2662 *Organometallics* **1990**, *9*, 2662-2672

Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ Complexes with Acetylenes. Synthesis and Decarbonylation of α,β-Unsaturated Bridging Acyl Complexes

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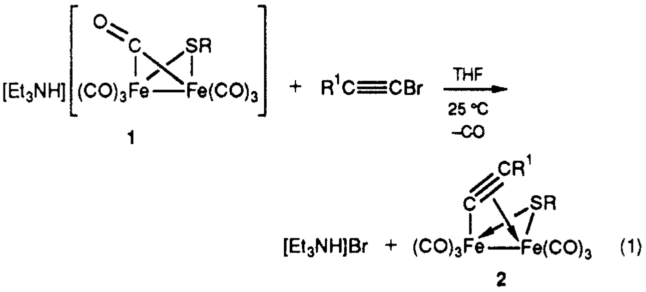
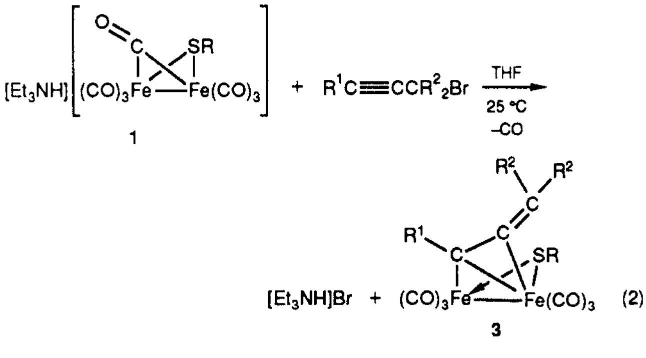
Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with alkyl- and arylacetylenes ($R^1C{\equiv}CR^2$) produced neutral μ-vinyl complexes of the type $(\mu\text{-}\sigma,\pi\text{-}R^1C{=}CHR^2)(\mu\text{-}RS)Fe_2(CO)_6$. Presumably, formation of these products resulted from the in situ protonation of an intermediate vinylic anion by the triethylammonium cation. ^1H NMR correlations have shown that overall addition of the diiron and proton units has occurred in a cis fashion. In some cases, reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with acetylenes generated the α,β-unsaturated acyl complexes $(\mu\text{-}R^2CHC{=}C(R^1)C{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ as well. Bridging acyl complexes of this general class were prepared directly by the reactions of α,β-unsaturated acid chlorides $R^1(R^2)C{=}CHC(O)Cl$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. In refluxing THF, these vinylacyl complexes underwent thermal decarbonylation to the respective μ-vinyl derivatives.

Introduction

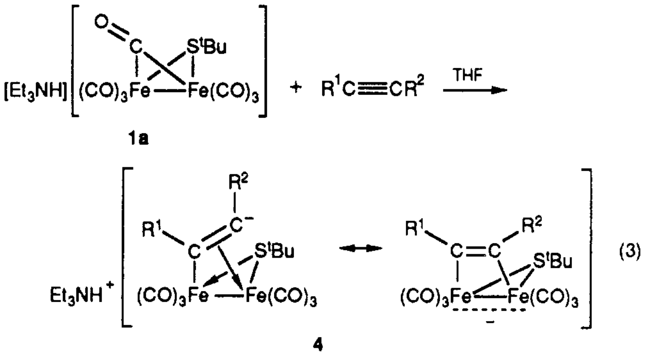
As described in a previous paper,[1a] the reaction of 1-bromoacetylenes, $R^1C{\equiv}CBr$, with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (1)[1b] generated, in good yields, the bridging acetylide complexes $(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR^1)(\mu\text{-}RS)Fe_2(CO)_6$ (2; eq 1). In related work, reactions of propargylic halides, $R^1C{\equiv}CCR^2{}_2X$, with this iron carbonyl salt produced bridging allenyl complexes of the type 3 (eq 2) in an S_N2' process.[1b] Since this reaction proceeded by way of attack of the iron carbonyl nucleophile at the terminal carbon atom of the C≡C bond of the propargylic halide, it was of interest to investigate reactions of the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ salt with acetylenes of type $R^1C{\equiv}CR^2$ and $R^1C{\equiv}CH$, which could only involve nucleophilic attack at the C≡C bond. We report here the results of such a study.

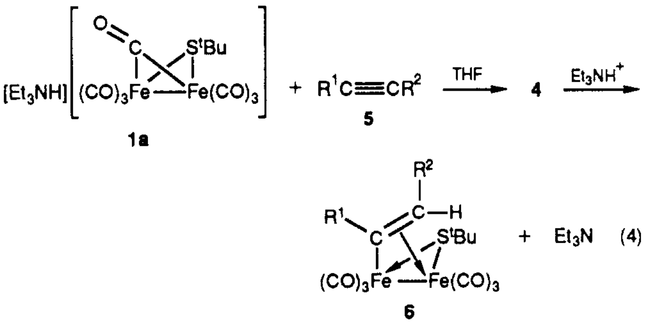




Results and Discussion

Reactions with Acetylenes. Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ (1a) with alkyl- and arylacetylenes, $R^1C{\equiv}CR^2$, might be expected to yield the anionic acetylene complex 4 (eq 3), in which the negative charge could be delocalized as shown. (Note that a similar negative charge delocalization occurs in the anion of salt 1.[1b]) However, such products were not obtained, but instead, the neutral bridging σ,π-vinyl complexes 6 were isolated (eq 4). (Some $\mu\text{-}\sigma,\pi$-vinyl complexes of this type had been prepared earlier by other procedures.[2,4]) Pre-





