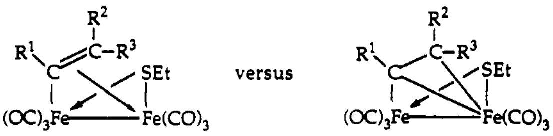


Figure 1. Two different representations of the bonding of the μ-σ,π-vinyl ligand to the $Fe_2(CO)_6$ framework.

All of the μ-σ,π-vinyl complexes were completely characterized spectroscopically. The ^1H NMR spectral data are given in Table IV. The protons attached to the μ-σ,π-vinyl ligand did not resonate in the region normally associated with olefinic protons (approximately 5–6 ppm).[5] Instead, the protons attached to the σ-bonded carbon atom (C_α) gave peaks shifted significantly downfield (at approximately 7–8 ppm), while the protons attached to the non-σ-bonded carbon atom (C_β) appeared significantly upfield (at approximately 2–4 ppm). This divergence results from the π-coordination of the vinyl ligand to the second iron atom, diminishing its double-bond character. As a result, the protons nearest to the electron-rich iron centers (those bonded to C_α) are deshielded while those farther away (bonded to C_β) are shielded. This diminution of double-bond character also was evident in the infrared spectra of these complexes, which showed no absorption in the region characteristic for free olefins (1667–1640 cm^{-1}).[6] The ^1H NMR data given in Table IV agree with other reports for similar μ-vinyl systems found in the literature.[7]

The ^{13}C NMR spectral data for the μ-σ,π-vinyl complexes are given in Table V. As was the case with the ^1H NMR data, the ^{13}C NMR chemical shifts for the carbon

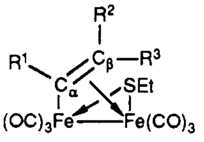
---

(5) *Spectrometric Determination of Organic Compounds*; Silverstein, R. M., Bassler, G. C., Merrill, T. C., Eds.; Wiley: New York, 1981; p 227.

(6) Reference 5, p 108.

(7) (a) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600. (b) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (c) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955. (d) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (e) Ros, J.; Vinas, J. M.; Mathieu, R.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **1988**, 281.

Table V. ^{13}C NMR Spectral Data for the μ-σ,π-Vinyl Complexes 8a–d



8

complex	R^1	R^2	R^3	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(SCH_2CH_3)$
8a	H	H	H	157.2 (d) J_{CH} = 150.7 Hz	73.9 (t) J_{CH} = 158.7 Hz	34.4 (t) J_{CH} = 145.4 Hz
8b	CH_3	H	H	183.12 (t) $^2J_{CH}$ = 5.0 Hz	72.17 (tq) J_{CH} = 158.1 Hz $^3J_{CH}$ = 6.4 Hz	34.28 (tq) J_{CH} = 139.8 Hz $^2J_{CH}$ = 5.1 Hz
8c	H	CH_3	H	151.47 (d) J_{CH} = 146.5 Hz	93.49 (d) J_{CH} = 158.7 Hz	33.71 (t) J_{CH} = 140.5 Hz
8b	CH_3	CH_3	H	176.30 (s)	88.27 (d) J_{CH} = 156.3 Hz	34.01 (t) J_{CH} = 140.6 Hz

atoms of the μ-σ,π-vinyl ligand did not appear in the region normally associated with free alkenes (approximately 100–140 ppm).[8] The signals associated with the σ-bonded carbon atoms (C_α) appeared downfield, in the range of 151–183 ppm, while those associated with the non-σ-bonded carbon atoms (C_β) appeared upfield, in the range 72–93 ppm. These results can be explained by the representations of the μ-σ,π-vinyl complexes in Figure 1. Drawing the π-bonded vinyl ligand as a metallacycle shows that C_α could have some carbene-like character, giving rise to a more downfield shift in the ^{13}C NMR spectrum. This is in contrast to C_β, which now appears to have some sp^3-like character, corresponding to a more upfield shift. The best representation would probably be somewhere between these two extremes. Finally, all of the complexes show a resonance for the methylene carbon atom of the ethanethiolate ligand (SCH_2CH_3) at 34 ppm, corresponding to an equatorial orientation of the thiolate bridge.[9]

There was some discrepancy in the ^{13}C NMR spectra of these μ-σ,π-vinyl complexes in the terminal carbonyl region. Some showed one resonance while others showed two. This can be explained by the fluxionality of the vinyl ligand in these complexes, which also has been observed by other researchers for similar μ-vinyl systems: (μ-$CH_3CH_2C{=}CCH_2CH_3CO_2)Fe_2(CO)_6$,[10a] (L-L′)$Fe_2(CO)_6$ (L-L′ = μ-$C_6H_5C{=}CC_6H_5$-S or μ-$C_6H_4CH_2NR$),[10b] (μ-H)(μ-σ,π-$CH{=}CH_2)Re_2(CO)_7(PPh_3)$,[10c] ($\mu$-H)($\mu$-$\sigma$,$\pi$-$CH{=}CH_2)Os_3(CO)_{10}$,[10d] ($\mu$-$\eta^1$,$\eta^3$-RC=CRC(O))$M_2$(CO)($\mu$-CO)$(C_5H_5)_2$ (M = Fe, Ru),[10e] (μ-σ,π-$CH_3CH_2OC{=}CH_2$)(μ-*t*-BuS)$Fe_2(CO)_6$,[10f] and (μ-η^1,η^2-$CH{=}C{=}C(CH_3)_2$(μ-*t*-BuS)$Fe_2(CO)_6$.[1a] A variable-temperature ^{13}C NMR study was performed on (μ-σ,π-$CH_3C{=}CH_2$)(μ-EtS)$Fe_2(CO)_6$ (Figure 2). At room temperature, one peak was observed in the terminal carbonyl region (δ_C 210.4 ppm), which broadened as the temperature was lowered. At −60 °C, the single peak was now resolved into two resonances. Assuming that the three carbonyl ligands on each iron atom are equilibrated, the two resonances observed at −60 °C can be assigned to the two inequivalent iron tricarbonyl fragments. At room temperature, these two peaks have coalesced, indicating that a fluxional process is occurring that equilibrates the two iron tricarbonyl fragments. A flipping motion of the vinyl ligand across the face of the

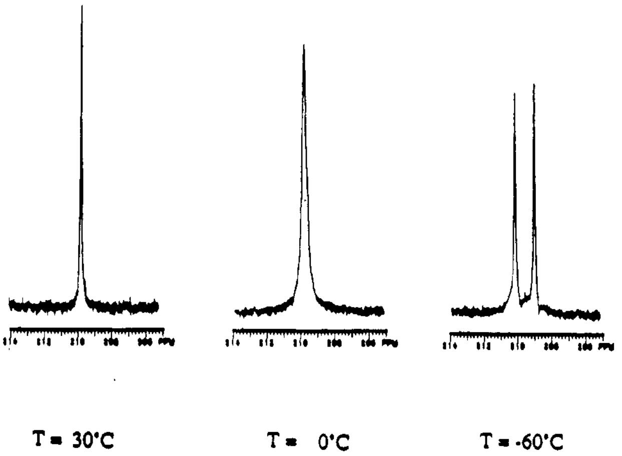
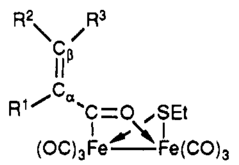


Figure 2. Variable-temperature ^{13}C NMR spectra for (μ-σ,π-$CH_3C{=}CH_2$)(μ-EtS)$Fe_2(CO)_6$ (**8b**).

Table VI. ^1H NMR Spectral Data for the Vinylacyl Complexes 7b–e[a]



7

complex	R^1	R^2	R^3	$\delta(R^1)$	$\delta(R^2)$	$\delta(R^3)$
7b	CH_3	H	H	1.45 (s) maj	5.90 (s) maj	5.86 (d) maj J_{HH} = 1.85 Hz
				1.52 (s) min	5.96 (s) min	5.92 (d) min J_{HH} = 1.79 Hz
7c	H	CH_3	H	5.96 (dd) maj J_{HH} = 15.49 Hz J_{HH} = 1.47 Hz 6.07 (dd) min J_{HH} = 14.95 Hz J_{HH} = 2.30 Hz	1.85 (s) both	6.57 (m) both
7d	CH_3	CH_3	H	1.34 (s) maj	1.78 (s) maj	4.98 (m) maj
				1.39 (s) min	1.87 (s) min	6.66 (m) min
7e	H	CH_3	CH_3	6.30 (s) maj	1.70 (s) maj	1.60 (s) maj
				6.38 (s) min	1.73 (s) min	1.67 (s) min

[a] Legend: min = minor isomer, maj = major isomer, both = both isomers.

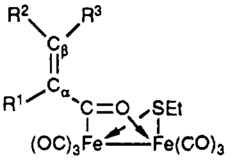
---

[8] Reference 5, p 289.

[9] The assignment of an equatorial orientation of the ethanethiolate ligand was based on ^{13}C NMR spectral data, which showed a resonance for SCH_2CH_3 at approximately δ_C 34 ppm for these compounds. See ref 1b and: Hoke, J. B. Ph.D. Dissertation, Massachusetts Institute of Technology, June 1987; Chapter 3.

[10] (a) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1155. (b) Hickey, J. P.; Huffman, J. C.; Todd, L. J. *Inorg. Chim. Acta* **1978**, *28*, 77. (c) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 3475. (d) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (e) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 409. (f) Hoke, J. B. Ph.D. Dissertation, Massachusetts Institute of Technology, June 1987; pp 108–110.

Table VII. ^{13}C NMR Spectral Data for the Vinylacyl Complexes 7b–e[a]



7

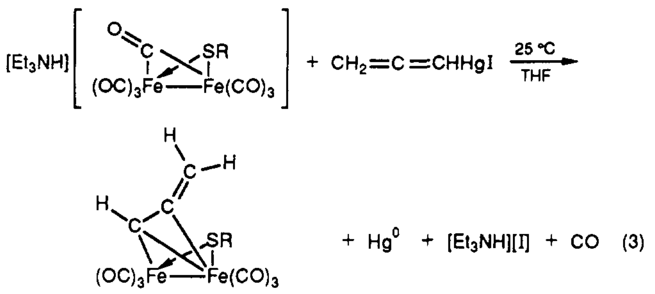
complex	R^1	R^2	R^3	$\delta_C(C_\alpha)$	$\delta_C(C_\beta)$	δ_C(C=O acyl)
7b	CH_3	H	H	151.86 (s) both	131.12 (t) both J_{CH} = 158.5 Hz	290.15 (s) maj 293.03 (s) min
7c	H	CH_3	H	143.91 (d) min J_{CH} = 154.3 Hz 145.03 (d) maj J_{CH} = 154.9 Hz	140.83 (d) maj J_{CH} = 158.8 Hz 141.33 (d) min J_{CH} = 160.4 Hz	284.94 (s) maj 287.74 (s) min
7d	CH_3	CH_3	H	147.04 (s) both	120.90 (d) maj J_{CH} = 153.6 Hz 124.30 (d) maj J_{CH} = 162.5 Hz	285.88 (s) min 299.32 (s) maj
7e	H	CH_3	CH_3	136.4 (d) maj J_{CH} = 158.0 Hz 136.6 (d) min J_{CH} = 158.0 Hz	147.2 (s) both	283.3 (s) maj 286.6 (s) min

[a] Legend: min = minor isomer, maj = major isomer, both = both isomers.

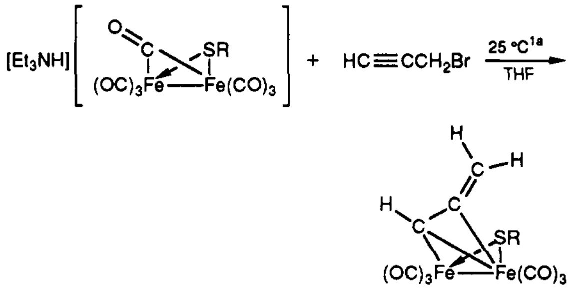
$Fe_2(CO)_6$ core would account for this equilibration. Thus, at −60 °C, the flipping motion has essentially ceased on the NMR time scale, giving rise to two signals, while at room temperature, the flipping motion occurs, giving rise to only one signal. However, there are other fluxional processes that are possible and the one suggested above is by no means proven.

The vinylacyl products 7 also were fully characterized spectroscopically. Their ^1H NMR and ^{13}C NMR spectral data are given in Tables VI and VII, respectively. Unlike the μ-σ,π-vinyl complexes, the vinylacyl complexes showed resonances in the ^1H NMR and ^{13}C NMR spectra for the protons and the carbon atoms of the vinyl ligand in the ranges normally observed for free olefins.[5,8] The ^{13}C NMR spectra also showed the characteristic resonances for the carbon atom of the acyl bridge far downfield (283–299 ppm), in the region normally assigned to μ-acyls, as was observed for alkyl and aryl μ-acyl complexes. Their infrared spectra also verified the presence of the μ-acyl bridge, showing strong absorptions for $\nu_{C=O}$(acyl) in the range normally associated with μ-acyl complexes (1465–1525 cm^{-1}).

Also examined during the course of this investigation were the reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with allenylmercuric iodide and allylmercuric iodide. The reaction of allenylmercuric iodide with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (R = *t*-Bu, Et) proceeded as before, with brisk gas evolution, a color change to brighter red, and formation of a white-gray precipitate. Two products were isolated, the first being the ubiquitous side product $(\mu\text{-}RS)_2Fe_2(CO)_6$, in moderate yield (R = *t*-Bu, 35%; R = Et, 43%; both yields based on S). The second product was an allenyl-bridged complex in which the organic ligand is much like a bridging σ,π-vinyl group with a pendant $=CH_2$ substituent (eq 3). These products, $(\mu\text{-}\eta^1,\eta^2\text{-}CH_2{=}C{=}CH)(\mu\text{-}RS)Fe_2(CO)_6$ (9), were isolated as air-stable red solids in moderately low yields (R = *t*-Bu, 28%; R = Et, 31%) and as only one geometric isomer (the thiolate ligand is equatorial). Their identities were confirmed by comparison of their ^1H NMR spectra with those of authentic samples that had been prepared earlier in these laboratories as shown in eq 4,[1a] a procedure obviously superior to that based on allenylmercuric iodide.



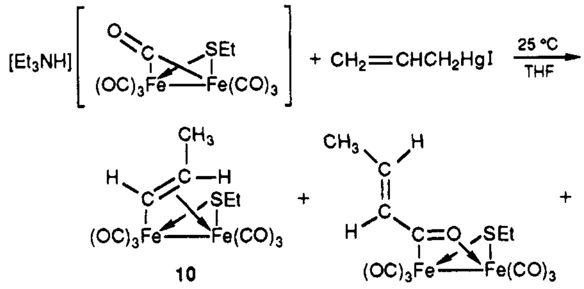
9 (R = *t*-Bu, 28%; R = Et 31%)



(4)

9 (R = *t*-Bu, 91%; R = Et, 92%)

The reaction of allylmercuric iodide and $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ also proceeded with brisk gas evolution, a color change to brighter red, and formation of elemental mercury and a white-gray precipitate (eq 5).



10

11

$$(\mu\text{-}EtS)_2Fe_2(CO)_6 + Hg^0 + [Et_3NH][I] \qquad (5)$$

Three products were isolated. The first was the μ-σ,π-propenyl complex $(\mu\text{-}\sigma,\pi\text{-}CH_3CH{=}CH)(\mu\text{-}EtS)Fe_2(CO)_6$ (10) in 15% yield, the second, the undesirable $(\mu\text{-}EtS)_2Fe_2(CO)_6$ in 61% yield (based on S), and the third, the propenylacyl complex $(\mu\text{-}CH_3CH{=}CHC{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$ (11) in 19% yield. As before, the formation of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ was promoted by the organomercuric halide electrophile. The *trans*-1-propenyl ligand resulted from a net 1,3-hydrogen migration from the α-carbon to the γ-carbon of the allyl group. As already noted, these complexes also are formed in the reaction of *trans*-1-propenylmercuric bromide, $CH_3CH{=}CHHgBr$, and $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$. It is interesting to

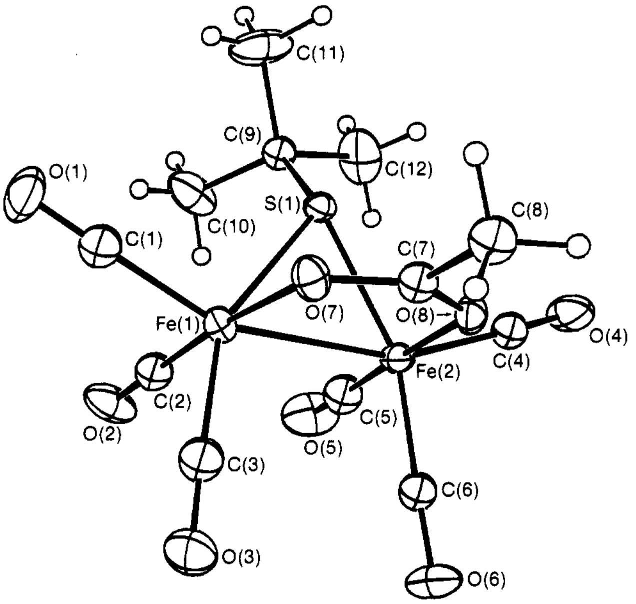
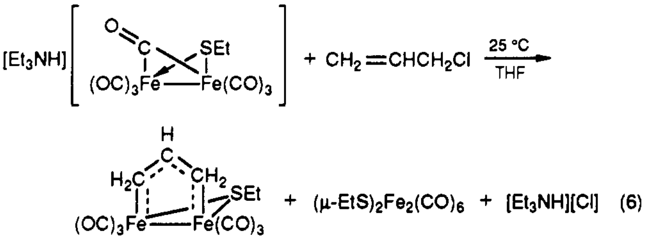


Figure 3. ORTEP plot of one of the independent molecules of (μ-CH$_3$CO$_2$)(μ-*t*-BuS)Fe$_2$(CO)$_6$ showing the atom numbering scheme. All atoms are shown with 20% thermal ellipsoids except hydrogens, which are shown artificially small.

compare the reaction of [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] with allylmercuric iodide with its reaction with allyl chloride. With allyl chloride only two products were formed, the bis(thiolate)-bridged product (μ-EtS)$_2$Fe$_2$(CO)$_6$ in 22% yield (based on S) and the allyl-bridged complex (μ-CH$_2$CHCH$_2$)(μ-EtS)Fe$_2$(CO)$_6$ (**12**) in 80% yield (eq 6).



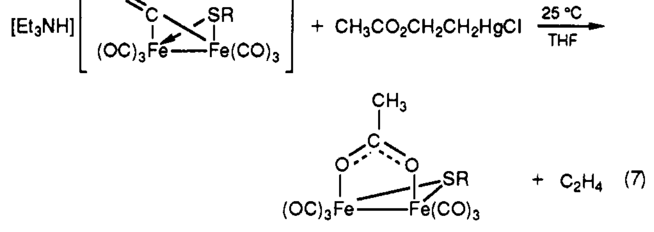
(6)

12

No 1,3-hydrogen migration in the allyl group was observed. The bridging allyl arrangement in **12** was confirmed by an X-ray structural analysis.[1a]

As indicated in Table I, HOCH$_2$CH$_2$HgCl and CH$_3$OCH$_2$CH$_2$HgCl, the hydroxy- and methoxymercuration products of ethylene, reacted with [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] to give the respective μ-acyl complexes. However, CH$_3$CO$_2$CH$_2$CH$_2$HgCl reacted differently. In the usual procedure, (2-acetoxyethyl)mercuric chloride was added as a solid against a positive flow of nitrogen to the [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] (R = *t*-Bu, Et) reagent solution. As usual, brisk gas evolution, a color change to brighter red, balls of elemental mercury, and a white-gray precipitate were observed. Similar to the cases of (2-methoxyethyl)- and (2-hydroxyethyl)mercuric chloride, TLC indicated the formation of two orange-red products. Chromatographic workup gave as the first eluted products the (μ-RS)$_2$Fe$_2$(CO)$_6$ (R = *t*-Bu, Et) complexes, but in much higher yields than had been observed previously. (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$ was isolated in 57% yield, while (μ-EtS)$_2$Fe$_2$(CO)$_6$ was isolated in 72% yield (both yields based on S).

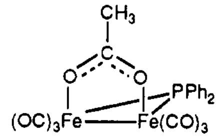
The second products to elute were initially believed to be the expected μ-acyl products (CH$_3$CO$_2$CH$_2$CH$_2$C=O)(μ-RS)Fe$_2$(CO)$_6$. The infrared spectra of these complexes showed stretching vibrations in the region normally associated with μ-acyl complexes (1520–1470 cm^{-1}), but approximately 10 cm^{-1} higher than had been previously observed: 1530 cm^{-1} (R = *t*-Bu) and 1532 cm^{-1} (R = Et). However, in neither spectrum was a peak observed at 1735 cm^{-1}, where $\nu_{C=O}$ stretches for esters are found and which would be expected for the acetoxy group in the postulated μ-acyl structure. In addition, the ^{1}H NMR spectra showed no resonances corresponding to the two methylene groups of the proposed μ-acyl bridge, CH$_3$CO$_2$CH_2CH_2C=O. But most significantly, the diagnostic resonances for the carbon atom of the μ-acyl ligand, found far downfield between 280 and 310 ppm, were absent in the ^{13}C NMR spectra. With use of the above spectroscopic information along with mass spectral data and elemental analyses obtained later, it was determined that the reaction of [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] with (2-acetoxyethyl)mercuric chloride did not give the expected μ-acyl products but, rather, diiron hexacarbonyl complexes containing the usual bridging thiolate ligand as well as a bridging acetate ligand, (μ-CH$_3$CO$_2$)(μ-RS)Fe$_2$(CO)$_6$ (**13**; eq 7).



(7)

13 (R = *t*-Bu, 40%; R = Et, 28%)

The infrared spectra of the two acetate complexes suggested the structure shown in eq 7. In the IR spectrum of (μ-CH$_3$CO$_2$)(μ-EtS)Fe$_2$(CO)$_6$ ν_{CO}(asym) and ν_{CO}(sym) were observed at 1551 and 1441 cm^{-1}, respectively. In the IR spectrum of (μ-CH$_3$CO$_2$)(μ-*t*-BuS)Fe$_2$(CO)$_6$ these bands occurred at 1548 and 1439 cm^{-1}. The differences between ν_{CO}(asym) and ν_{CO}(sym) were 110 and 109 cm^{-1}, respectively, which is in the range associated with bridging carboxylate ligands.[11] Convincing confirmation was provided by the IR spectrum of the known complex **14**, which,



14

as reported by Mott and Carty,[12] showed ν_{CO}(asym) and ν_{CO}(sym) at 1548 and 1431 cm^{-1}, respectively. Unambiguous proof of the structure shown in formula **13** was provided by a single-crystal X-ray diffraction study of (μ-CH$_3$CO$_2$)(μ-*t*-BuS)Fe$_2$(CO)$_6$. The molecule crystallizes in the space group $P\bar{1}$ with two independent molecules per asymmetric unit. An ORTEP plot of one of these molecules is given in Figure 3. Bond distances and angles are given in Tables VIII and IX. The data show that the two independent molecules are essentially identical. The molecule contains an Fe–Fe single bond (average Fe(1)–Fe(2) = 2.590 Å) and a slightly asymmetrical thiolate bridge (average Fe(1)–S(1) = 2.251 Å; average Fe(2)–S(1) = 2.239 Å), which is in an equatorial position.

The acetate ligand bridges both iron centers symmetrically, showing differences in the O(7)–C(7) and C(7)–O(8) bond distances of less than 2σ and differences in the

---

(11) Deacon, G. B.; Phillips, K. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(12) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1979**, *18*, 2926.

Table VIII. Intramolecular Bond Distances (Å) for $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ Involving the Non-Hydrogen Atoms

	molecule 1	molecule 2		molecule 1	molecule 2
Fe(1)-Fe(2)	2.589 (1)	2.590 (2)	O(1)–C(1)	1.108 (9)	1.14 (1)
Fe(1)–S(1)	2.252 (2)	2.250 (2)	O(2)–C(2)	1.147 (9)	1.12 (1)
Fe(1)–O(7)	1.992 (5)	1.991 (5)	O(3)–C(3)	1.146 (9)	1.12 (1)
Fe(1)–C(1)	1.843 (9)	1.81 (1)	O(4)–C(4)	1.117 (9)	1.11 (1)
Fe(1)–C(2)	1.773 (8)	1.79 (1)	O(5)–C(5)	1.13 (1)	1.129 (9)
Fe(1)–C(3)	1.807 (9)	1.81 (1)	O(6)–C(6)	1.157 (8)	1.12 (1)
Fe(2)–S(1)	2.238 (2)	2.240 (2)	O(7)–C(7)	1.243 (9)	1.258 (9)
Fe(2)–O(8)	2.004 (5)	1.998 (5)	O(8)–C(7)	1.253 (8)	1.275 (9)
Fe(2)–C(4)	1.817 (9)	1.85 (1)	C(7)–C(8)	1.52 (1)	1.49 (1)
Fe(2)–C(5)	1.77 (1)	1.757 (9)	C(9)–C(10)	1.48 (1)	1.49 (1)
Fe(2)–C(6)	1.789 (8)	1.80 (1)	C(9)–C(11)	1.53 (1)	1.51 (1)
S(1)–C(9)	1.865 (8)	1.873 (9)	C(9)–C(12)	1.52 (1)	1.54 (1)

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

Table IX. Intramolecular Bond Angles (deg)[a] for $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ Involving the Non-Hydrogen Atoms

	molecule 1	molecule 2
Fe(2)–Fe(1)–S(1)	54.54 (6)	54.94 (6)
Fe(2)–Fe(1)–O(7)	84.7 (2)	85.8 (1)
Fe(2)–Fe(1)–C(1)	158.9 (3)	159.1 (3)
Fe(2)–Fe(1)–C(2)	93.4 (3)	93.1 (3)
Fe(2)–Fe(1)–C(3)	97.7 (3)	98.1 (3)
S(1)–Fe(1)–O(7)	83.4 (1)	83.2 (2)
S(1)–Fe(1)–C(1)	104.6 (3)	104.6 (3)
S(1)–Fe(1)–C(2)	99.2 (3)	100.2 (3)
S(1)–Fe(1)–C(3)	151.3 (3)	151.2 (3)
O(7)–Fe(1)–C(1)	90.2 (3)	90.6 (4)
O(7)–Fe(1)–C(2)	175.0 (3)	175.0 (4)
O(7)–Fe(1)–C(3)	86.8 (3)	86.1 (4)
C(1)–Fe(1)–C(2)	93.2 (4)	92.2 (5)
C(1)–Fe(1)–C(3)	102.4 (4)	102.2 (5)
C(2)–Fe(1)–C(3)	88.9 (4)	89.3 (5)
Fe(1)–Fe(2)–S(1)	55.05 (6)	54.94 (6)
Fe(1)–Fe(2)–O(8)	84.7 (1)	84.1 (1)
Fe(1)–Fe(2)–C(4)	158.9 (3)	159.3 (3)
Fe(1)–Fe(2)–C(5)	96.0 (3)	95.7 (3)
Fe(1)–Fe(2)–C(6)	97.9 (3)	97.5 (3)
S(1)–Fe(2)–O(8)	84.6 (1)	84.8 (2)
S(1)–Fe(2)–C(4)	104.2 (3)	104.9 (3)
S(1)–Fe(2)–C(5)	97.0 (3)	96.4 (3)
S(1)–Fe(2)–C(6)	153.3 (3)	152.1 (3)
O(8)–Fe(2)–C(4)	90.1 (3)	90.2 (4)
O(8)–Fe(2)–C(5)	178.4 (4)	178.3 (3)
O(8)–Fe(2)–C(6)	87.3 (3)	88.5 (3)
C(4)–Fe(2)–C(5)	89.7 (4)	90.6 (4)
C(4)–Fe(2)–C(6)	102.3 (4)	102.2 (4)
C(5)–Fe(2)–C(6)	91.2 (4)	89.9 (4)
Fe(1)–S(1)–Fe(2)	70.40 (6)	70.48 (7)
Fe(1)–S(1)–C(9)	123.7 (2)	122.7 (3)
Fe(2)–S(1)–C(9)	121.5 (3)	122.1 (3)
Fe(1)–O(7)–C(7)	122.9 (5)	122.2 (5)
Fe(2)–O(8)–C(7)	122.1 (5)	123.4 (5)
Fe(1)–C(1)–O(1)	176.0 (9)	175 (1)
Fe(1)–C(2)–O(2)	175.0 (8)	173 (1)
Fe(1)–C(3)–O(3)	178.2 (8)	179 (1)
Fe(2)–C(4)–O(4)	175.5 (8)	179 (1)
Fe(2)–C(5)–O(5)	179 (1)	178.9 (9)
Fe(2)–C(6)–O(6)	178.2 (7)	176.4 (9)
O(7)–C(7)–O(8)	125.6 (7)	124.4 (7)
O(7)–C(7)–C(8)	117.6 (8)	118.4 (7)
O(8)–C(7)–C(8)	116.7 (7)	117.2 (7)
S(1)–C(9)–C(10)	115.0 (6)	116.7 (7)
S(1)–C(9)–C(11)	102.4 (6)	104.1 (7)
S(1)–C(9)–C(12)	108.6 (6)	105.7 (6)
C(10)–C(9)–C(11)	108.8 (8)	112 (1)
C(10)–C(9)–C(12)	113.6 (8)	108.6 (9)
C(11)–C(9)–C(12)	107.9 (8)	110 (1)

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

Table X. Further IR and ^{13}C NMR Spectral Data for $(\mu\text{-}CH_3CO_2)(\mu\text{-}RS)Fe_2(CO)_6$

complex	ν_{CO} terminal carbonyls, cm^{-1}	δ_C terminal carbonyls, ppm	δ_C acetate carbon, ppm
R = *t*-Bu	2080 (s), 2050 (vs), 2015 (vs), 1994 (vs), 1936 (vw)	204.97[a] 210.30[a] 213.34[a]	187.00[b]
R = Et	2085 (s), 2055 (vs), 2020 (vs), 1995 (vs), 1938 (vw)	208.84 209.65	187.40[c]

[a] Broad signals. [b] Singlet. [c] Quartet ($^2J_{CH}$ = 6.1 Hz).

Fe(1)–O(7) and Fe(2)–O(8) bond distances of less than 2.4σ in the two independent molecules. The carbon–oxygen bond distances of the acetate bridge are only slightly elongated from typical carbon–oxygen double bonds (average C–O distance in **13a** 1.257 Å compared to typical C=O distances in carboxylates of 1.23 ± 0.01 Å).[13] The two iron atoms and the acetate bridge are planar with mean deviations from planarity equal to 0.008 Å (molecule 1) and 0.023 Å (molecule 2). In addition, the sum of the interior angles of the Fe_2O_2C unit equals 540.0° for each of the independent molecules, in agreement with the expected value for a completely planar structure.

As discussed above, the acetate-bridged complexes $(\mu\text{-}CH_3CO_2)(\mu\text{-}RS)Fe_2(CO)_6$ (**13**) were fully characterized spectroscopically. Along with the infrared spectra data already presented, certain other infrared and ^{13}C NMR spectral data were very characteristic of this type of complex. As shown in Table X, the terminal carbonyl region in the infrared spectrum showed four very intense bands above 1990 cm^{-1} and a much weaker fifth band at lower frequency. This pattern of frequencies and intensities for ν_{CO} terminal carbonyl ligands is very representative of diiron hexacarbonyl complexes bridged by two different three-electron-donor ligands and corresponds nearly identically with the terminal carbonyl regions of the $(\mu\text{-}CH_3CO_2)(\mu\text{-}Ph_2P)Fe_2(CO)_6$ complex of Mott and Carty[12] discussed above. In the ^{13}C NMR spectra, the terminal carbonyl ligand signals appeared as two or three singlets (sometimes as very broad signals) while the carbon atom of the acetate bridge resonated at approximately 190 ppm downfield, in the region normally assigned to carboxylic acids.[14] These acetate carbon atoms appeared as singlets, although in **16b**, two-bond coupling to the methyl group of the acetate ligand was observed, giving rise to a quartet with $^2J_{CH}$ = 6.1 Hz.

We will return to the $(\mu\text{-}R'CO_2)(\mu\text{-}RS)Fe_2(CO)_6$ complexes and the mechanism of their formation from $R'CO_2CH_2CH_2HgCl$ compounds in a later section. This synthesis, in any case, was not a very satisfactory one, requiring preparation of $R'CO_2CH_2CH_2HgCl$ compounds and giving only moderate yields. Furthermore, this synthesis was not a general one. For instance, the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with $CH_3CO_2CH_2CH_2HgCl$ in THF at room temperature gave only $(\mu\text{-}PhS)_2Fe_2(CO)_6$ in quantitative yield. Since a $R'CO_2$–Hg intermediate most likely is involved in the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]/R'CO_2CH_2CH_2HgCl$ reactions, it seemed reasonable to see if the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with mercury(II) carboxylates might result in formation of the $(\mu\text{-}R'CO_2)(\mu\text{-}RS)Fe_2(CO)_6$ complexes. This proved to be the case with mercury(II) acetate, propionate, pivalate, and benzoate. The reactions were carried out by adding the solid mercury(II) carboxylates (since they were very poorly soluble in THF) to a

---

[13] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

[14] Reference 5, p 269.

Table XI. Yields of (μ-RS)$Fe_2(CO)_6$ and (μ-$R'CO_2$)(μ-RS)$Fe_2(CO)_6$ from the Reactions with Mercuric Carboxylates

	yield, %	
complex	(μ-RS)-$Fe_2(CO)_6$^{a}	(μ-$R'CH_2$)(μ-RS)-$Fe_2(CO)_6$^{b}
R' = CH_3, R = *t*-Bu	40	57
R' = CH_3, R = Et	57	42
R' = CH_3, R = Ph	84	14
R' = CH_2CH_3, R = *t*-Bu	56	44
R' = CH_2CH_3, R = Et	62	37
R' = $C(CH_3)_3$, R = *t*-Bu	46	49
R' = C_6H_5, R = *t*-Bu	64	32

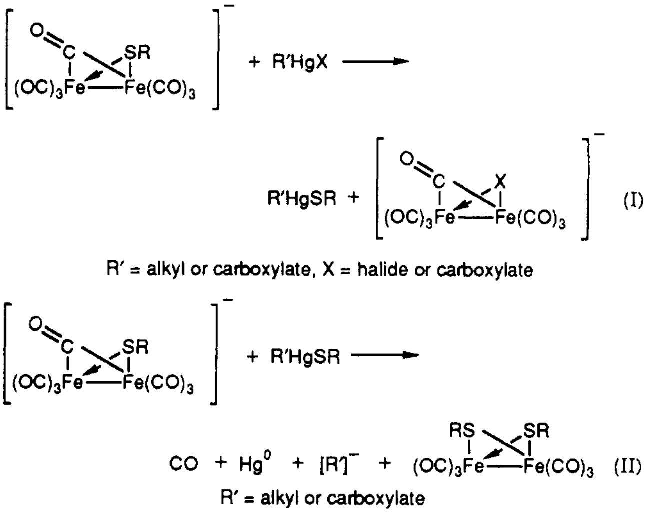
^{a}Based on S. ^{b}Based on Fe.

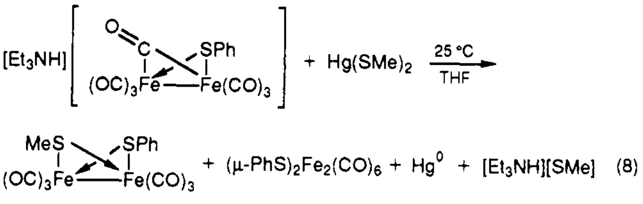
THF solution of the respective $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ (R = Et, *t*-Bu, Ph). As with the organomercuric halides, brisk gas evolution, a color change to bright red, and formation of balls of elemental mercury and of a white-gray precipitate were observed. TLC of the reaction mixtures indicated the formation of two orange-red products. Chromatographic workup gave, first, the ubiquitous side products $(\mu\text{-RS})_2Fe_2(CO)_6$, as usual, and second, the desired carboxylate-bridged products of type **13**. The yields of these products were only moderate (30–57%, except for R = Ph), and the respective $(\mu\text{-RS})_2Fe_2(CO)_6$ was formed as a major byproduct (40–84% yield) in all cases (Table XI). However, the $(\mu\text{-}R'CO_2)(\mu\text{-RS})Fe_2(CO)_6$ product yields were ~15% higher than when the $R'CO_2CH_2CH_2HgCl$ mercurial was used as the $R'CO_2$ source. In the case of $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$ the substitution of $Hg(O_2CCH_3)_2$ for $CH_3CO_2CH_2CH_2HgCl$ made all the difference: with the former $(\mu\text{-}CH_3CO_2)(\mu\text{-PhS})Fe_2(CO)_6$ was formed, albeit in only 14% yield, but with the latter it was not formed at all. However, this synthesis of $(\mu\text{-}R'CO_2)(\mu\text{-RS})Fe_2(CO)_6$ complexes also is not a general one. The reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ with $Hg(O_2CCF_3)_2$ gave $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$ as the only stable isolable product in 82% yield. The expected $(\mu\text{-}CF_3CO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ apparently had not been formed.

Finally, we address the problem of the formation of the $(\mu\text{-RS})_2Fe_2(CO)_6$ byproduct, which is found in so many reactions of the $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ complexes.[1] First, we note that these complexes by themselves are not stable in THF at room temperature, decomposing with time to give the respective $(\mu\text{-RS})_2Fe_2(CO)_6$ species. Indeed, the amount of $(\mu\text{-RS})_2Fe_2(CO)_6$ formed in a reaction with an electrophile seems to be a measure of the relative reactivity of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion toward the particular electrophile. When the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$/electrophile reactions are rapid, little or no $(\mu\text{-RS})_2Fe_2(CO)_6$ is formed. But when these reactions are slow (as indicated by slow development in the usually observed color change), the yield of $(\mu\text{-RS})_2Fe_2(CO)_6$ can become substantial.

The explanation may not be so simple when the electrophile is an inorganic or organometallic Hg(II) compound. The high yields of $(\mu\text{-RS})_2Fe_2(CO)_6$ formed in reactions of $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ with organomercuric halides, mercury(II) chloride, and mercury(II) carboxylates could be due to a facile RS ligand exchange from Fe to Hg as outlined in Scheme I. The thiophilicity of mercury is well-known.[2] Thus, in the presence of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion, R'HgX could exchange X (halide or carboxylate) with the thiolate ligand of the anion to form R'HgSR and a halide- or carboxylate-bridged diiron heptacarbonyl anion. Subsequent reaction of R'HgSR with another equivalent of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion would form $(\mu\text{-RS})_2Fe_2(CO)_6$ and carbon monoxide. The second step of this sequence was tested by experiment. A solution of $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$ was treated with bis(methanethiolato)mercury at room temperature. An immediate reaction ensued with brisk gas evolution, a color change to bright red, and formation of balls of elemental mercury (eq 8). Two products were isolated from this reaction: (1) the expected $(\mu\text{-PhS})_2Fe_2(CO)_6$ product in 16% yield (based on S) and (2) the mixed-thiolate-bridged product $(\mu\text{-MeS})(\mu\text{-PhS})Fe_2(CO)_6$ (**15**) in 73% yield. The formation of **15** clearly indicated ligand exchange between iron and mercury as was proposed in step 2 of Scheme I. Unfortunately, since this process was so facile at room temperature, formation of the undesirable $(\mu\text{-RS})_2Fe_2(CO)_6$ products in this chemistry seems unavoidable.