5a: EtOC≡CH	**6a**: R^1 = EtO, R^2 = H (84%)
b: $MeO_2CC{\equiv}CCO_2Me$	**b**: $R^1 = CO_2Me$, $R^2 = CO_2Me$ (67%)
c: $MeC{\equiv}CCO_2Me$	**c**: R^1 = Me, $R^2 = CO_2Me$ (60%)
d: $HC{\equiv}CC(O)_2Me$	**d**: R^1 = H, $R^2 = CO_2Me$ (61%)
e: HC≡CC(O)Me	**e**: R^1 = H, R^2 = C(O)Me (28%)
f: PhC≡CPh	**f**: R^1 = Ph, R^2 = Ph (42%)
g: HC≡CH	**g**: R^1 = H, R^2 = H (20%)

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[1] (a) Seyferth, D.; Hoke, J. B.; Wheeler, D. R. *J. Organomet. Chem.* **1988**, *341*, 421. (b) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430.

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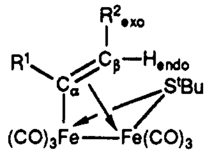
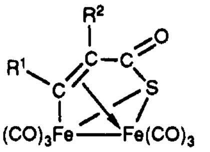
Table I. ^1H NMR Data for **6**



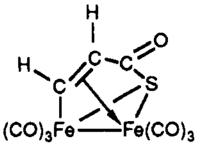
	R^1	R^2	$\delta_H(R^1)$	$\delta_H(R^2\text{-exo})$	δ_H(endo)
6a	EtO	H		3.22 (d, J = 5.03 Hz)	2.02 (d, J = 5.02 Hz)
6b	CO_2Me	CO_2Me			2.91 (s)
6c	Me	CO_2Me			2.91 (s)
6d	H	CO_2Me	8.83 (d, J = 12.2 Hz)		3.45 (d, J = 12.2 Hz)
6e	H	C(O)Me	8.88 (d, J = 11.7 Hz)		3.63 (d, J = 12.2 Hz)
6f	Ph	Ph			4.12 (s)
6g	H	H	7.7 (dd, J = 13.9 Hz, J = 9.2 Hz)	3.35 (d, J = 9.2 Hz)	3.08 (d, J = 13.9 Hz)

sumably, formation of the neutral products results from in situ deprotonation of the $[Et_3NH]^+$ cation by the intermediate anion **4**, i.e., by proton transfer from nitrogen to carbon. In general, the highest product yields were obtained with the functional acetylenes **5a–d**, which reacted with **1a** at room temperature. In contrast, reactions of diphenylacetylene and acetylene itself with **1a** required higher temperatures, i.e., that of refluxing THF, conditions under which salts such as **1a** are of limited stability.[1b] Hence, the yields of the respective σ,π-vinyl complexes **6f** and **6g** were somewhat lower. In the reactions of dimethyl acetylenedicarboxylate and acetylacetylene (3-butyn-2-one) with **1a**, complexes of type **7** also were isolated as unexpected byproducts in yields of 13 and 25%, respectively. The formation of these byproducts results from complex intramolecular processes involving the thiolate, vinyl, and carbonyl ligands of the intermediate anion **4**,[3] and such reactions, with more examples, will be discussed in detail in a later full paper.

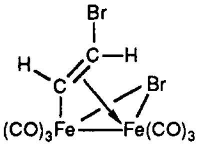


7a: $R^1 = R^2 = CO_2Me$
b: R^1 = H, R^2 = C(O)Me

From the proton NMR data for complexes of type **6** (Table I) it was determined that overall addition of the diiron unit and the proton to the acetylene occurred in a cis fashion. The ^1H NMR spectrum of the parent complex **6g** ($R^1 = R^2$ = H) was instrumental in defining the characteristic chemical shifts and coupling constants associated with the three possible types of vinyl protons (H_α, H_β(endo), and H_β(exo)). Subsequent comparison of these data with the ^1H NMR spectra of **6a–f** then provided a tool for ascertaining the geometry of the vinyl ligand and, hence, the geometry of addition to the acetylene. In the ^1H NMR spectrum of **6g**, the C_α proton signal appears as a low-field doublet of doublets, δ_H 7.77 (J_{trans} = 13.9 Hz and J_{cis} = 9.2 Hz), being coupled to both the cis and trans C_β protons. Correspondingly, the C_β proton signals are found upfield, δ_H(endo) 3.08 (d, J_{trans} = 13.9 Hz) and δ_H(exo) 3.35 (d, J_{cis} = 9.2 Hz). These data agree with those reported by King for other $(\mu\text{-}\sigma,\pi\text{-}HC{=}CH_2)(\mu\text{-}RS)Fe_2(CO)_6$ complexes,[4] and they are consistent with NMR data for other μ-vinyl systems as well.[5] Furthermore, for the two vinyl-bridged diiron complexes $(\mu\text{-}\sigma,\pi\text{-}HC{=}CHC(O)S\text{-})Fe_2(CO)_6$ (**7c**)[6] and $(\mu\text{-}\sigma,\pi\text{-}HC{=}CHBr)(\mu\text{-}Br)Fe_2(CO)_6$ (**8**),[7] in which the geometry of the vinyl ligand was determined by X-ray crystallography, cis (H_α/H_β(exo)) and trans (H_α/H_β(endo)) coupling constants of 6.7 and 10.5 Hz, respectively, were reported. In general, these values agree with known cis and trans coupling constants in free alkenes (J_{cis} = 6–12 Hz and J_{trans} = 12–18 Hz),[8] even though much of the double-bond character is lost in bridging the iron centers.[6,7] (In fact, the infrared spectra of all the new μ-vinyl complexes **6** show no absorption in the region characteristic for free olefins.[8]) Consequently, since the C_α proton signals of **6d** and **6e** both are observed in their ^1H NMR spectra as low-field doublets with trans coupling constants of 12.2 and 11.7 Hz, respectively, one can determine that overall cis addition of the diiron and proton units has occurred. Accordingly, the endo C_β proton resonances occur farther upfield as doublets having the corresponding trans coupling constants. For **6a**, **6b**, **6c**, and **6g**, the absence of any low-field resonances indicates that their vinyl protons are attached only to C_β, and as expected, the β-vinyl protons in **6a** show a geminal coupling of 5.02 Hz.