Scheme I. Proposed Ligand-Exchange Process between Iron and Mercury Resulting in the Formation of $(\mu\text{-RS})_2Fe_2(CO)_6$





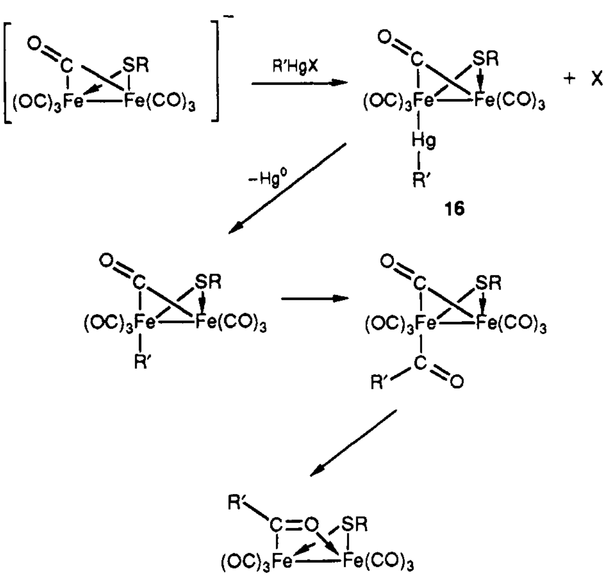
15

Considerations Concerning Reaction Course. As noted in the Introduction, the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion reacts as an iron nucleophile with most electrophiles that ultimately are capable of introducing a bridging three-electron-donor group in place of the CO bridge. Such a process in the case of an organomercuric chloride would give as a first intermediate **16** in Scheme II, a species containing an Fe–HgR bond. Such a reaction has literature precedent; a number of examples have been reported of the reactions of anionic transition-metal carbonyls with mercuric halides.[15] In the subsequent step of our suggested reaction course, elemental mercury is extruded and the organic group originally on mercury becomes bonded to iron. Here again, there is literature precedent for such Hg extrusion from L_nM–HgR systems.[16] In the third step

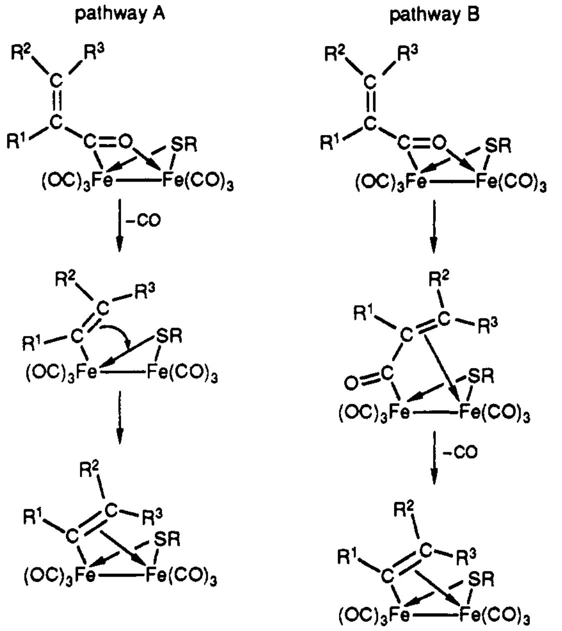
---

(15) (a) Glockling, F.; Mahale, V. R.; Sweeney, J. J. *J. Chem. Soc., Dalton Trans.* **1979**, 767. (b) Suleimanov, G. Z.; Sokolov, V. I.; Reutov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2837. (c) Schubert, U.; Kunz, E. *J. Organomet. Chem.* **1986**, *303*, C1.

Scheme II

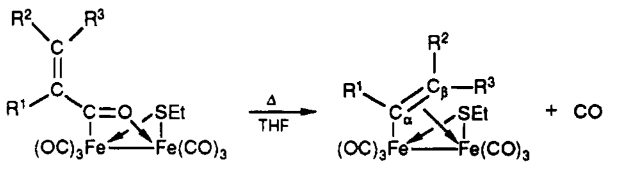


Scheme III. Possible Mechanisms of Decarbonylation for the Conversion of the Vinylacyl Complexes to the μ-σ,π-Vinyl complexes



of Scheme II, the organic substituent now on the iron atom migrates from iron to the carbon atom of a CO ligand. This is a well-known process in the chemistry of alkylmetal carbonyls[17] and one known to occur in dinuclear iron carbonyl systems.[18] In the final step of the proposed reaction course coordination of the σ-bonded acyl group to the other iron atom and migration of the bridging CO to a terminal position take place. We stress that this is a proposed reaction course based on literature precedent. No intermediates have been isolated or detected.

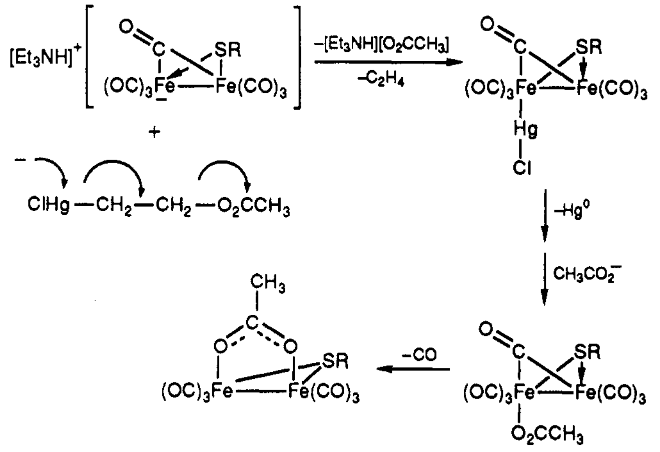
Table XII. Decarbonylation Rates in Refluxing THF



complex	time, h	conversion, %
$R^1 = R^2 = R^3 = H$	decarbonylation at room temp	
$R^1 = CH_3$, $R^2 = R^3 = H$	1.5	90
$R^1 = H$, $R^2 = CH_3$, $R^3 = H$	4.0	93
$R^1 = R^2 = CH_3$, $R^3 = H$	46.0	73[a]

[a] 33% after 4 h.

Scheme IV



When the organomercuric halide is vinylic, then the bridging acyl complex thus formed (7 in eq 2) in most cases is marginally stable at best and undergoes decarbonylation, giving the μ-σ,π-vinyl complex 8. Two likely pathways for this decarbonylation may be written (Scheme III). In a previous paper we have reported such decarbonylation reactions of $(\mu\text{-}R^2R^3C{=}CR^1C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ complexes that had been prepared by the reactions of $R^2R^3C{=}CR^1C(O)Cl$ or of $R^1C{\equiv}CR^2$ with the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anion.[1e] It was found that those complexes where R^1 and R^3 = H, i.e., $(\mu\text{-}R^2CH{=}CHC{=}O)(\mu\text{-}RS)Fe_2(CO)_6$, underwent relatively facile decarbonylation but that those of types $(\mu\text{-}R^2R^3C{=}CHC{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ and $(\mu\text{-}R^2CH{=}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$ were rather more stable to decarbonylation. Studies of the unsaturated acyl complexes 7 prepared in this investigation are in line with these findings, the times required for high conversion to the respective μ-σ,π-vinyl complexes being those shown in Table XII. Attempted thermal or photochemical decarbonylation of $(\mu\text{-}PhC{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$ and $(\mu\text{-}EtC{=}O)(\mu\text{-}PhS)Fe_2(CO)_6$ was unsuccessful. Only starting material and $(\mu\text{-}RS)_2Fe_2(CO)_6$ were recovered after 2 days of reflux in THF or 3 days of UV irradiation. Such decarbonylation of $(\mu\text{-}CH_3CH{=}CHC{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ complexes has been studied independently by Song et al.,[19] who

---

(16) (a) Sokolov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978**, *27*, 89. (b) Bashilov, V. V.; Sokolov, V. I.; Reutov, O. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1982**, 2069; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1982**, 1825. (c) Isaeva, L. S.; Morozova, L. N.; Bashilov, V. V.; Petrovskii, P. V.; Sokolov, V. I.; Reutov, O. A. *J. Organomet. Chem.* **1983**, *243*, 253. (d) Schlientz, W. J.; Ruff, J. K. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 215. (e) Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9. (f) Shul'pin, G. B.; Nizova, G. N. *J. Organomet. Chem.* **1984**, *276*, 109. (g) Rossell, O.; Sales, J.; Seco, M. *J. Organomet. Chem.* **1982**, *236*, 415. (h) Rossell, O.; Sales, J.; Seco, M. *J. Organomet. Chem.* **1981**, *205*, 133. (i) Cross, R. J.; Wardle, R. *J. Chem. Soc. A* **1970**, 840. (j) Cross, R. J.; Gemmill, J. *J. Chem. Soc., Dalton Trans.* **1984**, *199*, 205. (k) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707.

(17) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6.

(18) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* **1977**, *99*, 7381.

(19) Song, L.-C.; Liu, J.-T.; Wang, J.-T. *Acta Chim. Sin. (Engl. Ed.)* **1990**, 115.

established this process to be a first-order reaction.

Of some interest from the point of view of mechanism is the formation of (μ-CH_3CO_2)(μ-RS)$Fe_2(CO)_6$ in the reaction of $CH_3CO_2CH_2CH_2HgCl$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. ($\beta$-Carboxyethyl)mercuric halides are known to undergo facile β-elimination (as shown in Scheme IV) when attacked at mercury by nucleophilic reagents.[2] Such a process, when the attacking species is the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anion, would lead to an intermediate with an Fe–Hg bond. Anion exchange (–HgCl → –HgOAc) then would be followed by Hg extrusion and formation of the acetate bridge with loss of a CO ligand.

In summary, this investigation has shown that in those cases where a bridging acyl complex is formed, the net result is the C-alkylation of the bridging CO ligand, but without doubt, the reaction course that leads to this final product is quite different. A future paper will deal with the varied reactions of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anions with some acetylenic mercurials.

Finally, it should be noted that complexes of type (μ-R′CO)(μ-RS)$Fe_2(CO)_6$, where R = alkyl, aryl, or a vinyl group, can be prepared more readily in higher yield by the reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with the respective acid chloride, R′C(O)Cl.[1a,e]

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. Triethylamine was distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Ethyl, *tert*-butyl, and phenyl mercaptans were purged with nitrogen and used without further purification. Mercuric chloride (Alfa), mercuric acetate (Mallinckrodt), mercuric nitrate (Merck), and red mercuric oxide (Mallinckrodt) were used as received. Trifluoroacetic acid (Aldrich) and propionic acid (Fluka) were purified by vacuum distillation at room temperature and purged with nitrogen prior to use. Pivalic acid (Aldrich) and benzoic acid (Aldrich) were used as received. Ethylene, carbon monoxide, and methyl mercaptan were purchased from Matheson and used as received. Most organomercurials were available from our prior extensive work in organomercury chemistry. For leading references on the preparation of organomercuric halides (alkyl, aryl, and alkenyl), see ref 2 and 20.

The progress of all reactions was monitored by thin-layer chromatography (Baker Flex, Silica Gel 1B-F). Purification by filtration chromatography, in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh or Sigma SIL-R 100+ mesh silicic acid (ca. 200 mL) in a 350-mL glass fritted filter funnel, was used in most cases. Further purification by column chromatography was accomplished with a 300 × 25 mm or a 450 × 25 mm medium-pressure column containing Sigma S-0507 230–400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at –20 °C. All yields are based on Fe unless otherwise indicated.

Solution infrared spectra (NaCl solution cells) were obtained with a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on a JEOL FX-90Q, a Bruker WM-250, a Varian XL-300, or a Varian Gem-300 spectrometer operating at 90, 250, 300, or 300 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker WH-270, a Varian XL-300, a Varian Gem-300, or a Varian XL-400 spectrometer operating at 67.9, 75.4, 75.5, or 100.5 MHz, respectively. Broad-band proton-decoupled ^{31}P NMR spectra were obtained with a JEOL FX-90Q spectrometer operating at 36.2 MHz using a solution of 85% aqueous H_3PO_4 as an external reference. Broad-band proton-decoupled ^{19}F NMR spectra were obtained with a JEOL FX-90Q spectrometer operating at 89.6 MHz using a solution of $CFCl_3$ in $CDCl_3$ as an external reference. Electron impact mass spectra were obtained with a Finnigan 3200 mass spectrometer operating at 70 eV. Masses were correlated with use of the following isotopes: ^1H, ^{14}N, ^{12}C, ^{16}O, ^{19}F, ^{32}S, ^{31}P, ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus with use of analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory in Herlev, Denmark.

Standard in Situ Preparation of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. A 100-mL Schlenk flask equipped with a rubber septum and a stirbar was charged with 1.51 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 mL of THF, 0.42 mL (0.30 g, 3.00 mmol) of triethylamine, and 3.00 mmol of the appropriate thiol. The mixture was stirred for 30 min at room temperature, during which time slow gas evolution and a gradual color change from green to brown-red were observed. The resulting $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ reagent solution then was utilized in situ without further purification.

Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Alkyl- and Arylmercuric Halides. (a) When the Product is a Solid. The reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with phenylmercuric bromide is described as an example of the procedure used.

The $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ solution was generated with use of 1.00 g of $Fe_3(CO)_{12}$ (1.98 mmol), 0.20 g of Et_3N (2.00 mmol), and 0.19 g of $(CH_3)_3CSH$ (2.12 mmol) in 50 mL of THF at room temperature. After 30 min, 1.00 g of phenylmercuric bromide (2.80 mmol) was added as a solid (against a flow of nitrogen) to the stirred solution. The color of the solution changed from red-brown to red, and both a white precipitate and droplets of elemental mercury were observed in the bottom of the reaction mixture. The reaction mixture was stirred at room temperature overnight. The reaction solution was filtered through a pad of Celite, and the solvents then were removed in vacuo. The resulting residue was extracted with 90:10 pentane/CH_2Cl_2 (v/v) and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground-glass fritted funnel. Elution with pentane yielded one major band, which gave a red, crystalline, air-stable solid that was identified by comparison of its spectroscopic characteristics with those of a sample of the compound made by another method[1a] as $(\mu\text{-}C_6H_5C{=}O)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (0.840 g, 1.70 mmol, 86%).

(b) When the Product is an Oil. The reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with *n*-butylmercuric chloride is described as an example of the procedure used.

The $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ solution was generated with use of 1.50 g of $Fe_3(CO)_{12}$ (2.98 mmol), 0.31 g of Et_3N (3.01 mmol), and 0.27 g of *t*-BuSH (3.02 mmol) in 50 mL of THF at room temperature. After 30 min, 2.00 g of *n*-butylmercuric chloride (6.82 mmol) was added to the stirred solution as a solid against a flow of nitrogen. The color of the solution changed from red-brown to red, and both a white precipitate and droplets of elemental mercury were observed in the bottom of the reaction mixture. The reaction mixture was stirred at room temperature overnight, and then the solvents were removed in vacuo. The resulting residue was extracted with 80:20 pentane/CH_2Cl_2 (v/v) and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground glass fritted funnel. Elution with 80:20 pentane/CH_2Cl_2 (v/v) gave one broad band. This was reconcentrated, taken up in pentane, and rechromatographed on a silicic acid column (400 × 50 mm) with pentane as eluent. This gave two bands which ran closely together on the column. The first band gave a red-orange crystalline solid identified as the known compound $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ (0.12 g, 0.24 mmol, 8%). Next, a mixed fraction was collected (0.06 g), which was discarded. The last fraction gave a red-orange oil, which was identified as $(\mu\text{-}n\text{-}C_4H_9C{=}O)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (0.59 g, 1.30 mmol, 44%). ^1H NMR spectroscopy showed this to be a mixture of isomers: e/a approximately 1:1. ^1H NMR (400 MHz, $CDCl_3$): δ 0.70–1.56 (m, 16 H, $CH_3CH_2CH_2CH_2C{=}O$ and *t*-BuS including two singlets at 1.24 and 1.53 for the two isomers of *t*-BuS), 2.39–3.00 (complex m, 2 H, both isomers, $CH_3(CH_2)_2CH_2C{=}O$). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 13.6 (q, J_{CH} = 122.8 Hz, $CH_3(CH_2)_3C{=}O$), 21.9 (t, J_{CH} = 129.8 Hz, $CH_3CH_2CH_2CH_2C{=}O$), 25.9, 26.1 (overlapping t's

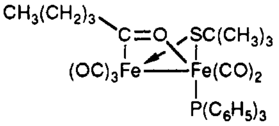
---

(20) Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer: Berlin, 1985; Chapter II.

J_{CH}'s ~122 Hz, $CH_3(CH_2)_2CH_2C{=}O$), 34.2 (q, J_{CH} = 126.5 Hz, one isomer, *t*-BuS), 34.7 (q, J_{CH} = 128.5 Hz, other isomer, *t*-BuS), 47.2 (s, *t*-BuS), 60.8 (t, J_{CH} = 127.4 Hz, one isomer, $CH_3(CH_2)_2CH_2C{=}O$), 61.1 (t, J_{CH} = 126.2 Hz, other isomer, $CH_3(CH_2)_2CH_2C{=}O$), 206.5, 209.4, 209.6, 210.1, 211.5, 212.1 (all s's, carbonyl C's), 300.7 (s, $CH_3(CH_2)_3C{=}O$).

A satisfactory analysis of the (μ-*n*-$C_4H_9C{=}O$)(μ-*t*-BuS)$Fe_2(CO)_6$ oil could not be obtained. Therefore, the solid mono(triphenylphosphine) derivative was prepared.

A solution of 0.210 g of triphenylphosphine (0.80 mmol) in THF (10 mL) was added via cannula to a stirred solution of 0.362 g of (μ-*n*-$C_4H_9C{=}O$)(μ-*t*-BuS)$Fe_2(CO)_6$ (0.80 mmol) in THF (20 mL) at room temperature, and the flask was rinsed with THF (5 mL) to ensure complete transfer of the triphenylphosphine to the iron-containing solution. This reaction mixture was stirred at room temperature for 24 h. The solution had changed from red-orange to dark red overnight. The solvents were removed in vacuo, and the residue was redissolved in pentane and chromatographed on a silicic acid pad packed in a 150-mL glass fritted funnel. Elution with pentane and then with 90:10 pentane/CH_2Cl_2 (v/v) gave one major dark red band. From this a dark red solid was obtained which could be recrystallized from pentane to give a red crystalline product (mp 108–110 °C), which was identified as the triphenylphosphine adduct (0.513 g, 0.74 mmol, 92%):



Anal. Calcd for $C_{32}H_{33}Fe_2O_6PS$: C, 55.84; H, 4.83. Found: C, 56.15; H, 5.03. ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.53–1.70 (m, 16 H, $CH_3(CH_2)_2CH_2C{=}O$ and *t*-BuS with a singlet at 1.59 for *t*-BuS), 3.13–3.35 (m, br, 2 H, $CH_3(CH_2)_2CH_2C{=}O$), 7.61–7.84 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 13.8 (q, J_{CH} = 122.9 Hz, $CH_3(CH_2)_3C{=}O$), 22.0 (t, J_{CH} = 123.2 Hz, $CH_3CH_2CH_2CH_2C{=}O$), 25.9 (t, J_{CH} = 126.4 Hz, $CH_3CH_2CH_2CH_2C{=}O$), 34.1 (q, J_{CH} = 126.4 Hz, $(CH_3)_3CS$), 48.5 (s, $(CH_3)_3CS$), 60.4 (t, J_{CH} = 127.9 Hz, $CH_3(CH_2)_2CH_2C{=}O$), 127.6–135.0 (m, aromatic C's), 209.9, 211.9, 214.6, 216.7, 218.1 (all s's, carbonyl C's), 299.8 (s, $CH_3(CH_2)_3C{=}O$). ^{31}P NMR (36.2 MHz, THF-d_8): δ_P 48.2.

With use of these procedures, the following complexes were prepared and characterized.

(μ-$CH_3OCH_2CH_2C{=}O$)(μ-EtS)$Fe_2(CO)_6$: red, oily compound; 3:1 e/a isomer mixture by ^{1}H NMR. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.36 (t, J_{HH} = 7.3 Hz, a-isomer, $-SCH_2CH_3$), 1.48 (t, J_{HH} = 7.3 Hz, e-isomer, $-SCH_2CH_3$), 2.56–3.39 (complex m, 6 H, both isomers, $-SCH_2CH_3$ and $CH_3O(CH_2)_2$), 3.18 (s, 3 H, CH_3O–). ^{13}C NMR (67.9 MHz, C_6D_6): δ_C 17.8 (q, J_{CH} = 127.8 Hz, a-isomer, $-SCH_2CH_3$), 18.2 (q, J_{CH} = 128.5 Hz, e-isomer, $-SCH_2CH_3$), 25.9 (t, J_{CH} = 141.2 Hz, a-isomer, $-SCH_2CH_3$), 33.0 (t, J_{CH} = 141.0 Hz, e-isomer, $-SCH_2CH_3$), 58.1 (q, J_{CH} = 140.5 Hz, both isomers, $-(CH_2)_2OCH_3$), 60.1 (t, J_{CH} = 128.2 Hz, e-isomer, $-CH_2CH_2OCH_3$), 60.4 (t, J_{CH} = 127.4 Hz, a-isomer, $-CH_2CH_2OCH_3$), 66.7 (t, J_{CH} = 142.8 Hz, both isomers, $-CH_2CH_2OCH_3$), 208.7, 209.0, 210.1, 210.7, 211.8 (all s's, carbonyl C's), 300.3, 301.9 (s's, both isomers, $-CH_3O(CH_2)_2C{=}O$).