7c



8

In the ^{13}C NMR spectra of these new σ,π-vinyl complexes, the C_α carbon signals are observed downfield, in the range of 154–216 ppm (Table II). Conversely, the C_β resonances are observed farther upfield, in the range of 50–90 ppm. Whereas the downfield shift of C_α may be explained in terms of the "carbene-like" character asso-

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[2] Ros, J.; Viñas, J. M.; Mathieu, R.; Solans, X.; Font-Bardia, M. *J. Chem. Soc., Dalton Trans.* **1988**, 281 (reaction of RSLi with $(\mu\text{-}\sigma,\pi\text{-}PhC{=}CHPh)(\mu\text{-}Cl)Fe_2(CO)_6$).

[3] Seyferth, D.; Hoke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895.

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

[5] (a) Andrianov, V. G.; Struchkov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1590. (b) Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Kaganovich, V. S.; Petrovskii, P. V. *J. Organomet. Chem.* **1971**, *31*, 257. (c) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (d) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955. (e) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29.

[6] Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 225.

[7] (a) Krüger, C.; Tsay, Y. H.; Grevels, F.-W.; von Gustorf, E. K. *Isr. J. Chem.* **1972**, *10*, 201. (b) Grevels, F. W.; Schulz, F.; von Gustorf, E. K.; Bunbury, D. S. *J. Organomet. Chem.* **1975**, *91*, 341.

[8] *Spectrometric Identification of Organic Compounds*; Bassler, G. C., Morrill, T. C., Silverstein, R. M., Eds.; Wiley: New York, 1981; pp 108, 227, 235.

Table II. ^{13}C **NMR Data for 6**[a]

	R^1	R^2	δ_{C_α}	δ_{C_β}
6a	EtO	H	216.71 (s)	50.94 (dd)
6b	CO_2Me	CO_2Me	176.55 (s)	67.99 (d)
6c	Me	CO_2Me	190.36 (s)	77.03 (d)
6d	H	CO_2Me	161.3 (d)	76.0 (d)
6e	H	C(O)Me	160.42 (d)	82.12 (d)
6f	Ph	Ph	176.58 (s)	90.25 (d)
6g	H	H	154.8 (d)	74.8 (dd)

[a] See diagram of **6** in Table I.

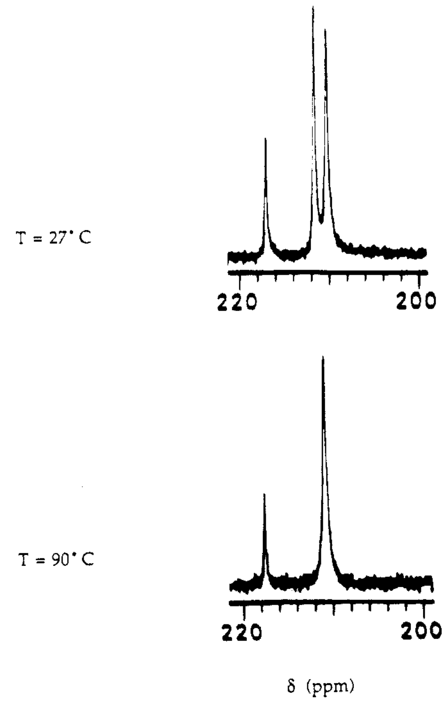
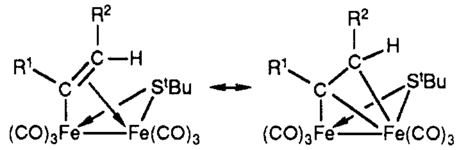


Figure 1. Variable-temperature ^{13}C NMR spectra of **6a**.

ciated with this carbon atom, as shown in the resonance hybrids **6x** and **6y**, the upfield shift of C_β may be attributed to a degree of "sp^3-like" character for this carbon atom. Similar shifts have been observed in other μ-vinyl systems.[5c,9a,b]