(μ-$CH_3OCH_2CH_2C{=}O$)(μ-EtS)$Fe_2(CO)_5PPh_3$: red crystals; mp 89.5–91.0 °C. Anal. Calcd for $C_{29}H_{27}Fe_2O_7PS$: C, 52.60; H, 4.11. Found: C, 52.96; H, 4.28. ^{1}H NMR (90 MHz, CD_2Cl_2): δ 1.12–3.06 (complex m, 12 H, $CH_3O(CH_2)_2C{=}O$ and $-SCH_2CH_3$), 7.35–7.56 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ_C 17.9 (q, J_{CH} = 127.6 Hz, $-SCH_2CH_3$), 31.3 (t, J_{CH} = 140.5 Hz, $-SCH_2CH_3$), 58.3, 59.8, 66.6, 66.8 (complex m, $CH_3O(CH_2)_2C{=}O$), 128.3–140.0 (m, aromatic C's), 209.6, 211.2, 213.9, 216.7, 216.8, 217.7 (all s's, carbonyl C's), 298.8 (s, $CH_3O(CH_2)_2C{=}O$). ^{31}P NMR (36.2 MHz, CD_2Cl_2): δ_P 54.2, 52.1 (major isomer).

(μ-$HOCH_2CH_2C{=}O$)(μ-EtS)$Fe_2(CO)_6$: red oil; a,e/e,e isomer mixture. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.27 Hz, 0.9 H, SCH_2CH_3, minor isomer), 1.49 (t, *J* = 7.27 Hz, 2.1 H, SCH_2CH_3, major isomer), 2.54–3.53 (complex m, 6 H, SCH_2CH_3 and $HOCH_2CH_2C{=}O$, both isomers), 3.86 (t, $^3J_{HH}$ = 5.48 Hz, 0.7 H, $HOCH_2CH_2C{=}O$, major isomer), 4.40 (t, $^3J_{HH}$ = 5.48 Hz, 0.3 H, $HOCH_2CH_2C{=}O$, minor isomer). Isomer ratio (major:minor): 2.1:1.0. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 16.17 (q, J_{CH} = 127.2 Hz, SCH_2CH_3, minor isomer), 18.28 (q, J_{CH} = 129.2 Hz, SCH_2CH_3, major isomer), 32.93 (t, J_{CH} = 140.0 Hz, SCH_2CH_3, both isomers), 57.06 (t, J_{CH} = 144.8 Hz, $HOCH_2CH_2{=}O$, major isomer), 57.97 (t, J_{CH} = 135.8 Hz, $HOCH_2CH_2C{=}O$, minor isomer), 62.89 (t, J_{CH} = 127.0 Hz, $HOCH_2CH_2C{=}O$, major isomer), 63.16 (t, J_{CH} = 126.5 Hz, $HOCH_2CH_2C{=}O$, minor isomer), 207.04, 208.78, 208.92, 209.09, 209.27, 210.87, and 211.42 (all s, terminal CO's, both isomers), 301.81 (s, acyl $C{=}O$, major isomer), 304.10 (s, acyl $C{=}O$, minor isomer).

(μ-$(CH_3)_3CC{=}O$)(μ-EtS)$Fe_2(CO)_6$: red-orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.86 (s, 9 H, $(CH_3)_3CC{=}O$), 1.48 (t, J_{HH} = 7.2 Hz, 3 H, $-SCH_2CH_3$), 2.58 (q, J_{HH} = 7.2 Hz, 2 H, $-SCH_2CH_3$). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 18.4 (q, J_{CH} = 128.1 Hz, $-SCH_2CH_3$), 26.0 (q, J_{CH} = 127.5 Hz, $(CH_3)_3CC{=}O$), 33.1 (t, J_{CH} = 140.6 Hz, $-SCH_2CH_3$), 55.7 (s, $(CH_3)_3CC{=}O$), 208.8, 209.4, 212.0 (all s's, carbonyl C's), 307.4 (s, $(CH_3)_3C{=}O$).

(μ-$(CH_3)_3CC{=}O$)(μ-EtS)$Fe_2(CO)_5PPh_3$: red solid; mp 147.5–149.0 °C. Anal. Calcd for $C_{30}H_{29}Fe_2O_6PS$: C, 54.58; H, 4.43. Found: C, 54.38; H, 4.47. ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.76 (s, 9 H, $(CH_3)_3CC{=}O$), 1.18 (t, J_{HH} = 7.5 Hz, 3 H, $-SCH_2CH_3$), 2.04 (q, J_{HH} = 7.7 Hz, 2 H, $-SCH_2CH_3$), 7.33–7.52 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 17.9 (q, J_{CH} = 127.0 Hz, $-SCH_2CH_3$), 26.0 (q, J_{CH} = 127.0 Hz, $(CH_3)_3CC{=}O$), 31.4 (t, J_{CH} = 135.8 Hz, $-SCH_2CH_3$), 55.1 (s, $(CH_3)_3CC{=}O$), 128.2–134.2 (m, aromatic C's), 210.4, 211.4, 214.2, 217.4, 217.8 (all s's, carbonyl C's), 307.0 (s, $(CH_3)_3CC{=}O$). ^{31}P NMR (36.2 MHz, $CDCl_3$): δ_P 53.8.

(μ-$FC_6H_4C{=}O$)(μ-EtS)$Fe_2(CO)_6$: red, oily solid; a,e/e,e isomer mixture. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.32 (t, J_{HH} = 7.2 Hz, a-isomer, $-SCH_2CH_3$), 1.57 (t, J_{HH} = 7.3 Hz, e-isomer, $-SCH_2CH_3$), 2.15–2.54 (m, a-isomer, $-SCH_2CH_3$), 2.67–2.88 (m, e-isomer, $-SCH_2CH_3$), 7.15–7.74 (m, aromatic H's). ^{13}C NMR (67.9 MHz, acetone-d_6): δ_C 18.2 (q, J_{CH} = 128.4 Hz, a-isomer, $-SCH_2CH_3$, 18.6 (q, J_{CH} = 127.9 Hz, e-isomer, $-SCH_2CH_3$), 26.5 (t, J_{CH} = 142.8 Hz, a-isomer, $-SCH_2CH_3$), 33.7 (t, J_{CH} = 140.5 Hz, e-isomer, $-SCH_2CH_3$), 115.4 (dd, J_{CH} = 160.8 Hz, J_{CF} = 18.7 Hz, a-isomer, β-carbon), 116.4 (dd, J_{CH} = 166.2 Hz, J_{CF} = 21.4 Hz, e-isomer, β-carbon), 131.0 (dd, J_{CH} = 163.0 Hz, J_{CF} = 7.7 Hz, e-isomer, α-carbon), 140.0 (dd, J_{CH} = 154.1 Hz, J_{CF} = 10.0 Hz, a-isomer, α-carbon), 141.8 (s, both isomers, ipso phenyl C), 162.9 (d, J_{CF} = 222.5 Hz, a-isomer, γ-carbon), 166.4 (d, J_{CF} = 238.4 Hz, e-isomer, γ-carbon), 210.1, 210.7, 212.1, 212.9 (all s's, carbonyl C's), 287.3 (s, e-isomer, $-FC_6H_4C{=}O$), 289.6 (s, a-isomer, $-FC_6H_4C{=}O$). ^{19}F NMR (89.6 MHz, CD_2Cl_2): δ_F −103.3.

(μ-$FC_6H_4C{=}O$)(μ-EtS)$Fe_2(CO)_5PPh_3$: red solid; mp 169–170 °C. Anal. Calcd for $C_{32}H_{24}FFe_2O_6PS$: C, 55.05; H, 3.46. Found: C, 55.20; H, 3.60. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.20 (t, J_{HH} = 7.2 Hz, 3 H, $-SCH_2CH_3$), 2.00–2.31 (m, 2 H, $-SCH_2CH_3$), 7.00–7.15 and 7.32–7.65 (m, 19 H, aromatic H's). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 17.8 (q, J_{CH} = 126.5 Hz, $-SCH_2CH_3$), 31.3 (t, J_{CH} = 140.8 Hz, $-SCH_2CH_3$), 113.6–141.0 (m, aromatic C's), 211.3, 212.5, 214.8, 217.2 (all s's, carbonyl C's), 286.6 (s, $FC_6H_4C{=}O$). ^{19}F NMR (89.6 MHz, $CDCl_3$): δ_F −105.9. ^{31}P NMR (36.2 MHz, $CDCl_3$): δ_P 54.6.

(μ-$Me_2NC_6H_4C{=}O$)(μ-EtS)$Fe_2(CO)_6$: red, oily solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.29 (t, J_{HH} = 7.1 Hz, a-isomer, $-SCH_2CH_3$), 1.50 (t, J_{HH} = 7.0 Hz, e-isomer, $-SCH_2CH_3$), 2.00–2.28 (m, a-isomer, $-SCH_2CH_3$), 2.58–2.75 (m, e-isomer, $-SCH_2CH_3$), 3.01 (s, 6 H, $-N(CH_3)_2$), 6.49–7.53 (m, 4 H, aromatic H's). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 18.4 (q, J_{CH} = 127.6 Hz, $-SCH_2CH_3$), 32.9 (t, J_{CH} = 141.9 Hz, $-SCH_2CH_3$), 40.0 (q, J_{CH} = 136.8 Hz, $-N(CH_3)_2$), 110.0 (d, J_{CH} = 160.0 Hz, aromatic C's ortho to $-N(CH_3)_2$), 130.5 (d, J_{CH} = 158.7 Hz, aromatic C's ortho to acyl group), 135.4 (s, $CN(CH_3)_2$), 155.6 (s, $CC{=}O$), 209.8, 211.2, 212.8 (all s's, carbonyl C's), 275.9 (s, $-C_6H_4C{=}O$).

(μ-$Me_2NC_6H_4C{=}O$)(μ-EtS)$Fe_2(CO)_5PPh_3$: red solid; mp 171–172 °C. Anal. Calcd for $C_{34}H_{30}Fe_2NO_6PS$: C, 56.46; H, 4.18. Found: C, 56.62; H, 4.38. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.20 (t, J_{HH} = 7.4 Hz, 3 H, $-SCH_2CH_3$), 2.19 (m, 2 H, $-SCH_2CH_3$), 3.00 (s, 6 H, $-N(CH_3)_2$), 6.48 (d, J_{HH} = 8.9 Hz, 2 H, phenylene H's ortho to $-NMe_2$), 7.24 (d, J_{HH} = 8.9 Hz, 2 H, phenylene H's ortho to acyl), 7.40–7.66 (m, 15 H, phosphine aromatic H's). ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ_C 18.2 (q, J_{CH} = 128.4 Hz, $-SCH_2CH_3$), 31.8 (t, J_{CH} = 139.6 Hz, $-SCH_2CH_3$), 40.2 (q, J_{CH} = 136.9 Hz, $-N(CH_3)_3$), 110.2 (d, J_{CH} = 158.6 Hz, phenyl C's ortho to $-N(CH_3)_2$), 127.6–142.0 (m, phenyl C's), 212.3, 215.8, 218.0, 218.4 (all s's, carbonyl C's), 277.9 (s, $-\mathrm{C_6H_4}\mathit{C}{=}\mathrm{O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ_P 54.1, 56.0.

$(\mu\text{-}(\mathrm{CH_3})_3\mathrm{CCH_2C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$: red oil; mixture of a,e and e,e isomers. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 0.74 (s, one isomer, $-\mathrm{CH_2C(C}\mathit{H}_3)_3$), 0.77 (s, other isomer, $-\mathrm{CH_2C(C}\mathit{H}_3)_3$), 1.28 (s, one isomer, *t*-BuS), 1.48 (s, other isomer, *t*-BuS), 2.44 and 3.28 (AB pattern, J_HH = 18.8 Hz, one isomer, $-\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_3}$), 2.48 and 2.82 (AB pattern, J_HH = 17.0 Hz, other isomer, $-\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_3}$). ^{13}C NMR (67.9 MHz, $\mathrm{C_6D_6}$): δ_C 26.6 (m, both isomers, *t*-BuS and $(\mathit{C}\mathrm{H_3})_3\mathrm{CCH_2C{=}O}$), 48.1 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{CH_2C{=}O}$), 49.5 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 74.2 (t, J_CH = 126.3 Hz, $(\mathrm{CH_3})_3\mathrm{C}\mathit{C}\mathrm{H_2C{=}O}$), 209.7, 210.1, 210.6, 210.8 (all s's, carbonyl C's), 302.3 (s, $-\mathrm{CH_2}\mathit{C}{=}\mathrm{O}$).

$(\mu\text{-}(\mathrm{CH_3})_3\mathrm{CCH_2C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_5PPh_3}$: red solid; mp 139–140 °C. Anal. Calcd for $\mathrm{C_{33}H_{35}Fe_2O_6PS}$: C, 56.44; H, 5.02. Found: C, 56.05; H, 5.13. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 0.41–1.53 (m, 18 H, *t*-BuS and $(\mathrm{C}\mathit{H}_3)_3\mathrm{CCH_2C{=}O}$), 1.72–3.54 (m, 2 H, $(\mathrm{CH_3})_3\mathrm{CC}\mathit{H}_2\mathrm{C{=}O}$), 7.32–7.81 (m, 15 H, phenyl H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 26.4–36.9 (m, *t*-BuS and $(\mathit{C}\mathrm{H_3})_3\mathrm{CCH_2C{=}O}$), 73.8 (t, J_CH = 125.0 Hz, $(\mathrm{CH_3})_3\mathrm{C}\mathit{C}\mathrm{H_2C{=}O}$), 127.1–142.0 (m, aromatic C's), 209.7, 211.7, 216.8, 218.0 (s's, carbonyl C's), 301.3 (s, $-\mathrm{CH_2}\mathit{C}{=}\mathrm{O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ_P 48.2.

$(\mu\text{-}\mathrm{CH_2{=}CH(CH_2)_4C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$: red oil; mixture of a,e and e,e isomers. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.88–1.96 (m, 15 H, *t*-BuS and $\mathrm{CH_2{=}CH(C}\mathit{H}_2)_3\mathrm{CH_2C{=}O}$), 2.45–3.00 (m, 2 H, $-\mathrm{C}\mathit{H}_2\mathrm{C{=}O}$), 4.86–4.97 (m, 2 H, $-\mathrm{CH{=}C}\mathit{H}_2$), 5.71 (m, 1 H, $-\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$). ^{13}C NMR (67.9 MHz, $\mathrm{C_6D_6}$): δ 11.7–37.5 (m, hexenyl C's and *t*-BuS), 49.7 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 61.1, 61.3 (both t's, both J_CH = 126.0 Hz, both isomers, $\mathit{C}\mathrm{H_2C{=}O}$), 114.8 (t, J_CH = 156.9 Hz, $-\mathrm{CH{=}}\mathit{C}\mathrm{H_2}$), 138.3 (d, J_CH = 142.6 Hz, $\mathit{C}\mathrm{H{=}CH_2}$), 210.0, 210.6, 210.8, 211.9, 212.5 (all s's, carbonyl C's), 300.4 (s, $-\mathrm{CH_2}\mathit{C}{=}\mathrm{O}$).

$(\mu\text{-}\mathrm{CH_2{=}CH(CH_2)_4C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_5PPh_3}$: a red oil. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 0.73–1.78 (m, 15 H, *t*-BuS and $\mathrm{CH_2{=}CH(C}\mathit{H}_2)_3\mathrm{CH_2C{=}O}$), 2.40–2.58 (m, 2 H, $-\mathrm{C}\mathit{H}_2\mathrm{C{=}O}$), 4.82–4.92 (m, 2 H, $-\mathrm{CH{=}C}\mathit{H}_2$), 5.57–5.62 (m, 1 H, $-\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$), 7.30–7.65 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 11.0–38.5 (m, $\mathrm{CH_2{=}CH(}\mathit{C}\mathrm{H_2)_3CH_2C{=}O}$ and *t*-BuS), 49.8 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 61.0 (t, J_CH = 130.6 Hz, $-\mathit{C}\mathrm{H_2C{=}O}$), 115.0 (t, J_CH = 156.7 Hz, $-\mathrm{CH{=}}\mathit{C}\mathrm{H_2}$), 127.2–140.0 (m, aromatic C's and $-\mathit{C}\mathrm{H}$<<db$\mathrm{CH_2}$), 210.5, 212.4, 215.0, 215.6, 217.4 (all s's, carbonyl C's), 299.7, 301.1 (both s's, isomers, $-\mathrm{CH_2}\mathit{C}{=}\mathrm{O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ_P 48.4, 55.2.

$(\mu\text{-c-}\mathrm{C_6H_{11}C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$: red-orange oil; two isomers. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 0.80–2.25 (complex m, 19 H, ring H's and *t*-BuS including a singlet at δ 1.53 for *t*-BuS), 2.56 (complex m, 1 H, $-\mathrm{C}\mathit{H}\mathrm{C{=}O}$). ^{13}C NMR (67.9 MHz, $\mathrm{C_6D_6}$): δ_C 25.4 (t, J_CH = 133.4 Hz), 25.8 (t, J_CH = 122.8 Hz), 28.2 (t, J_CH = 126.0 Hz) (preceding peaks are for ring C's), 30.2 (q, J_CH = 126.6 Hz, *t*-BuS), 49.6 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 68.2 (d, J_CH = 132.7 Hz, $-\mathit{C}\mathrm{HC{=}O}$), 210.6, 210.7, 212.5 (s's, carbonyl C's), 304.1 (s, c-$\mathrm{C_6H_{11}}\mathit{C}{=}\mathrm{O}$).

$(\mu\text{-c-}\mathrm{C_6H_{11}C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_5PPh_3}$: red solid; mp 154.5–155.5 °C. Anal. Calcd for $\mathrm{C_{34}H_{35}Fe_2O_6PS}$: C, 57.16; H, 4.94. Found: C, 57.03; H, 4.98. ^{1}H NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 0.53–1.64 (m, 19 H, ring H's and singlet at 1.18 for *t*-BuS), 2.52 (t, J_HH = 8.23 Hz, 1 H, $\mathrm{C}\mathit{H}\mathrm{C{=}O}$), 7.41–7.83 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CD_2Cl_2}$): δ_C 24.0–30.3 (m, ring C's), 34.3 (q, J_CH = 126.7 Hz, *t*-BuS), 49.1 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 67.6 (d, J_CH = 131.1 Hz, $\mathit{C}\mathrm{HC{=}O}$), 127.6–140.2 (m, phenyl C's), 210.9, 212.7, 215.2, 217.3, 218.9 (all s's, carbonyl C's), 304.0 (s, $=\mathrm{CH}\mathit{C}{=}\mathrm{O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CD_2Cl_2}$): δ_P 48.2.

$(\mu\text{-}\mathrm{HOCH_2CH_2C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$: red oil; mixture of e,a and e,e isomers. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.29 (s, 4.1 H, $\mathrm{SC(C}\mathit{H}_3)_3$, minor isomer), 1.50 (s, 4.9 H, $\mathrm{SC(C}\mathit{H}_3)_3$, major isomer), 2.74–3.56 (complex m, 4 H, $\mathrm{HOC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C{=}O}$, both isomers), 4.07 (t, $^3J_\mathrm{HH}$ = 6.49 Hz, 0.6 H, $\mathit{H}\mathrm{OCH_2CH_2C{=}O}$, major isomer), 4.37 (t, $^3J_\mathrm{HH}$ = 6.49 Hz, $\mathit{H}\mathrm{OCH_2CH_2C{=}O}$, minor isomer). Isomer ratio (major:minor): 1.2:1.0. ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$): δ_C 34.14 (q, J_CH = 123.3 Hz, $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$, major isomer), 34.73 (q, J_CH = 125.4 Hz, $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$, minor isomer), 48.02 (s, $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$, minor isomer), 49.83 (s, $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$, major isomer), 57.21 (t, J_CH = 144.6 Hz, $\mathrm{HO}\mathit{C}\mathrm{H_2CH_2C{=}O}$, major isomer), 57.43 (t, J_CH = 150.4 Hz, $\mathrm{HO}\mathit{C}\mathrm{H_2CH_2C{=}O}$, minor isomer), 62.78 (t, J_CH = 127.5 Hz, $\mathrm{HOCH_2}\mathit{C}\mathrm{H_2C{=}O}$, minor isomer), 63.03 (t, J_CH = 128.4 Hz, $\mathrm{HOCH_2}\mathit{C}\mathrm{H_2C{=}O}$, major isomer), 206.28, 208.87, 209.28, 209.89, 211.06, and 211.61 (all s, terminal *C*O's, both isomers), 300.91 (s, acyl $\mathit{C}{=}\mathrm{O}$, minor isomer), 301.67 (s, acyl $\mathit{C}{=}\mathrm{O}$, major isomer).

$(\mu\text{-}\textit{trans}\text{-}2\text{-}\mathrm{MeO\text{-}c\text{-}C_6H_{10}C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$: red, oily compound. ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$): δ 0.58–2.15 (m, 17 H, ring H's; s at δ 1.48 for *t*-BuS), 2.86–3.18 (m, 5 H, with s at δ 3.14 for $-\mathrm{OC}\mathit{H}_3$). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 23.9, 25.0, 27.2, 29.6 (m, ring C's), 34.3 (q, J_CH = 126.6 Hz, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 49.3 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 56.2 (q, J_CH = 141.9 Hz, $-\mathrm{O}\mathit{C}\mathrm{H_3}$), 73.2 (d, J_CH = 133.9 Hz, $=\mathit{C}\mathrm{HC{=}O}$), 79.9 (d, J_CH = 142.9 Hz, $=\mathit{C}\mathrm{HCOCH_3}$), 209.8, 210.3, 210.8 (all s's, carbonyl C's), 305.1 (s, acyl C).

$(\mu\text{-}\textit{trans}\text{-}2\text{-}\mathrm{MeO\text{-}c\text{-}C_6H_{10}C{=}O})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_5PPh_3}$: red solid; mp 137.5–139 °C. Anal. Calcd for $\mathrm{C_{35}H_{37}Fe_2O_7PS}$: C, 56.48; H, 5.01. Found: C, 56.47; H, 5.07. ^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$): δ 0.57–1.98 (m, 17 H, ring H's; s at δ 1.22 for *t*-BuS), 2.61–3.37 (m, 5 H, methoxy resonance is at 3.11 ppm), 7.25–7.81 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): 22.1–29.7 (m, ring C's), 34.0 (q, J_CH = 126.4 Hz, *t*-BuS), 48.3 (s, $(\mathrm{CH_3})_3\mathit{C}\mathrm{S}$), 56.5 (q, J_CH = 140.1 Hz, $-\mathrm{O}\mathit{C}\mathrm{H_3}$), 72.0 (d, J_CH = 130.8 Hz, $=\mathit{C}\mathrm{HC{=}O}$), 79.7 (d, J_CH = 141.8 Hz, $=\mathit{C}\mathrm{HOCH_3}$), 127.1–134.8 (m, aromatic C's), 210.5, 212.1, 213.3, 217.0, 218.1 (all s's, carbonyl C's), 304.1 (s, acyl C). ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ_P 49.0.

$(\mu\text{-}\mathrm{EtC{=}O})(\mu\text{-}\mathrm{PhS})\mathrm{Fe_2(CO)_6}$: red solid; mp 80.5–81.5 °C; a 1:1 e,a/e,e isomer mixture. Anal. Calcd for $\mathrm{C_{15}H_{10}Fe_2O_7S}$: C, 40.40; H, 2.26. Found: C, 40.70; H, 2.36. ^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$): δ 0.31 (t, J_HH = 7.6 Hz, e-isomer, $-\mathrm{SCH_2C}\mathit{H}_3$), 0.81 (t, J_HH = 7.6 Hz, a-isomer, $-\mathrm{SCH_2C}\mathit{H}_3$), 2.20–3.00 (complex m, 2 H, both isomers, $-\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$), 7.18–7.66 (m, 5 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CD_2Cl_2}$): δ_C 7.8 (q, J_CH = 126.3 Hz, e-isomer, $\mathit{C}\mathrm{H_3CH_2C{=}O}$), 8.1 (q, J_CH = 128.4 Hz, a-isomer, $\mathit{C}\mathrm{H_3CH_2C{=}O}$), 54.9, 55.0 (overlapping t's, J_CH's ~128 Hz, $\mathrm{CH_3}\mathit{C}\mathrm{H_2C{=}O}$), 127.7–140.1 (m, aromatic C's), 207.8, 208.9, 209.6, 209.9, 211.8, 212.4 (all s's, carbonyl C's), 302.2, 302.5 (s, both isomers $\mathrm{Et}\mathit{C}{=}\mathrm{O}$).

$(\mu\text{-c-}\mathrm{C_3H_5C{=}O})(\mu\text{-}\mathrm{PhS})\mathrm{Fe_2(CO)_6}$: red solid; mp 71–72 °C. Anal. Calcd for $\mathrm{C_{16}H_{10}Fe_2O_7S}$: C, 41.96; H, 2.20. Found: C, 42.05; H, 2.32. ^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$): δ −0.16 to +0.94 (m, 4 H, c-$(\mathrm{C}\mathit{H}_2)_2\mathrm{CHC{=}O}$), 2.41–2.58 (complex m, 1 H, $\mathrm{C}\mathit{H}\mathrm{C{=}O}$), 7.20–7.47 (m, 5 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CD_2Cl_2}$): δ_C 13.4 (t, J_CH = 167.8 Hz, one ring $=\mathit{C}\mathrm{H_2}$), 14.3 (t, J_CH = 170.2 Hz, other ring $=\mathit{C}\mathrm{H_2}$), 37.6 (d, J_CH = 172.6 Hz, $=\mathit{C}\mathrm{HC{=}O}$), 127.7–133.5 (m, aromatic C's), 206.4, 209.7, 210.5, 212.4 (all s's, carbonyl C's), 297.0 (s, c-$\mathrm{C_3H_5}\mathit{C}{=}\mathrm{O}$).

$(\mu\text{-}\mathrm{Et(Me)CHC{=}O})(\mu\text{-}\mathrm{PhS})\mathrm{Fe_2(CO)_6}$: red oil; mixture of e,a and e,e isomers. ^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$): δ 0.58–1.45 (m, 8 H, both isomers, $\mathrm{C}\mathit{H}_3\mathrm{C}\mathit{H}_2\mathrm{CH(C}\mathit{H}_3\mathrm{)C{=}O}$), 2.08–2.78 (m, 1 H, both isomers, $\mathrm{CH_3CH_2C}\mathit{H}\mathrm{(CH_3)C{=}O}$), 7.20–7.50 (m, 5 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CD_2Cl_2}$): δ_C 11.3 (q, J_CH = 122.7 Hz, e-isomer, $\mathrm{CHCH_2C}\mathit{H}_3$), 25.5 (q, J_CH = 124.9 Hz, a-isomer, $\mathrm{CHCH_2C}\mathit{H}_3$), 29.8, 30.7, 33.9, 34.3 (complex m, both isomers, $\mathrm{C(O)}\mathit{C}\mathrm{H(}\mathit{C}\mathrm{H_3)CH_2CH_3}$), 59.5 (t, J_CH = 127.5 Hz, one isomer, $\mathrm{C(O)CH(CH_3)}\mathit{C}\mathrm{H_2CH_3}$), 59.8 (t, J_CH = 129.5 Hz, other isomer, $\mathrm{C(O)CH(CH_3)}\mathit{C}\mathrm{H_2CH_3}$), 127.8–139.9 (m, aromatic C's), 207.6, 209.1, 209.8, 211.8, 212.4 (all s's, carbonyl C's), 302.3, 302.9 (s's, both isomers, *s*-$\mathrm{C_4H_9}\mathit{C}{=}\mathrm{O}$).

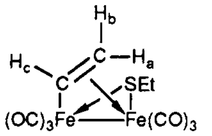
$(\mu\text{-}\mathrm{Et(Me)CHC{=}O})(\mu\text{-}\mathrm{PhS})\mathrm{Fe_2(CO)_5PPh_3}$: red solid; mp 132–133 °C. Anal. Calcd for $\mathrm{C_{34}H_{29}Fe_2O_6PS}$: C, 57.66; H, 4.13. Found: C, 58.59; H, 4.53. ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 0.61–1.91 (m, 8 H, $\mathrm{C}\mathit{H}_3\mathrm{C}\mathit{H}_2\mathrm{CH(C}\mathit{H}_3\mathrm{)C{=}O}$), 2.62 (m, br, 1 H, $\mathrm{CH_3CH_2C}\mathit{H}\mathrm{(CH_3)C{=}O}$), 6.70–7.65 (m, 20 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_C 12.3 (q, J_CH = 125.5 Hz, one isomer, $\mathit{C}\mathrm{H_3CH_2CH(CH_3)C{=}O}$), 19.0 (q, J_CH = 124.7 Hz, other isomer, $\mathit{C}\mathrm{H_3CH_2CH(CH_3)C{=}O}$), 29.0, 30.1, 30.6, 34.0 (complex m, both isomers, $\mathrm{CH_3CH_2}\mathit{C}\mathrm{H(}\mathit{C}\mathrm{H_3)C{=}O}$), 59.2 (t, J_CH = 128.4 Hz, $\mathrm{CH_3}\mathit{C}\mathrm{H_2CH(CH_3)C{=}O}$), 126.7–140.5 (m, aromatic C's), 210.0, 210.9, 214.9, 216.6, 218.3 (all s's, carbonyl C's), 301.8, 302.4 (both s's, both isomers, $(\mathrm{CH_3CH_2CH(CH_3)}\mathit{C}{=}\mathrm{O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CD_2Cl_2}$): δ_P 50.2.

$(\mu\text{-}\mathrm{MeOCH_2CH_2C{=}O})(\mu\text{-}\mathrm{PhS})\mathrm{Fe_2(CO)_6}$: red-orange solid; mp 58–59 °C; an approximately 1:1 mixture of e,a and e,e isomers. Anal. Calcd for $\mathrm{C_{16}H_{12}Fe_2O_8S}$: C, 40.38; H, 2.54. Found: C, 39.70; H, 2.60. ^{1}H NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 2.79–3.40 (complex m, 7 H, $-(\mathrm{C}\mathit{H}_2)_2\mathrm{OC}\mathit{H}_3$, with two singlets at 3.04 and 3.19 for $-\mathrm{OC}\mathit{H}_3$), 7.16–7.50 (m, 5 H, phenyl H's). ^{13}C NMR (67.9 MHz, $\mathrm{C_6D_6}$): δ_C 58.0, 58.2 (q, J_CH = 126.5 Hz, both isomers, $-(\mathrm{CH_2})_2\mathrm{O}\mathit{C}\mathrm{H_3}$), 60.4 (t, J_CH = 127.5 Hz, both isomers, $-\mathit{C}\mathrm{H_2CH_2OCH_3}$), 66.5, 66.8 (t, J_CH = 138.4 Hz, both isomers, $-\mathrm{CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 127.7–133.1 (m, phenyl C's, 207.5, 208.8, 209.5, 211.0, 211.7, 215.2 (all s's, carbonyl C's), 301.9 (s, $-\mathrm{CH_3O(CH_2)_2}\mathit{C}{=}\mathrm{O}$).

(μ-MeOCH$_2$CH$_2$C=O)(μ-PhS)Fe$_2$(CO)$_5$PPh$_3$: red solid; mp 131.5–132.5 °C; e,a and e,e isomer mixture. Anal. Calcd for $C_{33}H_{27}Fe_2O_7PS$: C, 55.81; H, 3.83. Found: C, 55.90; H, 4.00. ^{1}H NMR (270 MHz, acetone-d_6): δ 2.80–3.21 (m, 7 H, CH_3O(CH_2)$_2$C=O), 6.83–7.76 (m, 20 H, aromatic H's). ^{13}C NMR (67.9 MHz, acetone-d_6): δ_C 58.5, 60.8, 67.1, 67.3, 71.7, 81.8 (complex m, isomers, CH$_3$O(CH$_2$)$_2$C=O), 127.2–142.9 (m, aromatic C's), 210.0, 211.4, 214.3, 215.0, 216.9, 218.6 (all s's, carbonyl C's), 301.4, 303.2 (both s's, isomers, CH$_3$OCH$_2$CH$_2$$C$=O). ^{31}P NMR (36.2 MHz, acetone-d_6): δ_P 48.7 (major isomer), 53.3 (minor isomer).

(μ-*p*-ClC$_6$H$_4$C=O)(μ-PhS)Fe$_2$(CO)$_6$: red solid; mp 105–106 °C. Anal. Calcd for $C_{19}H_9ClFe_2O_7S$: C, 43.19; H, 1.72. Found: C, 43.52; H, 2.03. ^{1}H NMR (90 MHz, CD$_2$Cl$_2$): δ 6.98–8.00 (m, all H's). ^{13}C NMR (67.9 MHz, CD$_2$Cl$_2$): δ_C 127.8–140.8 (m, aromatic C's), 208.9, 209.2, 210.1, 212.4 (all s's, carbonyl C's), 290.7 (s, ClC$_6$H$_4$$C$=O).

Reaction of CH$_2$=CHHgBr with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The anion was generated with use of 1.50 g of Fe$_3$(CO)$_{12}$ (2.98 mmol), 0.31 g of Et$_3$N (3.01 mmol), and 0.18 g of EtSH (2.97 mmol) in 50 mL of THF at room temperature. After 30 min, 1.07 g of vinylmercuric bromide (3.48 mmol) was added to the stirred solution as a solid against a flow of nitrogen. The color of the solution changed from red-brown to red, and both a white precipitate and droplets of elemental mercury were observed in the bottom of the flask. The reaction mixture was stirred at room temperature for 4 h, and then the solvents were removed in vacuo. The resulting residue was extracted with pentane and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground-glass fritted funnel. Elution with pentane gave one red-orange band, from which was isolated a red-orange oily compound. This was identified as (μ-σ,π-CH$_2$=CH)(μ-EtS)Fe$_2$(CO)$_6$ (0.75 g, 1.90 mmol, 64%) and was purified for elemental analysis by short-path distillation (0.05 mmHg):

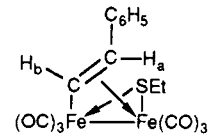


Anal. Calcd for $C_{10}H_8Fe_2O_6S$: C, 32.65; H, 2.19. Found: C, 32.42; H, 2.29. ^{1}H NMR (90 MHz, CDCl$_3$): δ 1.30 (t, J_{HH} = 7.4 Hz, 3 H, –SCH$_2$CH_3), 2.35 (q, J_{HH} = 7.3 Hz, 2 H, –SCH_2CH$_3$), 2.84 (dd, J_{HH} = 9.2, 2.1 Hz, 1 H, H$_a$), 3.79 (dd, J_{HH} = 13.8, 2.1 Hz, 1 H, H$_b$), 8.17 (dd, J_{HH} = 9.2, 13.8 Hz, 1 H, H$_c$). ^{13}C NMR (67.9 MHz, CD$_2$Cl$_2$): δ_C 18.2 (q, J_{CH} = 128.8 Hz, –SCH$_2$$CH_3$), 34.4 (t, J_{CH} = 145.4 Hz, –SCH$_2$CH$_3$), 73.9 (t, J_{CH} = 158.7 Hz, CH$_2$=CH–), 157.2 (d, J_{CH} = 150.7 Hz, CH$_2$=CH–), 209.6, 210.7 (s's, carbonyl C's).

A similar reaction between CH$_2$=CHHgBr and [Et$_3$NH][(μ-CO)(μ-PhS)Fe$_2$(CO)$_6$] in THF gave (μ-CH$_2$=CH)(μ-PhS)Fe$_2$(CO)$_6$: red-orange solid; mp 66–67 °C; 35% yield. Anal. Calcd for $C_{14}H_8Fe_2O_6S$: C, 40.43; H, 1.94. Found: C, 40.49; H, 2.01. ^{1}H NMR (90 MHz, acetone-d_6): δ 3.10 (dd, J_{HH} = 14.1, 1.8 Hz, 1 H, H$_a$), 4.09 (dd, J_{HH} = 9.4, 1.8 Hz, 1 H, H$_b$), 7.24–7.52 (m, 5 H, aromtic H's), 8.17 (dd, J_{HH} = 9.4, 14.1 Hz, 1 H, H$_c$). ^{13}C NMR (67.9 MHz, CD$_2$Cl$_2$): δ_C 73.7 (t, J_{CH} = 159.8 Hz, CH$_2$=CH–), 128.2–140.5 (m, aromatic C's), 156.9 (d, J_{CH} = 150.6 Hz, CH$_2$=CH–), 210.4, 210.6 (s's, carbonyl C's).

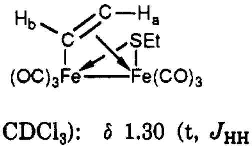
From a second band, also eluted with pentane, was obtained (μ-PhS)$_2$Fe$_2$(CO)$_6$ in 38% yield.

Reaction of *trans*-β-Styrylmercuric Chloride with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The anion solution was generated on the same scale as in the experiment above. After 30 min, 1.10 g of *trans*-β-styrylmercuric chloride (3.24 mmol) was added to the stirred solution as a solid against a flow of nitrogen. The reaction mixture was stirred at room temperature for 24 h, and then the solvents were removed in vacuo to give a red residue. This was extracted with 60:40 pentane/CH$_2$Cl$_2$ and subjected to filtration chromatography on a pad of silicic acid (2 cm) packed in a 350-mL ground-glass fritted funnel. Elution with 60:40 pentane/CH$_2$Cl$_2$ gave one broad red-orange band. This residue was taken up in pentane and the solution rechromatographed on a pad of silicic acid (7 cm) with pentane as eluent. The first band to elute gave a red-orange crystalline solid, which was identified as the μ-σ,π-vinyl compound (μ-σ,π-*trans*-β-C$_6$H$_5$CH=CH)(μ-EtS)Fe$_2$(CO)$_6$ (0.62 g, 1.39 mmol, 47%):



Anal. Calcd for $C_{16}H_{12}Fe_2O_6S$: C, 43.28; H, 2.72. Found: C, 43.34; H, 2.77. ^{1}H NMR (90 MHz, CD$_2$Cl$_2$): δ 1.38 (m, 3 H, both isomers, –SCH$_2$CH_3), 2.40 (m, 2 H, both isomers, –SCH_2CH$_3$), 4.38 (d, J_{HH} = 13.5 Hz, 1 H, H$_a$), 7.28 (s, 5 H, aromatic H's), 8.50 (d, J_{HH} = 13.5 Hz, 1 H, H$_b$). ^{13}C NMR (67.9 MHz, CH$_2$Cl$_2$): δ_C 18.4 (q, J_{CH} = 129.3 Hz, –SCH$_2$$CH_3$), 34.4 (t, J_{CH} = 140.6 Hz, –SCH$_2$CH$_3$), 95.7 (d, J_{CH} = 158.7 Hz, C$_6$H$_5$CH=CH–), 126.4–129.5 (m, aromatic C's), 140.1 (s, ipso phenyl C's), 144.9 (d, J_{CH} = 147.5 Hz, C$_6$H$_5$$C$H=CH–), 210.1, 210.3 (s's, carbonyl C's).

Reaction of *trans*-ClCH=CHHgCl with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The anion solution was generated as in the experiments above. After 30 min, 1.00 g of *trans*-(β-chlorovinyl)mercuric chloride (3.36 mmol) was added to the stirred solution as a solid against a flow of nitrogen. The reaction mixture was stirred at room temperature for 10 h, and then the solvents were removed in vacuo to give a red oily residue. This was extracted with pentane and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground-glass fritted funnel. Elution with pentane gave one broad band. The resulting red, oily residue was taken up in pentane and was rechromaatographed on a silica gel column (30 × 300 mm) with pentane as eluent. Two red-orange bands that eluted close together were separated on this column. The first band gave a red-orange, unstable oil, which was identified as (μ-σ,π-*trans*-CHCl=CH)(μ-EtS)Fe$_2$(CO)$_6$ (0.26 g, 0.64 mmol, 21%):

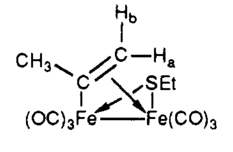


^{1}H NMR (90 MHz, CDCl$_3$): δ 1.30 (t, J_{HH} = 6.5 Hz, 3 H, –SCH$_2$CH_3), 2.31 (q, J_{HH} = 7.3 Hz, 2 H, –SCH_2CH$_3$), 4.34 (d, J_{HH} = 10.6 Hz, 1 H, H$_a$), 7.83 (d, J_{HH} = 10.5 Hz, 1 H, H$_b$). ^{13}C NMR (67.9 MHz, CDCl$_3$): δ_C 17.9 (q, J_{CH} = 129.4 Hz, –SCH$_2$$CH_3$), 34.0 (t, J_{CH} = 141.6 Hz, –SCH$_2$CH$_3$), 87.1 (d, J_{CH} = 200.0 Hz, =CHCl), 149.4 (d, J_{CH} = 154.5 Hz, –CH=CHCl), 208.3 (s, carbonyl C's). Mass spectrum (EI; *m/z* (relative intensity)): 402 (M$^+$, 9), 374 (M$^+$ – CO, 6), 346 (M$^+$ – 2CO, 12), 318 (M$^+$ – 3CO, 27), 290 (M$^+$ – 4CO, 36), 262 (M$^+$ – 5CO, 18), 234 (M$^+$ – 6CO, 26), 206 (Fe$_2$SC$_2$H$_3$Cl$^+$, 73), 180 (Fe$_2$(SH)(Cl)$^+$, 100), 144 (Fe$_2$S$^+$, 45).