6x **6y**

Like the bridging acetylide complexes described previously,[1] these new bridging vinyl complexes show fluxionality of the unsaturated ligand. This is illustrated in the variable-temperature ^{13}C NMR spectra of the ethoxyvinyl derivative **6a** (Figure 1). Typical for most of the μ-vinyl products isolated, the room-temperature ^{13}C NMR spectrum shows two signals (δ_C 210.24 and 211.63) in the terminal carbonyl region. (In some cases, one broad resonance was observed.) However, at 90 °C, one observes the coalescence of these two peaks into one, indicative of a fluxional process. When the temperature then is lowered back to 25 °C, the motion of the vinyl ligand slows on the NMR time scale, the $Fe(CO)_3$ fragments once again become inequivalent, and the single carbonyl resonance is split into the two original signals. Three processes may be considered as the cause for these observations: vinyl group flipping over the face of the Fe_2S core, trigonal rotation or pairwise exchange of CO ligands on each Fe, and inversion at sulfur. More work is required in order to demonstrate which of these processes is operative. Related fluxional behavior has been observed in other vinyl systems.[5c,9]

Table III. ^1H **NMR Data for 6h, 6h′, 6i, and 6i′**[a]

	R^1	R^2	$\delta_H(R^1)$	$\delta_H(R^2\text{-exo})$	$\delta_H(\text{endo})$
6h	Ph	H		3.58 (d, J = 2.5 Hz)	2.79 (d, J = 2.5 Hz)
6h′	H	Ph	8.30 (d, J = 13.7 Hz)		4.68 (d, J = 13.7 Hz)
6i	Me_3Si	H		4.05 (d, J = 3.5 Hz)	3.30 (d, J = 3.6 Hz)
6i′	H	Me_3Si	8.25 (d, J = 15.1 Hz)		3.47 (d, J = 15.2 Hz)

[a] See diagram of **6** in Table I.

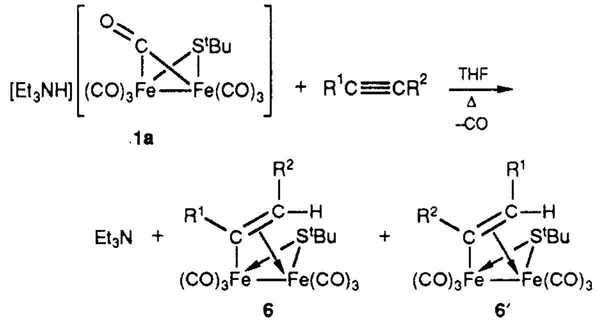
Table IV. ^{13}C **NMR Data for 6h, 6h′, 6i, and 6i′**[a]

	R^1	R^2	δ_{C_α}	δ_{C_β}
6h	Ph	H	185.0 (s)	68.8 (dd)
6h′	H	Ph	141.5 (d)	96.6 (d)
6i	Me_3Si	H	181.19 (s)	78.19 (t)
6i′	H	Me_3Si	159.71 (d)	91.40 (d)

[a] See diagram of **6** in Table I.

As expected, in the reactions of activated terminal acetylenes with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}{}^tBuS)Fe_2(CO)_6]$ (**1a**) addition of the diiron and proton units was regiospecific in that only one of the two possible positional isomers of addition was formed. This observation is consistent with exclusive attack of an iron-centered nucleophile at one carbon atom of the triple bond. In the case of methyl propiolate, methyl 2-butynoate, and 3-butyn-2-one, this occurs in a fashion consistent with Michael addition to the activated acetylene. In the case of ethoxyacetylene, charge distribution of the triple bond[10] directs nucleophilic attack to the α-carbon atom, consistent with Markovnikov addition to the acetylene.

In the reactions of **1a** with unactivated acetylenes such as PhC≡CH and $Me_3SiC≡CH$, addition of the diiron and proton units was not regiospecific in that both possible positional isomers of addition were isolated (eq 5). Al-



(5)

6h: R^1 = Ph, R^2 = H (29% (**6**), 20% (**6′**))
i: R^1 = Me_3Si, R^2 = H (17% (**6**), 17% (**6′**))

though physical separation of the two isomers by chromatography or recrystallization was impossible, spectroscopic characterization of these new vinyl complexes was straightforward. As expected, assignments for vinyl proton

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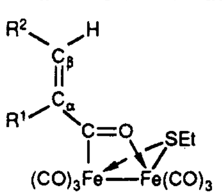
(10) Dickstein, J. I.; Miller, S. I. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; Vol. 2, p 827.

Table V. ^1H and ^{13}C NMR Data for **10**

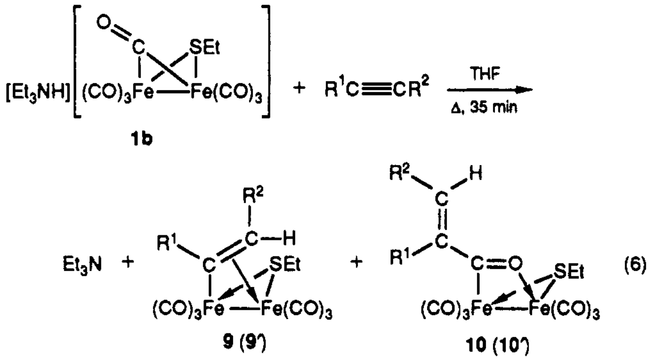


	R^1	R^2	δ_{H_β}	δ_{C_α}	δ_{C_β}
10a	^nPr	^nPr	6.54 (t) 6.71 (t)	150.26 (s) 150.85 (s)	153.08 (dd) 154.68 (d)
10b	Et	Et	6.64 (t) 6.78 (t)	151.69 (s) 151.21 (s)	153.98 (d) 155.56 (d)
10c	Me	Et	6.55 (m)	145.33[a]	153.49[a]
10c′	Et	Me	6.62 (t)	147.32[a]	154.53[a]