Because of the instability of this material, a satisfactory elemental analysis could not be obtained. Attempted synthesis of a phosphine substitution product by the room-temperature reaction between this compound and triphenylphosphine gave only decomposition products. The mass spectrum of this compound, however, showed the presence of the correct parent ion and ions due to the loss of carbonyl ligand which exhibited the correct isotope pattern for a monochlorinated compound.

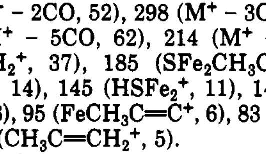
The second red-orange band gave a red-orange crystalline solid identified as the known compound (μ-EtS)$_2$Fe$_2$(CO)$_6$ (0.54 g, 1.34 mmol, 44%).

Reaction of CH$_2$=C(CH$_3$)HgBr with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The standard [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (2.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, CH$_2$=C(CH$_3$)HgBr (1.09 g, 3.40 mmol) was added as a solid. An immediate reaction ensued with gas evolution and a color change to deep red-brown. After the reaction mixture had been stirred for 2 h at room temperature, the solution had changed to bright red and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of three orange-red products. The solvent was removed in vacuo to yield a red oil, which was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator gave a red oil, which was purified by medium-pressure chromatography. Pentane eluted a red-orange band, which gave 0.23 g (0.59 mmol, 20%) of (μ-σ,π-CH$_3$C=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$ as a slightly air-sensitive red oil:



Anal. Calcd for $C_{11}H_{10}Fe_2O_6S$: C, 34.59; H, 2.64. Found: C, 34.99; H, 2.64. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.32 (t, J = 7.55 Hz, 3 H, $SCH_2C\mathit{H}_3$), 2.30 (q, J = 7.42 Hz, 2 H, $SC\mathit{H}_2CH_3$), 2.42 (d, $^2J_{HH}$ = 2.34 Hz, 1 H, $CH_3C{=}C\mathit{H}_aH_b$ endo), 2.61 (s, 3 H, $C\mathit{H}_3C{=}CH_aH_b$), 3.48 (d, $^2J_{HH}$ = 2.22 Hz, 1 H, $CH_3C{=}CH_a\mathit{H}_b$ exo). ^{13}C NMR ($CDCl_3$ 75.4 MHz): δ_C 17.98 (qt, J_{CH} = 128.1 Hz, $^2J_{CH}$ = 5.4 Hz, $SCH_2\mathit{C}H_3$), 34.28 (tq, J_{CH} = 139.8 Hz, $^2J_{CH}$ = 5.1 Hz, $S\mathit{C}H_2CH_3$), 42.98 (qt, J_{CH} = 127.3 Hz, $^3J_{CH}$ = 8.2 Hz, $\mathit{C}H_3C{=}CH_2$), 72.17 (tq, J_{CH} = 158.1 Hz, $^3J_{CH}$ = 6.4 Hz, $CH_3C{=}\mathit{C}H_2$), 183.12 (t, $^2J_{CH}$ = 5.0 Hz, $CH_3\mathit{C}{=}CH_2$), 210.40 (s, terminal *C*O's). Mass spectrum (EI; m/z (relative intensity)): 382 (M^+, 36), 354 ($M^+ - CO$, 27), 326 ($M^+ - 2CO$, 52), 298 ($M^+ - 3CO$, 47), 270 ($M^+ - 4CO$, 69), 242 ($M^+ - 5CO$, 62), 214 ($M^+ - 6CO$, 100), 186 ($HSFe_2CH_3C{=}CH_2^+$, 37), 185 ($SFe_2CH_3C{=}CH_2^+$, 7), 184 ($SFe_2CH_3C{=}CH^+$, 14), 145 ($HSFe_2^+$, 11), 144 (SFe_2^+, 79), 97 ($FeCH_3C{=}CH_2^+$, 8), 95 ($FeCH_3C{=}C^+$, 6), 83 ($FeHC{=}CH_2^+$, 6), 57 (FeH^+, 10), 41 ($CH_3C{=}CH_2^+$, 5).

Further elution with pentane gave 0.14 g (0.35 mmol, 23% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$ as an orange-red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Continued elution with pentane then gave 0.41 g (1.00 mmol, 34%) of (μ-$CH_2{=}C(CH_3)C{=}O$)(μ-EtS)Fe$_2$(CO)$_6$ (a mixture of two inseparable isomers) as a slightly air-sensitive red oil. Due to the facile loss of carbon monoxide, analytically pure (μ-$CH_2{=}C(CH_3)C{=}O$)(μ-EtS)Fe$_2$(CO)$_6$ could not be obtained:



^1H NMR (250 MHz, $CDCl_3$): δ 1.32 (t, J = 7.27 Hz, 0.8 H, $SCH_2C\mathit{H}_3$, minor isomer), 1.45 (s, 2.2 H, $H_2C{=}CC\mathit{H}_3C{=}O$, major isomer), 1.50 (t, J = 7.30 Hz, 2.2 H, $SCH_2C\mathit{H}_3$, major isomer), 1.52 (s, 0.8 H, $H_2C{=}CC\mathit{H}_3C{=}O$, minor isomer), 2.04–2.26 and 2.54–2.70 (complex m, 2 H, $SC\mathit{H}_2CH_3$, both isomers), 5.86 (d, $^2J_{HH}$ = 1.85 Hz, 0.7 H, $\mathit{H}_aH_bC{=}CCH_3C{=}O$ endo, major isomer), 5.90 (s, 0.7 H, $H_a\mathit{H}_bC{=}CCH_3C{=}O$ exo, major isomer), 5.92 (d, $^2J_{HH}$ = 1.79 Hz, 0.3 H, $\mathit{H}_aH_bC{=}CCH_3C{=}O$ endo, minor isomer), 5.96 (s, 0.3 H, $H_a\mathit{H}_bC{=}CCH_3C{=}O$ exo, minor isomer). Isomer ratio (major:minor): 2.8:1.0. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 16.68 (q, J_{CH} = 128.7 Hz, $H_2C{=}C\mathit{C}H_3C{=}O$, minor isomer), 16.85 (q, J_{CH} = 122.7 Hz, $H_2C{=}C\mathit{C}H_3C{=}O$, major isomer), 17.84 (q, J_{CH} = 128.6 Hz, $SCH_2\mathit{C}H_3$, minor isomer), 18.38 (q, J_{CH} = 127.7 Hz, $SCH_2\mathit{C}H_3$, major isomer), 26.41 (t, J_{CH} = 143.0 Hz, $S\mathit{C}H_2CH_3$, minor isomer), 32.96 (t, J_{CH} = 140.3 Hz, $S\mathit{C}H_2CH_3$, major isomer), 131.12 (t, J_{CH} = 158.5 Hz, $H_2\mathit{C}{=}CCH_3C{=}O$, both isomers), 151.86 (s, $H_2C{=}\mathit{C}CH_3C{=}O$, both isomers), 207.80, 209.48, 209.61, 210.18, 210.40, 210.59, 211.56, and 212.17 (all s, terminal *C*O's, both isomers), 290.15 (s, acyl $\mathit{C}{=}O$, major isomer), 293.03 (s, acyl $\mathit{C}{=}O$, minor isomer). Mass spectrum (EI; m/z (relative intensity)): 410 (M^+, 9), 382 ($M^+ - CO$, 20), 354 ($M^+ - 2CO$, 28), 326 ($M^+ - 3CO$, 43), 298 ($M^+ - 4CO$, 38), 270 ($M^+ - 5CO$, 57), 242 ($M^+ - 6CO$, 96), 240 ($M^+ - 6CO - 2H$, 23), 214 ($HSFe_2CH_3C{=}CH_2C{=}O^+$, 66), 213 ($HSFe_2CH_3C{=}CHC{=}O^+$ 7), 212 ($HSFe_2CH_3C{=}CC{=}O^+$, 46), 186 ($HSFe_2CH_3C{=}CH_2^+$, 44), 185 ($HSFe_2CH_3C{=}CH+$, 11), 184 ($HSFe_2CH_3C{=}C^+$, 16), 145 ($HSFe_2^+$, 43), 144 (SFe_2^+, 100), 142 (18), 71 (26), 69 ($CH_3C{=}CH_2C{=}O^+$, 25), 57 (FeH^+, 36), 56 (Fe^+, 18), 41 ($CH_3C{=}CH_2^+$, 30), 39 ($CH_3C{=}C^+$, 19).

Reaction of *trans*-$CH_3CH{=}CHHgBr$ with [Et_3NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The standard [Et_3NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $CH_3CH{=}CHHgBr$ (0.65 g, 2.01 mmol) was added as a solid. An immediate reaction ensued with gas evolution and a color change to deep red-brown. After 2 h at room temperature, TLC indicated the formation of three orange-red products. The solvent was removed in vacuo to yield a red oil, which was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent gave a red oil, which was purified by medium-pressure chromatography. Pentane eluted a red-orange band, which gave 0.38 g (0.99 mmol, 50%) of (μ-σ,π-$CH{=}CHCH_3$)(μ-EtS)Fe$_2$(CO)$_6$ as a slightly air-sensitive red oil, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[1e] Further elution with pentane gave 0.09 g (0.22 mmol, 22% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$ as an orange-red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Continued elution with pentane then gave 0.20 g (0.49 mmol, 25%) of (μ-$CH_3CH{=}CHC{=}O$)(μ-EtS)Fe$_2$(CO)$_6$ as an air-sensitive red oil, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[1e]

Reaction of *cis*-$CH_3CH{=}C(CH_3)HgBr$ with [Et_3NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The standard [Et_3NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (2.99 mmol) was generated at room temperature. Against a positive flow of nitrogen, $CH_3CH{=}C(CH_3)HgBr$ (1.02 g, 3.04 mmol) was added as a solid. An immediate reaction ensued with gas evolution and a color change to deep red-brown. After the reaction mixture had been stirred for 2 h at room temperature, TLC indicated the formation of three orange-red products. The solvent was removed in vacuo to yield a red oil, which was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent gave a red oil, which was purified by medium-pressure chromatography. Pentane eluted a red-orange band, which gave 0.15 g (0.39 mmol, 13%), of (μ-σ,π-$CH_3C{=}CHCH_3$)(μ-EtS)Fe$_2$(CO)$_6$ as a slightly air-sensitive red oil. Anal. Calcd for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05. Found: C, 36.00; H, 3.44. ^1H NMR (250 MHz, $CDCl_3$): δ 1.32 (t, J = 7.45 Hz, 3 H, $SCH_2C\mathit{H}_3$), 1.66 (d, J = 6.09 Hz, 3 H, $CH_3C{=}CHC\mathit{H}_3$), 2.33 (q, J = 7.40 Hz, 2 H, $SC\mathit{H}_2CH_3$), 2.57 (s, 3 H, $C\mathit{H}_3C{=}CHCH_3$), 3.05 (q, J = 6.09 Hz, 1 H, $CH_3C{=}C\mathit{H}CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 18.03 (q, J_{CH} = 128.0 Hz, $SCH_2\mathit{C}H_3$), 32.37 (q, J_{CH} = 125.6 Hz, $CH_3C{=}CH\mathit{C}H_3$), 34.01 (t, J_{CH} = 140.6 Hz, $S\mathit{C}H_2CH_3$), 34.83 (q, J_{CH} = 124.5 Hz, $\mathit{C}H_3C{=}CHCH_3$), 88.27 (d, J_{CH} = 156.3 Hz, $CH_3C{=}\mathit{C}HCH_3$), 176.30 (s, $CH_3\mathit{C}{=}CHCH_3$), 209.62 and 210.33 (both s, terminal *C*O's). Mass spectrum (EI; m/z (relative intensity)): 396 (M^+, 25), 368 ($M^+ - CO$, 19), 340 ($M^+ - 2CO$, 43), 312 ($M^+ - 3CO$, 36), 284 ($M^+ - 4CO$, 64), 256 ($M^+ - 5CO$, 51), 228 ($M^+ - 6CO$, 100), 200 ($HSFe_2CH_3C{=}CHCH_3^+$, 46), 199 ($SFe_2CH_3C{=}CHCH_3^+$, 6), 198 ($SFe_2CH_3C{=}CCH_3^+$, 32), 172 ($HSFe_2HC{=}CH_2^+$, 7), 171 ($SFe_2HC{=}CH_2^+$, 5), 170 ($SFe_2HC{=}CH^+$, 12), 145 ($HSFe_2^+$, 13), 144 (SFe_2^+, 63), 55 ($CH_3C{=}CHCH_3^+$, 3), 54 ($CH_3C{=}CCH_3^+$, 2), 41 ($C_3H_5^+$, 1), 39 ($C_3H_3^+$, 1).

Further elution with pentane gave 0.13 g (0.31 mmol, 20% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$ as an orange-red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Continued elution with pentane then gave 0.58 g (1.38 mmol, 46%) of (μ-$CH_3CH{=}C(CH_3)C{=}O$)(μ-EtS)Fe$_2$(CO)$_6$ (a mixture of two inseparable isomers) as a slightly air-sensitive red oil. Due to the facile loss of carbon monoxide, analytically pure (μ-$CH_3CH{=}C(CH_3)C{=}O$)(μ-EtS)Fe$_2$(CO)$_6$ could not be obtained. ^1H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, J = 7.46 Hz, 1.1 H, $SCH_2C\mathit{H}_3$, minor isomer), 1.34 (s, 1.9 H, $CH_3CH{=}C(C\mathit{H}_3)C{=}O$, major isomer), 1.39 (s, 1.1 H, $CH_3CH{=}C(C\mathit{H}_3){=}O$, minor isomer), 1.50 (t, J = 7.33 Hz, 1.9 H, $SCH_2C\mathit{H}_3$, major isomer), 1.78 (s, 1.9 H, $C\mathit{H}_3CH{=}C(CH_3)C{=}O$, major isomer), 1.87 (s, 1.1 H, $C\mathit{H}_3CH{=}C(CH_3)C{=}O$, minor isomer), 2.51–2.72 (complex m, 2 H, $SC\mathit{H}_2CH_3$, both isomers), 4.94–5.02 (complex m, 0.6 H, $CH_3C\mathit{H}{=}C(CH_3)C{=}O$, major isomer), 6.62–6.70 (complex m, 0.4 H, $CH_3C\mathit{H}{=}C(CH_3)C{=}O$, minor isomer). Isomer ratio (major:minor): 1.7:1.0. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.57 (q, J_{CH} = 126.6 Hz, $\mathit{C}H_3CH{=}C(CH_3)C{=}O$, major isomer), 15.01 (q, J_{CH} = 123.8 Hz, $\mathit{C}H_3CH{=}C(CH_3)C{=}O$, minor isomer), 17.76 (q, J_{CH} = 123.1 Hz, $SCH_2\mathit{C}H_3$, minor isomer), 18.32 (q, J_{CH} = 127.20 Hz, $SCH_2\mathit{C}H_3$, major isomer), 19.35 (q, J_{CH} = 126.2 Hz, $CH_3CH{=}C(\mathit{C}H_3)C{=}O$, both isomers), 26.44 (t, J_{CH} = 138.8 Hz, $S\mathit{C}H_2CH_3$, minor isomer), 33.12 (t, J_{CH} = 143.2 Hz, $S\mathit{C}H_2CH_3$, major isomer), 120.90 (d, J_{CH} = 153.6 Hz, $CH_3\mathit{C}H{=}C(CH_3)C{=}O$, major isomer), 124.30 (d, J_{CH} = 162.5 Hz, $CH_3\mathit{C}H{=}C(CH_3)C{=}O$, minor isomer), 147.04 (s, $CH_3CH{=}\mathit{C}(CH_3)C{=}O$, both isomers), 208.05, 209.33, 209.69, 210.70, 210.98, 212.02, 212.56 (all s, terminal *C*O's, both isomers), 285.88 (s, aryl $\mathit{C}{=}O$, minor isomer), 299.32 (s, acyl $\mathit{C}{=}O$, major isomer). Mass spectrum (EI; m/z (relative intensity)): 424 (M^+, 9), 396 ($M^+ - CO$, 11), 368 ($M^+ - 2CO$, 22), 340 ($M^+ - 3CO$, 33), 312 ($\mathrm{M^+}$ - 4CO, 35), 284 ($\mathrm{M^+}$ - 5CO, 51), 256 ($\mathrm{M^+}$ - 6CO, 100), 228 ($\mathrm{HSFe_2CH_3C{=}CHCH_3C{=}O^+}$, 52), 226 ($\mathrm{SFe_2CH_3C{=}CCH_3C{=}O^+}$, 16), 200 ($\mathrm{HSFe_2CH_3C{=}CHCH_3^+}$, 39), 198 ($\mathrm{SFe_2CH_3C{=}CCH_3^+}$, 28), 183 ($\mathrm{SFe_2C{=}CCH_3^+}$, 7), 170 ($\mathrm{HSFe_2C{=}CH^+}$, 8), 145 ($\mathrm{HSFe_2^+}$, 16), 144 ($\mathrm{SFe_2^+}$, 44), 55 ($\mathrm{CH_3C{=}CHCH_3^+}$, 6), 39 ($\mathrm{C{=}CCH_3^+}$, 6).

Decarbonylation Reactions. $(\mu\text{-}\mathrm{CH_2{=}C(CH_3)C{=}O})(\mu\text{-}\mathrm{EtS})\mathrm{Fe_2(CO)_6}$. In a 100-mL round-bottomed flask, $(\mu\text{-}\mathrm{H_2C{=}C(CH_3)C{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (0.014 g, 0.035 mmol) was dissolved in 10 mL of THF. This deep red solution was cannulated into a dry and degassed 100-mL Schlenk flask equipped with a stirbar and a rubber septum and stirred at room temperature. After 18 h, the reaction mixture was still deep red and TLC indicated that only starting material was present. At this point, the reaction mixture waas cannulated into a dry and degassed 100-mL three-necked round-bottomed flask equipped with a reflux condenser, a gas inlet adapter, stirbar, and a rubber septum and then heated at reflux. After 1.5 h of heating, the reaction mixture was still deep red but TLC indicated complete conversion to the corresponding vinyl compound. The solvent was removed in vacuo to yield a red oil, which was purified by filtration chromatography. Pentane eluted a red band, which gave 0.012 g (0.032 mmol, 90%) of $(\mu\text{-}\sigma,\pi\text{-}\mathrm{CH_3C{=}CH_2})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample (above).

$(\mu\text{-}\textit{trans}\text{-}\mathrm{CH_3CH{=}CHC{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$. $(\mu\text{-}\mathrm{CH_3CH{=}CHC{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (0.11 g, 0.27 mmol) was dissolved in 10 mL of THF. This deep red solution was cannulated into a dry and degassed 100-mL Schlenk flask equipped with a stirbar and a rubber septum and stirred at room temperature. After 14 h, the reaction mixture was still deep red and TLC indicated that only starting material was present. The reaction mixture was transferred to another flask (as above) and heated at reflux. After 4 h of heating, the reaction mixture was still deep red but TLC indicated complete conversion to the corresponding vinyl compound. The solvent was removed in vacuo to yield a red oil, which was purified by filtration chromatography. Pentane eluted a red band, which gave 0.10 g (0.25 mmol, 93%) of $(\mu\text{-}\sigma,\pi\text{-}\mathrm{CH{=}CHCH_3})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[1e]

$(\mu\text{-}\mathrm{CH_3CH{=}C(CH_3)C{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$. $(\mu\text{-}\mathrm{CH_3CH{=}C(CH_3)C{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (0.17 g, 0.40 mmol) was dissolved in 10 mL of THF. This deep red solution was cannulated into a dry and degassed 100-mL Schlenk flask equipped with a stirbar and a rubber septum and stirred at room temperature. After 18 h, the reaction mixture was still deep red and TLC indicated that only starting material was present. At this point, the reaction mixture was transferred to another flask (as above) and heated at reflux. After 46 h of heating, the reaction mixture was still deep red but TLC indicated complete conversion to the corresponding vinyl compound. The solvent was removed in vacuo to yield a red oil, which was purified by filtration chromatography. Pentane eluted a red band, which gave 0.12 g (0.29 mmol, 73%) of $(\mu\text{-}\sigma,\pi\text{-}\mathrm{CH_3C{=}CHCH_3})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample (above).