[a] From $^{13}C\{^1H\}$ NMR spectrum.

and carbon signals could be made in the corresponding ^1H and ^{13}C NMR spectra consistent with **6a–g** (Tables III and IV). In general, steric considerations and the ability of both the phenyl and trimethylsilyl groups to stabilize α-carbanions favor β-attack of the iron nucleophile and subsequent formation of isomer **6′** upon protonation. Conversely, charge distribution in the triple bonds favors α-attack of the iron nucleophile and subsequent formation of isomer **6**. Neither effect predominates, and hence both isomers are formed in roughly equal amounts.

Surprisingly, reaction of $[Et_3NH][\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ (**1b**) with the electron-rich internal alkylacetylenes 2-pentyne, 3-hexyne, and 4-octyne in refluxing THF yielded not only the expected μ-vinyl complexes **9** but also the new α,β-unsaturated acyl complexes of the type $(\mu\text{-}R^2CH{=}C(R^1)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$ (**10**; eq 6). Certainly, isolation of the acyl complexes was unexpected in that insertion of carbon monoxide into an iron–vinyl bond had occurred. Typically, these μ-acyl products were obtained as a mixture of two inseparable isomers presumably resulting from either an axial (a) or equatorial (e) orientation of the organic thiolate group and lone electron pair on sulfur with respect to the Fe_2S plane (Figure 2). For the reaction of 2-pentyne, four isomers were obtained; two (**9c** and **9c′**) result from opposite addition to the acetylene, and each of these products then exists as the e/a isomer pair. As noted in the Experimental Section, purification of the new μ-vinyl and μ-acyl complexes **9** and **10** by chromatography was a problem since the common byproduct, $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (**11**), typically had similar eluting behavior. Furthermore, because **10a** and **10c**/**10c′** were isolated as unstable oils, analytically pure samples for carbon/hydrogen combustion analysis could not be obtained. In refluxing THF (4 h), these α,β-unsaturated acyl complexes undergo decarbonylation to the respective μ-σ,π-vinyl complexes **9** in low yield (eq 7). A large amount of acyl complex (21–35%) remained unconverted, and the reaction was complicated by the isolation of large quantities of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (**11**; 18–36%).



a: $R^1 = {}^nPr$, $R^2 = {}^nPr$ (31% (**9**), 26% (**10**))
b: R^1 = Et, R^2 = Et (43% (**9**), 31% (**10**))
c: R^1 = Me(Et), R^2 = Et(Me) (12% (**9**), 8% (**9′**) 11% (**10**), 13% (**10′**))

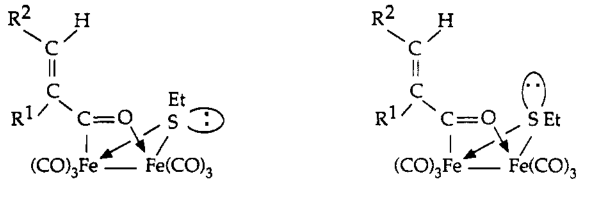
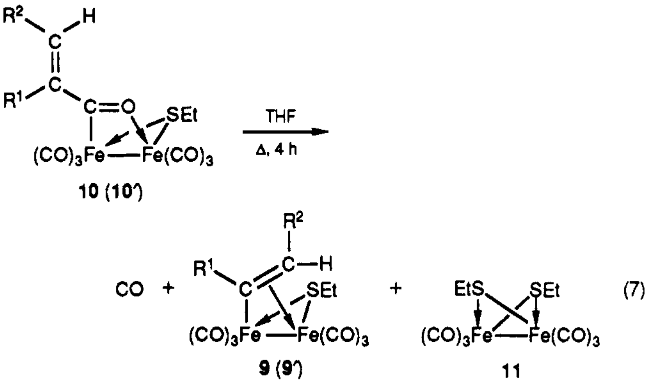


Figure 2.



9a: $R^1 = {}^nPr$, $R^2 = {}^nPr$ (18% (**9**), 36% (**11**))
b: R^1 = Et, R^2 = Et (14% (**9**), 42% (**11**))
c: R^1 = Me(Et), R^2 = Et(Me) (12% (**9**), 15% (**9′**) 18% (**11**))

In the reactions summarized by eq 6 the SEt rather than the SBu^t compounds were used. There was a reason for this: in our prior work[1b] we had found that complexes of type $(\mu\text{-}R^1CO)(\mu\text{-}R^2S)Fe_2(CO)_6$ were more likely to be solids rather than oils when R^2 = Et. In this instance, however, the α,β-unsaturated acyl complexes also were oils when R^2 = Et.

Structural characterization of the new μ-vinyl complexes **9** was straightforward and consistent with **6a–i**. However, subsequent characterization of the new α,β-unsaturated acyl complexes **10** was less straightforward. The electron impact mass spectra of all complexes **10** showed the correct molecular ion with subsequent loss of seven carbonyl ligands. Furthermore, assignments could be made for the vinyl protons and carbons in the respective ^1H and ^{13}C NMR spectra (Table V). In the ^1H NMR spectra, the β-proton signal of the vinyl ligand was observed downfield ($\delta_H \sim 6.6$) in the region typical for protons on uncoordinated double bonds.[8] In contrast to the vinyl resonances of the μ-vinyl complexes of **6** and **9**, both the α- and β-vinyl carbon signals of the vinylacyl products were observed downfield in the range of 145–156 ppm in the corresponding ^{13}C NMR spectra (compare Tables II and V). The infrared spectra all showed an absorption in the region of 1600 cm^{-1}, which could be assigned to the C–C stretch of an uncoordinated carbon–carbon double bond. No bridging carbonyl band was observed, and in the ^{13}C NMR spectra, a singlet was observed far downfield ($\delta_C \sim 288$) that could not be attributed to a bridging carbonyl ligand. In comparison to the chemical shifts of related acyl carbon atoms in other thiolate-bridged diiron compounds, this peak could be assigned to the bridging acyl carbon of **10**.[2,11]

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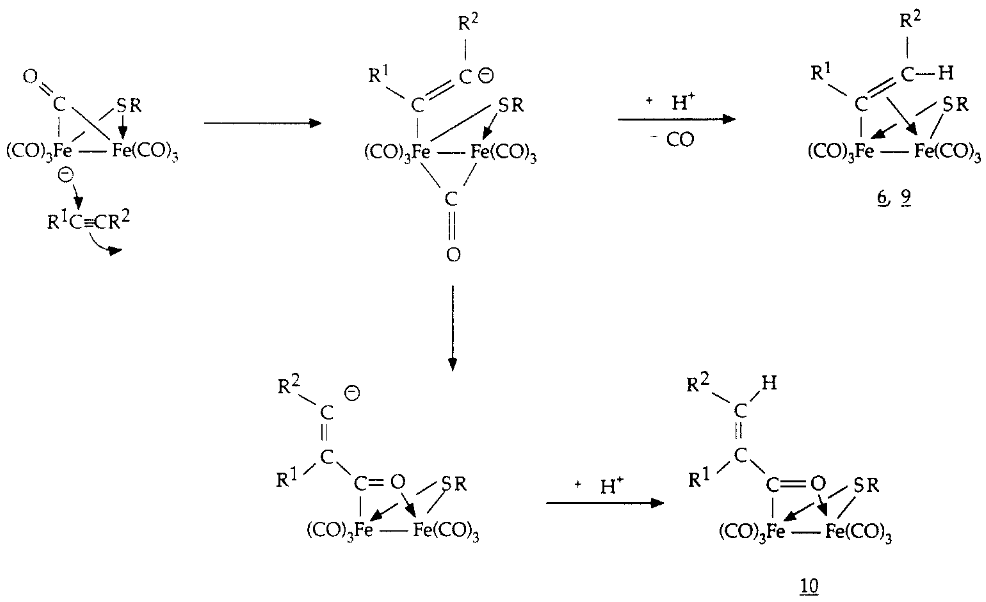
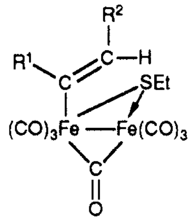
[11] (a) Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572. (b) Archer, C. M. Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1986, pp 122–126, 209–215.

Scheme I



(Although shifted to lower frequency, the corresponding acyl carbonyl absorptions were observed in the IR spectra with some difficulty in the region around 1455 cm^{-1}).[2,11] On the basis of this spectroscopic evidence, the α,β-unsaturated bridging acyl structure **10** was assigned to these products, rather than the isomeric **12** with an η^1 σ-bonded vinyl ligand. These data are consistent with the analytical and spectroscopic data for the related ethoxyvinyl derivative (μ-$CH_2{=}C(EtO)C{=}O$)(μ-^tBuS)$Fe_2(CO)_6$ (**13**), which was prepared by an independent route and characterized by X-ray crystallography.[12] Other vinylacyl complexes also are known.[13,14a]