Reaction of $\mathrm{(CH_3)_2C{=}CHHgBr}$ with $[\mathrm{Et_3NH}][(\mu\text{-CO})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}]$. The anion was generated with use of 1.50 g of $\mathrm{Fe_3(CO)_{12}}$ (2.98 mmol), 0.31 g of $\mathrm{Et_3N}$ (3.01 mmol), and 0.18 g of EtSH (2.97 mmol) in 50 mL of THF at room temperature. After 30 min 1.00 g of isobutenylmercuric bromide (2.98 mmol) was added to the stirred solution as a solid against a flow of nitrogen. The reaction mixture was stirred at room temperature for 16 h, and then the solvents were removed in vacuo to give a red solid residue. This was extracted with pentane and subjected to filtration chromatography on a pad of silicic acid (7 cm) packed in a 350-mL ground-glass fritted funnel. Elution with pentane first gave two red-orange bands, which were collected together to give a crystalline sample that was identified as the two isomers of the known compound $(\mu\text{-EtS})_2\mathrm{Fe_2(CO)_6}$ (0.75 g, 0.65 mmol, 22%). A third red band then eluted to give a red oil, which was identified as the acyl compound $(\mu\text{-}\mathrm{(CH_3)_2C{=}CHC{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (0.75 g, 1.77 mmol, 59%). ^{1}H NMR spectroscopy showed this to be a mixture of isomers, 2:1 e/a. A satisfactory elemental analysis could not be obtained for this compound. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 1.34 (t, J_{HH} = 7.3 Hz, e-isomer, $-\mathrm{SCH_2C}H_3$), 1.48 (t, J_{HH} = 7.3 Hz, a-isomer, $-\mathrm{SCH_2C}H_3$), 1.60 (s, e-isomer, *trans*-$\mathrm{C}H_3\mathrm{C{=}CH}$–), 1.67 (s, a-isomer, *trans*-$\mathrm{C}H_3\mathrm{C{=}CH}$–), 1.70 (s, e-isomer, *cis*-$\mathrm{C}H_3\mathrm{C{=}CH}$–), 1.73 (s, a-isomer, *cis*-$\mathrm{C}H_3\mathrm{C{=}CH}$–), 2.10–2.68 (m, 2 H, both isomers, $-\mathrm{SC}H_2\mathrm{CH_3}$), 6.30 (s, e-isomer, $\mathrm{(CH_3)_2C{=}C}H$–), 6.38 (s, a-isomer, $\mathrm{(CH_3)_2C{=}C}H$–). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_{C} 17.9 (q, J_{CH} = 123.0 Hz, a-isomer, $-\mathrm{SCH_2C}H_3$), 18.4 (q, J_{CH} = 125.2 Hz, e-isomer, $-\mathrm{SCH_2C}H_3$), 21.5 (overlapping q's J_{CH}'s could not be determined accurately, both isomers, *trans*-$C\mathrm{H_3C{=}CH}$–), 26.8 (q, J_{CH} could not be determined, a-isomer, *cis*-$C\mathrm{H_3C{=}CH}$–), 27.0 (q, J_{CH} = 124.9 Hz, e-isomer, *cis*-$C\mathrm{H_3C{=}CH}$–), 33.0 (t, J_{CH} = 141.0 Hz, $-\mathrm{SC}H_2\mathrm{CH_3}$), 136.4 (d, J_{CH} = 158.0 Hz, e-isomer, $\mathrm{(CH_3)_2C{=}}C\mathrm{H}$–), 136.6 (d, J_{CH} = 158.0 Hz, a-isomer, $\mathrm{(CH_3)_2C{=}}C\mathrm{H}$–), 147.2 (s, both isomers [?], $\mathrm{(CH_3)_2}C\mathrm{{=}CH}$–), 207.8, 209.3, 209.8, 210.4, 212.1 (s's, carbonyl C's), 293.8, 286.6 (s's, $-\mathrm{C{=}CH}C\mathrm{{=}O}$). Mass spectrum (EI; m/z (relative intensity)): 396 ($\mathrm{M^+}$ - CO, 1), 368 ($\mathrm{M^+}$ - 2CO, 2), 340 ($\mathrm{M^+}$ - 3CO, 7), 312 ($\mathrm{M^+}$ - 4CO, 4), 284 ($\mathrm{M^+}$ - 5CO, 8), 256 ($\mathrm{M^+}$ - 6CO, 18), 228 ($\mathrm{M^+}$ - 7CO, 17), 200 ($\mathrm{HSFe_2C_4H_7^+}$, 24), 144 ($\mathrm{Fe_2S^+}$, 55), 83 ($\mathrm{C_5H_7O^+}$, 100), 55 ($\mathrm{C_5H_7^+}$, 97).

The triphenylphosphine derivative was prepared.

A solution of 0.22 g of triphenylphosphine (0.85 mmol) in THF (10 mL) was added via cannula to a stirred solution of 0.35 g of $(\mu\text{-}\mathrm{(CH_3)_2C{=}CHC{=}O})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (0.83 mmol) in THF (10 mL) at room temperature, and the flask was rinsed with THF (5 mL) to ensure complete transfer of the triphenylphosphine to the iron complex containing solution. This reaction mixture was stirred at room temperature for 4 h. The solution changed from red-orange to dark red. The solvents were removed in vacuo. The residue was taken up in 70:30 pentane/$\mathrm{CH_2Cl_2}$ (v/v) and the solution chromatographed on a silicic acid pad packed in a 150-mL glass fritted funnel. The column was eluted first with pentane to remove unreacted starting material and then with 70:30 pentane/$\mathrm{CH_2Cl_2}$ (v/v) to give one dark red band. This give a red solid, which was recrystallized from pentane to give a red crystalline product (mp 129–130 °C). This was identified as the triphenylphosphine adduct (0.465 g, 0.72 mmol, 87%). Anal. Calcd for $\mathrm{C_{30}H_{27}Fe_2O_6PS}$: C, 57.74; H, 4.14. Found: C, 58.13; H, 4.26. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 1.16 (t, J_{HH} = 7.3 Hz, 3 H, $-\mathrm{SCH_2C}H_3$), 1.17 (s, 3 H, *cis*-$\mathrm{C}H_3\mathrm{C{=}}$), 1.63 (s, 3 H, *trans*-$\mathrm{C}H_3\mathrm{C{=}}$), 2.00–2.30 (m, 2 H, $-\mathrm{SC}H_2\mathrm{CH_3}$), 6.36 (s, 1 H, $-\mathrm{(CH_3)_2C{=}C}H\mathrm{C{=}O}$), 7.32–7.66 (m, 15 H, aromatic H's). ^{13}C NMR (67.9 MHz, $\mathrm{CDCl_3}$): δ_{C} 15.0–25.0 (complex m, $-\mathrm{S}C\mathrm{H_2}C\mathrm{H_3}$ and $(C\mathrm{H_3})_2\mathrm{C{=}CH}$–), 127.2–148.0 (m, aromatic and vinyl C's), 210.2, 214.3, 215.8, 217.1, 217.9 (all s's, carbonyl C's), 285.3 (s, $\mathrm{(CH_3)_2C{=}CH}C\mathrm{{=}O}$). ^{31}P NMR (36.2 MHz, $\mathrm{CD_2Cl_2}$): δ_{P} 52.1.

Reaction of $\mathrm{CH_3CO_2CH_2CH_2HgCl}$ with $[\mathrm{Et_3NH}][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})\mathrm{Fe_2(CO)_6}]$. The standard $[\mathrm{Et_3NH}][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})\mathrm{Fe_2(CO)_6}]$ reagent solution (2.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $\mathrm{CH_3CO_2CH_2CH_2HgCl}$ (1.11 g, 3.45 mmol) was added as a solid. An immediate reaction ensued with brisk gas evolution and a color change to brighter red. After the reaction mixture had been stirred for 3 h at room temperature, the solution had changed to a deeper red-brown and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of two orange-red products. The solvent was removed in vacuo to yield a brown-red solid, which was purified by filtration chromatography. Pentane eluted an orange-red band, which gave 0.39 g (0.86 mmol, 57% based on S) of $(\mu\text{-}t\text{-BuS})_2\mathrm{Fe_2(CO)_6}$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. Further elution with pentane/$\mathrm{CH_2Cl_2}$ (2:1 v/v) gave 0.51 g (1.19 mmol, 40%) of $(\mu\text{-}\mathrm{CH_3CO_2})(\mu\text{-}t\text{-BuS})\mathrm{Fe_2(CO)_6}$ as an orange-red solid after recrystallization from pentane; mp 34.0–35.0 °C. Anal. Calcd for $\mathrm{C_{12}H_{12}Fe_2O_8S}$: C, 33.68; H, 2.83. Found: C, 33.66; H, 2.87. IR ($\mathrm{CCl_4}$, $\mathrm{cm^{-1}}$): 2960 (w), 2925 (w), 2900 (w), 2860 (w), 1548 (w), 1439 (m), 1368 (w), 1155 (w), 625 (w), 600 (w). Terminal carbonyl region ($\mathrm{CCl_4}$, $\mathrm{cm^{-1}}$): 2080 (s), 2050 (vs), 2015 (vs), 1994 (vs), 1936 (vw). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.56 (s, 3 H, $\mathrm{O_2CC}H_3$), 1.58 (s, 9 H, $\mathrm{SC(C}H_3)_3$). ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$): δ_{C} 23.72 (q, J_{CH} = 129.2 Hz, $\mathrm{O_2C}C\mathrm{H_3}$), 34.73 (q, J_{CH} = 128.1 Hz, $\mathrm{SC(}C\mathrm{H_3)_3}$), 49.15 (s, $\mathrm{S}C\mathrm{(CH_3)_3}$), 187.00 (s, $\mathrm{O_2}C\mathrm{CH_3}$), 204.97, 210.30, 213.4 (all s, broad, terminal CO's). Mass spectrum (EI; m/z (relative intensity)): 428 ($\mathrm{M^+}$, 15), 400 ($\mathrm{M^+}$ - CO, 34), 372 ($\mathrm{M^+}$ - 2CO, 51), 344 ($\mathrm{M^+}$ - 3CO, 52), 316 ($\mathrm{M^+}$ - 4CO, 63), 288 ($\mathrm{M^+}$ - 5CO, 66), 260 ($\mathrm{M^+}$ - 6CO, 100), 204 ($\mathrm{HSFe_2O_2CCH_3^+}$, 100), 203 ($\mathrm{SFe_2O_2CCH_3^+}$, 98), 202 ($\mathrm{SFe_2O_2CCH_2^+}$, 66), 176 ($\mathrm{HSFe_2OCH_3^+}$, 54), 161 ($\mathrm{HSFe_2O^+}$, 82), 145 ($\mathrm{HSFe_2^+}$, 19), 144

(SFe_2^+, 53), 60 ($CH_3CO_2H^+$, 18), 57 (*t*-Bu$^+$, 60), 42 ($C_3H_6^+$, 51), 41 ($C_3H_5^+$, 93), 40 ($C_3H_4^+$, 10), 39 ($C_3H_3^+$, 40).

The same procedure was used to effect the reaction of $CH_3CO_2CH_2CH_2HgCl$ with $[Et_3NH][(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]$. TLC indicated the formation of two orange-red products. The solvent was removed in vacuo to yield an orange-red solid, which was purified by filtration chromatography. Pentane eluted an orange-red band, which gave 0.45 g (1.11 mmol, 72% based on S) of $(\mu\text{-EtS})_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Further elution with pentane/CH_2Cl_2 (2:1 v/v) gave 0.34 g (0.84 mmol, 28%) of $(\mu\text{-}CH_3CO_2)(\mu\text{-EtS})Fe_2(CO)_6$ as an orange-red solid after recrystallization from pentane; mp 50.0–51.0 °C. Anal. Calcd for $C_{10}H_8Fe_2O_8S$: C, 30.03; H, 2.02. Found: C, 30.13; H, 2.14. IR (CCl_4, cm^{-1}): 2965 (m), 2930 (m), 2870 (w), 2860 (w), 1551 (m), 1441 (s), 1380 (w), 1354 (w), 1260 (m), 1050 (w), 970 (w), 700 (m), 628 (s), 595 (m, br). Terminal carbonyl region (CCl_4, cm^{-1}): 2085 (s), 2055 (vs), 2020 (vs), 1995 (vs), 1938 (vw). ^1H NMR (300 MHz, $CDCl_3$): δ 1.57 (s, 3 H, O_2CCH_3), 1.60 (t, J = 7.4 Hz, 3 H, SCH_2CH_3), 2.66 (q, J = 7.3 Hz, 2 H, SCH_2CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 18.54 (q, J_{CH} = 127.3 Hz, SCH_2CH_3), 23.38 (q, J_{CH} = 129.6 Hz, O_2CCH_3), 31.02 (t, J_{CH} = 139.9 Hz, SCH_2CH_3), 187.40 (q, $^2J_{CH}$ = 6.1 Hz, O_2CCH_3), 208.84 and 209.65 (both s, terminal CO's). Mass spectrum (EI; m/z (relative intensity)): 400 (M^+, 3), 372 ($M^+ - CO$, 10), 344 ($M^+ - 2CO$, 14), 316 ($M^+ - 3CO$, 13), 288 ($M^+ - 4CO$, 18), 260 ($M^+ - 5CO$, 16), 232 ($M^+ - 6CO$, 55), 206 ($H_3SFe_2O_2CCH_3^+$, 12), 205 ($H_2SFe_2O_2CCH_3^+$, 11), 204 ($HSFe_2O_2CCH_3^+$, 100), 203 ($SFe_2O_2CCH_3^+$, 22), 202 ($SFe_2O_2CCH_2^+$, 14), 178 ($H_3SFe_2OCH_3^+$, 11), 177 ($H_2SFe_2OCH_3^+$, 5), 176 ($HSFe_2OCH_3^+$, 16), 154 ($Fe_2OCCH_2^+$, 61), 145 ($HSFe_2^+$, 4), 144 (SFe_2^+, 6), 122 (81), 121 (20), 115 ($FeO_2CCH_3^+$, 23), 94 (62), 93 (36), 89 ($HSFe^+$, 45), 66 ($H_2S_2^+$, 75), 64 (S_2^+, 23), 62 ($CH_3CH_2SH^+$, 46), 61 ($CH_3CH_2S^+$, 93), 60 ($CH_3CO_2H^+$, 65), 59 ($CH_3CO_2^+$, 23), 56 (Fe^+, 14), 45 (CO_2H^+, 55), 44 (CO_2^+, 32), 43 (CH_3CO^+, 70).

A similar reaction of $CH_3O_2CCH_2CH_2HgCl$ with $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$ gave the usual balls of mercury and the gray-white precipitate, but the only iron carbonyl product was $(\mu\text{-PhS})_2Fe_2(CO)_6$, which was isolated in 100% yield, based on S.

Reaction of Mercuric Acetate with $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$. The standard $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ reagent solution (1.99 mmol) was generated at room temperature. Against a positive flow of nitrogen, $Hg(O_2CCH_3)_2$ (0.65 g, 2.05 mmol) was added as a solid. An immediate reaction ensued with brisk gas evolution and a color change to deep red. After the reaction mixture had been stirred for 20 h at room temperature, the solution had changed to bright red and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of two orange-red products. The solvent was removed in vacuo to yield an orange-red solid, which was purified by filtration chromatography. Pentane eluted an orange-red band, which gave 0.19 g (0.41 mmol, 40% based on S) of $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Further elution with pentane/CH_2Cl_2 (2:1 v/v) gave 0.48 g (1.13 mmol, 57%) of $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ as an orange-red solid after recrystallization from pentane. Its identity was verified by comparing its ^1H NMR spectrum with that of an authentic sample (above).

The following other μ-carboxylato complexes were prepared by this procedure.

$(\mu\text{-}CH_3CO_2)(\mu\text{-EtS})Fe_2(CO)_6$: 42% yield, together with byproduct $(\mu\text{-EtS})_2Fe_2(CO)_6$ (57%).

$(\mu\text{-}CH_3CO_2)(\mu\text{-PhS})Fe_2(CO)_6$: orange-red solid; mp 101.0–103.0 °C (from pentane) in 14% yield (together with $(\mu\text{-PhS})_2Fe_2(CO)_6$ in 84% yield). The $\mu\text{-}CH_3CO_2$ complex was a mixture of e,a and e,e isomers. Anal. Calcd for $C_{14}H_8Fe_2O_8S$: C, 37.54; H, 1.80. Found: C, 37.67; H, 1.89. ^1H NMR (250 MHz, acetone-d_6): δ 0.90 (s, 1.4 H, O_2CCH_3, minor isomer), 1.63 (s, 1.6 H, O_2CCH_3, major isomer), 7.25–7.40 and 7.69–7.72 (m, C_6H_5, both isomers). Isomer ratio (major:minor): 1.1:1.0. ^{13}C NMR (75.4 MHz, C_6D_6): δ_C 22.08 (q, J_{CH} = 130.1 Hz, O_2CCH_3, minor isomer), 22.98 (q, J_{CH} = 130.3 Hz, O_2CCH_3, major isomer), 126.18–138.29 (m, SC_6H_5, both isomers), 186.86 (s, O_2CCH_3, minor isomer), 188.31 (s, O_2CCH_3, major isomer), 203.88, 204.40, 207.96, 208.75, 213.58, 214.07 (all s, broad, terminal CO's).

The following compounds were prepared with use of mercuric propionate.

$(\mu\text{-}EtCO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$: orange-red solid; mp 53.0–54.0 °C; 44% yield (together with $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$ in 56% yield). Anal. Calcd for $C_{13}H_{14}Fe_2O_8S$: C, 35.33; H, 3.19. Found: C, 35.44; H, 3.28. ^1H NMR (300 MHz, $CDCl_3$): δ 0.72 (t, J = 7.32 Hz, 3 H, $O_2CCH_2CH_3$), 1.57 (s, 9 H, $SC(CH_3)_3$), 1.79 (q, J = 7.11 Hz, 2 H, $O_2CCH_2CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 9.77 (q, 127.3 Hz, $O_2CCH_2CH_3$), 30.72 (t, J_{CH} = 125.7 Hz, $O_2CCH_2CH_3$), 34.81 (q, J_{CH} = 128.0 Hz, $SC(CH_3)_3$), 49.09 (s, $SC(CH_3)_3$), 190.29 (t, $^2J_{CH}$ = 6.9 Hz, $O_2CCH_2CH_3$), 204.72, 209.96, 213.00 (all s, broad, terminal CO's).

$(\mu\text{-}EtCO_2)(\mu\text{-EtS})Fe_2(CO)_6$: orange-red oil; 37% yield (together with $(\mu\text{-EtS})_2Fe_2(CO)_6$ in 62% yield). Anal. Calcd for $C_{11}H_{10}Fe_2O_8S$: C, 31.92; H, 2.43. Found: C, 31.26; H, 2.92. ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (t, J = 7.38 Hz, 3 H, $O_2CCH_2CH_3$), 1.61 (t, J = 6.84 Hz, 3 H, SCH_2CH_3), 1.81 (q, J = 7.36 Hz, 2 H, $O_2CCH_2CH_3$), 2.66 (q, J = 6.67 Hz, 2 H, SCH_2CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 9.78 (J_{CH} = 129.1 Hz, $O_2CCH_2CH_3$), 18.52 (q, J_{CH} = 127.7 Hz, SCH_2CH_3), 30.38 (t, J_{CH} = 127.4 Hz, $O_2CCH_2CH_3$), 31.02 (t, J_{CH} = 141.3 Hz, SCH_2CH_3), 190.68 (s, $O_2CCH_2CH_3$), 205.71, 209.60, 213.26 (all s, broad, terminal CO's). Mass spectrum (EI; m/z (relative intensity)): 414 (M^+, 4), 386 ($M^+ - CO$, 10), 358 ($M^+ - 2CO$, 16), 330 ($M^+ - 3CO$, 14), 302 ($M^+ - 4CO$, 19), 274 ($M^+ - 5CO$, 21), 246 ($M^+ - 6CO$, 62), 219 ($H_2SFe_2O_2CH_2CH_3^+$, 12), 218 ($HSFe_2O_2CCH_2CH_3^+$, 100), 217 ($SFe_2O_2CCH_2CH_3^+$, 20), 216 ($SFe_2O_2CCH_2CH_2^+$, 13), 162 ($HSFe_2OH^+$, 13), 161 ($HSFe_2O^+$, 9), 145 ($HSFe_2^+$, 9), 144 (SFe_2^+, 8), 111 (14), 109 (10), 97 ($FeCCH_2CH_3^+$, 20), 95 (13), 85 (14), 83 (15), 81 (11), 71 (20), 69 (17), 57 ($CH_3CH_2CO^+$, 27), 43 (CH_3CO^+, 8), 41 ($CH_3CH_2C^+$, 3).