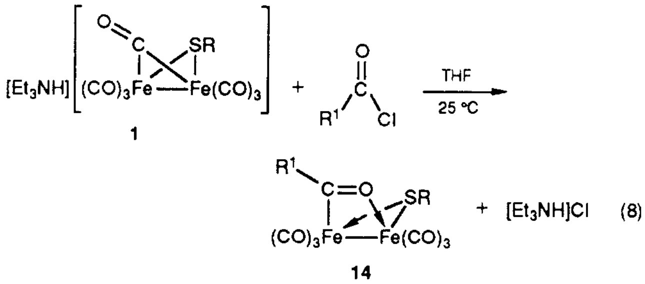


12

A possible mechanism incorporating the formation of both the μ-vinyl and μ-acyl products is outlined in Scheme I. Initially, attack of the iron nucleophile at the acetylene likely generates an intermediate vinylic anion where the negative charge is localized on the β-carbon atom of the uncoordinated vinyl ligand. This vinyl ligand can then form a π-bond to the adjacent iron atom concurrent with expulsion of carbon monoxide and protonation of the β-carbon to give the μ-vinyl complexes (μ-σ,π-$R^1C{=}CHR^2$)(μ-RS)$Fe_2(CO)_6$ (**6** or **9**) isolated in all cases. Alternatively, in the case of the electron-rich acetylenes, migratory insertion of CO into the iron–vinyl bond may occur, yielding an anionic acyl intermediate where the negative charge also is localized on the β-carbon of the vinyl ligand.[13b,14] Subsequent protonation at this site then gives the neutral α,β-unsaturated acyl complexes (μ-$R^2CH{=}C(R^1)C{=}O$)(μ-EtS)$Fe_2(CO)_6$ (**10**). (The exact order of protonation vs bridging/insertion for the two separate reaction pathways cannot be determined with certainty. Protonation may occur prior to bridging or insertion.) The fact that the neutral μ-acyl derivatives decarbonylate only poorly to the corresponding μ-vinyl derivatives also suggests that they do not function as general intermediates in the synthesis of the μ-vinyl complexes.

It is interesting to note that formation of the α,β-unsaturated acyl complexes **10** is not promoted by the presence of free carbon monoxide in solution. For instance, reaction of a CO-saturated solution containing [Et_3NH][μ-CO)(μ-EtS)$Fe_2(CO)_6$] (**1b**) with 3-hexyne yielded **9b** and **10b** in 47 and 34% yields, respectively. In comparison to the original reaction (eq 6), a significant increase in the production of the acyl complex was not observed. This would suggest that formation of the acyl derivatives results entirely from an intramolecular insertion process. Since coordinative unsaturation resulting from insertion of CO can be satisfied by formation of the bridging acyl ligand, such a mechanism is entirely plausible.

Reactions with α,β-Unsaturated Acid Chlorides. As reported earlier,[2] the reaction of acid chlorides, $R^1C(O)Cl$, with [Et_3NH][(μ-CO)(μ-RS)$Fe_2(CO)_6$] (**1**) is a general method for the synthesis of a wide variety of alkylacyl- and arylacyl-bridged diiron complexes (μ-$R^1C{=}O$)(μ-RS)$Fe_2(CO)_6$ (**14**; eq 8). In the light of the results just described, it was of interest to determine if reaction of α,β-unsaturated acid chlorides with **1** would proceed analogously. As expected, reaction of α,β-unsaturated acid chlorides,



R = R^1 = alkyl, aryl

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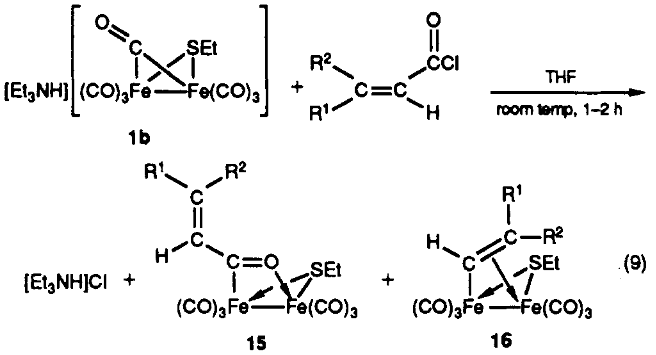
[12] Hoke, J. B. Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1987; to be submitted for publication.

[13] (a) Mitsudo, T.; Nakanishi, H.; Inubushi, T.; Morishima, I.; Watanabe, Y.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 416. (b) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189.

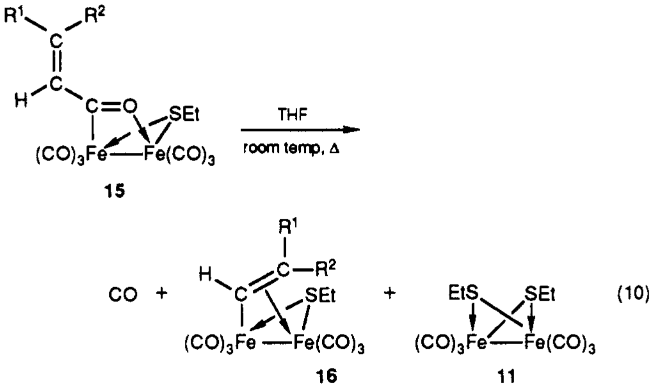
[14] (a) *Principles and Applications of Organotransition Metal Chemistry*; Collman, J. P.; Hegedus, L. S., Norton, J. R.; Finke, R. G., Eds.; University Science Books: Mill Valley, CA, 1987; pp 355–380. (b) Collman, J. P.; Rothrock, R.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* 1977, *99*, 7381.