The following compound was prepared with use of mercuric pivalate.

$(\mu\text{-}(CH_3)_3CCO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$: orange-red oil; 49% yield (together with $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$ in 46% yield). Anal. Calcd for $C_{15}H_{18}Fe_2O_8S$: C, 38.33; H, 3.86. Found: C, 38.24; H, 3.67. ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (s, 9 H, $O_2C(CH_3)_3$), 1.56 (s, 9 H, $SC(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 27.00 (q, J_{CH} = 127.7 Hz, $O_2CC(CH_3)_3$), 34.62 (q, J_{CH} = 128.0 Hz, $SC(CH_3)_3$), 40.39 (q, $^2J_{CH}$ = 2.8 Hz, $O_2CC(CH_3)_3$), 48.71 (q, $^2J_{CH}$ = 7.8 Hz, $SC(CH_3)_3$), 915.28 (q, $^3J_{CH}$ = 4.4 Hz, $O_2CC(CH_3)_3$), 210.05, 211.25 (both s, terminal CO's). Mass spectrum (EI; m/z (relative intensity)): 470 (M^+, 5), 442 ($M^+ - CO$, 8), 414 ($M^+ - 2CO$, 16), 386 ($M^+ - 3CO$, 19), 358 ($M^+ - 4CO$, 25), 330 ($M^+ - 5CO$, 24), 302 ($M^+ - 6CO$, 94), 247 ($H_2SFe_2O_2CC(CH_3)_3^+$, 12), 246 ($HSFe_2O_2CC(CH_3)_3^+$, 100), 245 ($SFe_2O_2CC(CH_3)_3^+$, 4), 162 ($H_2SFe_2O^+$, 4), 161 ($HSFe_2O^+$, 2), 90 (HS-*t*-Bu$^+$, 4), 57 (*t*-Bu$^+$, 78), 56 (Fe^+ or *t*-Bu – H$^+$, 16), 55 ($C_4H_7^+$, 4).

The following complex was prepared with use of mercuric benzoate.

$(\mu\text{-}PhCO_2)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$: orange-red solid; mp 98.0–99.0 °C; 32% yield (together with $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$ in 64% yield). Anal. Calcd for $C_{17}H_{14}Fe_2O_8S$: C, 41.67; H, 2.88. Found: C, 41.94; H, 2.88. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.63 (s, 9 H, $SC(CH_3)_3$), 7.25–7.52 (m, 5 H, $O_2CC_6H_5$). ^{13}C NMR (CD_2Cl_2, 75.4 MHz): δ_C 35.04 (q, J_{CH} = 127.3 Hz, $SC(CH_3)_3$), 49.72 (s, $SC(CH_3)_3$), 127.11–133.59 (m, $O_2CC_6H_5$), 181.68 (s, $O_2CC_6H_5$), 205.16, 210.03, 214.00 (all s, broad, terminal CO's). Mass spectrum (EI; m/z (relative intensity)): 490 (M^+, 2), 462 ($M^+ - CO$, 6), 434 ($M^+ - 2CO$, 14), 406 ($M^+ - 3CO$, 14), 378 ($M^+ - 4CO$, 11), 350 ($M^+ - 5CO$, 10), 322 ($M^+ - 6CO$, 52), 267 ($H_2SFe_2O_2CC_6H_5^+$, 14), 266 ($HSFe_2O_2CC_6H_5^+$, 100), 265 ($SFe_2O_2CC_6H_5^+$, 13), 222 ($HSFe_2C_6H_5^+$, 29), 221 ($SFe_2C_6H_5^+$, 37), 161 ($HSFe_2O^+$, 9), 160 (SFe_2O^+, 8), 145 ($HSFe_2^+$, 7), 144 (SFe_2^+, 58), 122 ($C_6H_5CO_2H^+$, 10), 105 ($C_6H_5CO^+$, 21), 77 ($C_6H_5^+$, 24), 57 (*t*-Bu$^+$, 33), 56 (Fe^+ or *t*-Bu – H$^+$, 12), 51 ($C_4H_3^+$, 12), 42 ($C_3H_6^+$, 30), 41 ($C_3H_5^+$, 47), 39 ($C_3H_3^+$, 27).

The following mercury(II) compounds gave only the respective $(\mu\text{-RS})_2Fe_2(CO)_6$ species on reaction with a THF solution of $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ (% yield of $(\mu\text{-RS})_2Fe_2(CO)_6$ in parentheses): mercuric chloride (100%); mercuric trifluoroacetate (82%); mercuric oxalate (99%); mercuric malonate (63%); CH_3O_2CHgCl (93%).

Reaction of $Hg(SMe)_2$ with $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$. The standard $[Et_3NH][(\mu\text{-CO})(\mu\text{-PhS})Fe_2(CO)_6]$ reagent solution (2.98 mmol) was generated at room temperature. Against

Table XIII. Crystal Data and Intensity Measurements for $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$

empirical formula	$C_{12}H_{12}Fe_2O_8S$
fw	427.99
cryst dimens, mm	0.346 × 0.240 × 0.190
cryst syst	irregular triclinic prism
lattice params	a = 13.608 (2) Å b = 16.945 (2) Å c = 8.599 (1) Å α = 98.52 (1)° β = 99.00 (1)° γ = 113.03 (1)° V = 1753.8 Å^3
space group	$P\bar{1}$ (No. 2)
Z value	4
D_{calc}, g/cm^3	1.621
abs coeff, cm^{-1}	15.965
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.71069 Å)
temp, °C	22
detector aperture, mm	2.00 + (1.00 tan θ) horizontal, 4.00 vertical
Scan Type	$\theta/2\theta$
Scan Rate, deg/min	1.33–6.67
$2\theta_{max}$, deg	50.0
no. of rflns measd	total 5839, unique 3310
H atom treatment	included in calc positions (d_{C-H} = 0.95 Å)
refinement	full-matrix least-squares
p	0.04
anomalous dispersion	all non-H atoms
transmissn coeff	0.871–1.190
final no. of params	325
error in observn of unit wt	2.562
residuals: R, R_w	0.055, 0.093

Table XIV. Final Positional Parameters and B(eq) Values for $(\mu\text{-}CH_3CO_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$

atom	x	y	z	B(eq),[a] Å^2
Fe(1)	0.2250 (1)	0.43179 (9)	0.8789 (2)	3.47 (4)
Fe(2)	0.2972 (1)	0.5630 (1)	0.7428 (2)	3.41 (4)
Fe(1)′	−0.2456 (1)	−0.0399 (1)	0.8880 (2)	4.48 (5)
Fe(2)′	−0.3653 (1)	−0.1618 (1)	0.6304 (2)	4.11 (4)
S(1)	0.1283 (2)	0.4527 (2)	0.6640 (3)	3.11 (6)
S(1)′	−0.3404 (2)	−0.0210 (2)	0.6689 (4)	3.89 (7)
O(1)	0.0663 (7)	0.2698 (6)	0.943 (1)	7.4 (3)
O(2)	0.3321 (6)	0.3348 (5)	0.721 (1)	7.1 (3)
O(3)	0.4144 (8)	0.4990 (6)	1.160 (1)	7.7 (3)
O(4)	0.2920 (7)	0.6786 (6)	0.523 (1)	7.8 (3)
O(5)	0.3967 (7)	0.4844 (7)	0.530 (1)	8.6 (3)
O(6)	0.5089 (6)	0.6678 (6)	0.979 (1)	6.4 (3)
O(7)	0.1667 (6)	0.5049 (4)	1.0043 (9)	4.2 (2)
O(8)	0.2314 (5)	0.6190 (4)	0.8923 (9)	3.9 (2)
O(1)′	−0.142 (1)	0.1372 (7)	1.105 (1)	11.2 (5)
O(2)′	−0.0393 (7)	−0.0163 (9)	0.803 (1)	10.3 (4)
O(3)′	−0.2061 (9)	−0.1532 (7)	1.091 (1)	10.7 (4)
O(4)′	−0.5293 (9)	−0.2525 (8)	0.318 (1)	10.5 (4)
O(5)′	−0.1888 (7)	−0.1437 (6)	0.471 (1)	7.8 (3)
O(6)′	−0.3379 (8)	−0.3070 (5)	0.746 (1)	9.5 (3)
O(7)′	−0.3848 (6)	−0.0673 (5)	0.9608 (9)	4.3 (2)
O(8)′	−0.4868 (5)	−0.1774 (5)	0.7438 (9)	4.4 (2)
C(1)	0.1268 (9)	0.3320 (7)	0.925 (1)	4.9 (3)*
C(2)	0.2886 (9)	0.3736 (7)	0.776 (1)	4.6 (3)*
C(3)	0.3400 (9)	0.4720 (8)	1.052 (2)	5.4 (3)*
C(4)	0.2946 (9)	0.6372 (7)	0.611 (1)	4.5 (3)*
C(5)	0.359 (1)	0.5159 (8)	0.614 (2)	5.7 (3)*
C(6)	0.4265 (8)	0.6257 (7)	0.885 (1)	4.2 (2)*
C(7)	0.1811 (8)	0.5801 (7)	0.988 (1)	4.1 (2)*
C(8)	0.134 (1)	0.6290 (8)	1.092 (2)	5.2 (3)*
C(9)	0.0780 (8)	0.3776 (7)	0.459 (1)	4.0 (2)*
C(10)	0.119 (1)	0.3085 (9)	0.440 (2)	8.2 (4)
C(11)	−0.046 (1)	0.333 (1)	0.443 (2)	9.0 (5)
C(12)	0.099 (1)	0.433 (1)	0.334 (2)	8.8 (5)
C(1)′	−0.182 (1)	0.0673 (9)	1.027 (2)	7.2 (4)*
C(2)′	−0.121 (1)	−0.0238 (9)	0.828 (2)	6.4 (3)*
C(3)′	−0.221 (1)	−0.1093 (9)	1.014 (2)	6.8 (4)*
C(4)′	−0.467 (1)	−0.2175 (9)	0.435 (2)	6.5 (4)*
C(5)′	−0.2573 (9)	−0.1499 (8)	0.534 (2)	5.1 (3)*
C(6)′	−0.352 (1)	0.02528 (8)	0.701 (2)	5.9 (3)*
C(7)′	−0.4745 (8)	−0.1286 (7)	0.880 (1)	4.2 (2)*
C(8)′	−0.5745 (9)	−0.1447 (7)	0.945 (1)	4.9 (3)*
C(9)′	−0.272 (1)	−0.0524 (8)	0.538 (2)	5.3 (3)*
C(10)′	−0.155 (1)	0.072 (1)	0.544 (2)	8.9 (6)
C(11)′	−0.288 (2)	0.1346 (9)	0.589 (2)	14.0 (6)
C(12)′	−0.340 1)	0.005 (1)	0.364 (2)	10.1 (6)

[a] Values marked with an asterisk denote atoms refined isotropically. Unprimed atoms refer to molecule 1; primed atoms refer to molecule 2.

a positive flow of nitrogen, $Hg(SMe)_2$ (0.91 g, 3.08 mmol) was added as a solid. An immediate reaction ensued with brisk gas evolution and a color change to deep red-brown. After the reaction mixture had been stirred for 2 h at room temperature, the color of the solution was bright red and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of two orange-red products, which moved in pentane. The solvent was removed in vacuo to yield a red-brown solid, which was purified by filtration chromatography. Pentane eluted a large red band, which gave 0.95 g (2.18 mmol, 73%), of $(\mu\text{-}PhS)(\mu\text{-}MeS)Fe_2(CO)_6$ (a mixture of three inseparable isomers identified by comparison of its ^1H NMR spectrum and melting point (82.0–83.0 °C; lit.[21] mp 83.0–85.0 °C) with those of an authentic sample. Elution with pentane/CH_2Cl_2 (9:1 v/v) gave 0.12 g (0.24 mmol, 16% based on S) of $(\mu\text{-}PhS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

Stability of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ in THF Solution. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reagent solution (1.99 mmol) was generated at room temperature and stirred under a nitrogen atmosphere for 7 days. At this point, the solution was bright red. TLC analysis of the reaction mixture indicated the formation of one major product, which moved in pentane, followed by three other very faint orange products. The solvent was removed in vacuo to yield a red-brown oily solid, which was purified by filtration chromatography. Pentane eluted one large red band, which gave 0.19 g (0.42 mmol, 41% based on S) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Further elution with CH_2Cl_2/acetone (1:1 v/v) gave a bright red-rose solid. Due to its instability and lack of organic resonances in its ^1H NMR spectrum, further characterization was not pursued.

Reaction of $CH_2{=}C{=}CHHgI$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $CH_2{=}C{=}CHHgI$ (1.60 g, 4.37 mmol) was added as a solid. An immediate reaction ensued with brisk gas evolution and a color change to deeper red-brown. After the reaction mixture had been stirred for 1 h at room temperature, the solution had changed to bright red and a white-gray precipitate had formed. TLC indicated the formation of two orange-red products. The solvent was removed in vacuo to yield a red-brown solid, which was dissolved in pentane/CH_2Cl_2 (2:1 v/v) and filtered through a thin pad of silicic acid. Removal of the solvent left a dark red solid, which was purified by medium-pressure chromatography. Pentane eluted an orange-red band, which gave 0.24 g (0.53 mmol, 35% based on S) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Further elution with pentane gave 0.34 g (0.83 mmol, 28%) of $(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CH_2)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ as a red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[1a]

A similar reaction of allenylmercuric iodide with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ gave $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (43% yield) and $(\mu\text{-}\eta^1,\eta^2\text{-}CH_2{=}C{=}CH)(\mu\text{-}EtS)Fe_2(CO)_6$, a red solid,[1a] in 31% yield.

Reaction of $CH_2{=}CHCH_2HgI$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $CH_2{=}CHCH_2HgI$ (1.20 g, 3.25 mmol) was added as a solid. An immediate reaction ensued with brisk gas evolution and a color change to deeper red-brown. After the reaction mixture had been stirred for 23 h at room temper-

---

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

Organometallics 1991, 10, 3380–3384

ature, the solution had changed to bright red and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of three orange-red products. The solvent was removed in vacuo to yield a red oily solid, which was dissolved in pentane/CH_2Cl_2 (2:1 v/v) and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a dark red oily solid, which was purified by preparative thin-layer chromatography with pentane as the eluent. The first red band gave 0.17 g (0.4 mmol, 15%) of (μ-σ,π-CH=$CHCH_3$)(μ-EtS)-$Fe_2(CO)_6$ as a slightly air-sensitive red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[1e] The second band was orange-red and gave 0.38 g (0.94 mmol, 61% based on S) of (μ-EtS)$_2Fe_2(CO)_6$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. The third red band gave 0.23 g (0.57 mmol, 19%) of (μ-CH_3CH=CHC=O)(μ-EtS)$Fe_2(CO)_6$ (a mixture of two inseparable isomers) as a slightly air-sensitive red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[1e]

X-ray Crystallography. Structure of (μ-CH_3CO_2)(μ-*t*-BuS)$Fe_2(CO)_6$. Orange crystals of (μ-CH_3CO_2)(μ-*t*-BuS)$Fe_2(CO)_6$ were grown from pentane at −18 °C over several days. A suitable single crystal was mounted in air on a glass fiber with use of epoxy resin. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $16.0 \leq 2\theta \leq 26.0°$. A triclinic crystal system was established by the usual peak search and reflection indexing program, and the lack of systematic absences established the space group as $P1$ or $P\bar{1}$, the latter of which was established by the satisfactory refinement of the structure. A cell reduction failed to show the presence of a higher symmetry cell.

Intensity data were collected on the CAD4 diffractometer using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak width on either side of the scan. The intensities of three standard reflections were measured every 60 min of X-ray exposure time; no significant change in these standards occurred, so no correction was applied. The data were processed in the usual manner with a value of 0.04 for p.[22] A total of 5839 unique reflections were measured, of which 3310 were observed and used in subsequent calculations. A summary of data collection details and crystal data appears in Table XIII.

The structure was solved with use of MULTAN 82 to locate the four independent Fe and the two S atoms of the two crystallographically independent complex molecules. All remaining atoms (including hydrogens) were located by the usual sequence of least-squares and difference Fourier calculations.[23] Hydrogen atoms were input in positions idealized from the observed positions, assuming tetrahedral geometries about the carbon atoms and using C–H distances of 0.95 Å. Hydrogens were assigned isotropic thermal parameters 20% larger than those of the attached carbon. All non-hydrogen atoms with the exception of the carbonyl carbon atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[24] An absorption correction was applied to the data by using the method of Walker and Stuart.[25] The final model in the space group $P\bar{1}$ converged to $R = 0.055$ and $R_w = 0.093$ with 325 parameters varied. The asymmetric unit contains two independent (μ-CH_3CO_2)(μ-*t*-BuS)$Fe_2(CO)_6$ molecules having essentially identical sets of bond distances and angles.

The positional and isotropic thermal parameters for the independent molecules, labeled molecules 1 and 2, are given in Table XIV.

Acknowledgment. The authors at the Massachusetts Institute of Technology are grateful to the National Science Foundation for generous support of this work, while those at the University of Alberta thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support.

Supplementary Material Available: Tables of infrared and mass spectra for new compounds and anisotropic thermal parameters and hydrogen atom positions for **13a** (19 pages); a listing of the observed and calculated structure factors for **13a** (17 pages). Ordering information is given on any current masthead page.

---

[22] Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

[23] Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

[24] (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. (c) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[25] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

Gold in Organic Synthesis. Preparation of Symmetrical and Unsymmetrical Biaryls via C–C Coupling from *cis*-Diarylgold(III) Complexes

José Vicente,* María Dolores Bermúdez, and Jaime Escribano

Grupo de Química Organometálica, Departamento de Química Inorgánica,
Facultad de Ciencias Químicas, Universidad de Murcia, 30171 Espinardo, Murcia, Spain

Received December 5, 1990

At room temperature, reacting *cis*-[Au(Ar)(Ar′)Cl] with [$PhCH_2PPh_3$]Cl (1:1), with PPh_3 plus $NaClO_4{\cdot}H_2O$ (1:2:1), or with PPh_3 (1:1) leads to a reductive elimination giving gold(I) complexes [$PhCH_2PPh_3$][$AuCl_2$], [$Au(PPh_3)_2$]ClO_4, or [$AuCl(PPh_3)$], respectively, and in high yields, the corresponding biaryls Ar–Ar′ [Ar = C_6H_4N=NPh-2, Ar′ = Ar (**1**), $C_6H_4NO_2$-2 (**2**), C_6F_5 (**3**); Ar = Ar′ = C_6H_3(N=NC_6H_4Me-4′)-2, Me-5 (**4**); Ar = $C_6H_4CH_2NMe_2$-2, Ar′ = Ph (**5**), C_6H_4N=NPh-2 (**6**), C_6H_3(N=NC_6H_4Me-4′)-2, Me-5 (**7**)].

Introduction

The synthesis of biaryls has a long history from the old Pschorr reaction (1896)[1] to the last report of Caubère (1989).[2] Most of the reported methods require the use of metals or metal complexes. Thus, the Ullmann reaction[3] or some of its modifications use copper or organocopper

---

[1] See for example: Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509.

[2] Lourak, M.; Vanderese, R.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4840, 4844.

[3] See for example: Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613; *Synthesis* **1974**, 63. Normant, J. F. *Synthesis* **1972**, 63. Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.

0276-7333/91/2310-3380$02.50/0