R^{1}R^{2}C=CHC(O)Cl, with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] (**1b**) yielded the μ-acyl complexes (μ-R^{1}R^{2}C=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15**) in variable yield (eq 9). In some cases, the corresponding vinyl-bridged species (μ-σ,π-HC=CR^{1}R^2)(μ-EtS)Fe$_2$(CO)$_6$ (**16**) also were isolated, presumably resulting from decarbonylation of the μ-acyl complexes **15**. In comparison to the case for the acyl products prepared from the electron-rich acetylenes, subsequent structural characterization of the new acyl complexes was straightforward. Because the characteristic downfield chemical shift of the μ-acyl carbon atom (δ_C ~289) was easily identified, ^{13}C NMR spectroscopy was the most useful tool in determining the general structure. The corresponding ^{1}H NMR spectra also were helpful in assigning a trans geometry to the vinyl ligand. Furthermore, the acyl carbonyl stretch in the infrared spectra was typically observed in the region of 1455 cm^{-1} while the vinyl double-bond stretch was observed as a strong and a weak band in the range of 1600–1640 cm^{-1}. As in the reactions of the electron-rich acetylenes, purification of these new μ-vinyl and μ-acyl products by chromatography was at times a problem since the common byproduct (μ-EtS)$_2$Fe$_2$(CO)$_6$ (**11**) had similar eluting properties.



a: R^1 = H, R^2 = H (38% (**15**), 51% (**16**))
b: R^1 = Ph, R^2 = H (59% (**15**), 38% (6h') (**16**))
c: R^1 = Me, R^2 = H (80% (**15**), 13% (**16**))
d: R^1 = Me, R^2 = Me (93% (**15**))

Excluding **15d**, the new acyl complexes undergo facile decarbonylation to the corresponding μ-vinyl derivatives **16** (eq 10). This behavior is in contrast to the corresponding poor conversions of the acetylene-derived acyls **10**, described earlier (eq 7). Such a difference in behavior may be ascribed to electronic effects involving the acyl bridge. Electron-donating groups are known to stabilize acyl ligands.[14a] Compounds **10a–c** all contain two alkyl groups on the double bond, which makes the vinyl ligand electron rich and hence stabilizes the acyl complex toward decarbonylation. However, since **15a** and **15c** contain only a monosubstituted vinyl ligand and **15b** contains an unsubstituted vinyl ligand, the acyl bridges are not as electron rich in comparison to those in **10a–c** and are destabilized. Subsequently, decarbonylation is much more facile as reflected in the high conversion yields (eq 10). In the case of **15d**, steric factors probably also are involved in the low conversion yield. In addition to **15d** having a disubstituted vinyl ligand, the substitution is such that the resulting μ-vinyl ligand will contain a methyl group pointing directly at the thiolate bridge (in all the other μ-vinyl complexes prepared, a proton occupied this position). Obviously, this creates a sterically unfavorable interaction and hence the observed decarbonylation yield is quite low. Similarly, the trans geometry of the vinyl ligand was maintained after decarbonylation in the cases of **15b** and **15c**. Because of their facile decarbonylation, purification of **15a–c** was a problem. Since these acyl derivatives also were isolated as slightly air-sensitive oils, analytically pure samples, and hence accurate C/H combustion analyses, could not be obtained.



a: R^1 = H, R^2 = H (92% (**16**))
b: R^1 = Ph, R^2 = H (82% (**16**))
c: R^1 = Me, R^2 = H (95% (**16**), 36% (**11**))
d: R^1 = Me, R^2 = Me (33% (**16**))

In all of the reactions that we have described, the cation present in the salt was [Et$_3$NH]$^+$, a species that readily transferred a proton to the vinylic ligand formed in the reaction. In view of this, it was of interest to investigate some of these reactions of the [(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]$^-$ anion with use of a system in which such proton transfer would not occur, for instance, with the known Li[(μ-CO)(μ-RS)Fe$_2$(CO)$_6$].[2] Such studies have been carried out; preliminary accounts have been published,[3,15] and full details will be reported in due course.

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 and *tert*-butyl mercaptans were purged with nitrogen and used without further purification. Acryloyl, crotonyl, 3,3-dimethylacryloyl, and cinnamoyl chlorides (all purchased from Aldrich) were purged with nitrogen prior to use. Dimethyl acetylenedicarboxylate, methyl propiolate, methyl 2-butynoate, 3-butyn-2-one, and ethoxyacetylene (all purchased from Farchan Labs) were purged with nitrogen after purification by vacuum distillation (at room temperature) when necessary. Phenylacetylene (Fluka), (trimethylsilyl)acetylene (Aldrich), 3-hexyne (Farchan), 4-octyne (Aldrich), and 2-pentyne (Aldrich) were purged with nitrogen and used without further purification. Diphenylacetylene (Aldrich) was used as obtained. Acetylene was bubbled through sulfuric acid and then passed through a column of potassium hydroxide (pellets) prior to use. Triiron dodecacarbonyl was prepared by a literature procedure.[16]

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 100–300 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 350 × 25 mm gravity column or a 450 × 25 mm medium-pressure column containing Mallinckrodt 100 mesh silicic acid or Sigma 230–400 mesh silica gel. All chromatography was completed without the exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at −20 °C.

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[15] Hoke, J. B.; Dewan, J. C.; Seyferth, D. *Organometallics* **1987**, *6*, 1816.

[16] McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

Solution infrared spectra (NaCl windows) 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, or a Varian XL-300 spectrometer operating at 90, 250, or 300 MHz, respectively. Carbon-13 NMR spectra were recorded on a Bruker WH-270, a Varian XL-300, or a Varian XL-400 spectrometer operating at 67.9, 75.4, or 100.5 MHz, respectively. Electron impact mass spectra were obtained with a Finnigan 3200 mass spectrometer operating at 70 eV. FAB mass spectra were obtained with a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated with use of the following isotopes: ^{1}H, ^{12}C, ^{28}Si, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Standard in Situ Preparation of $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{RS})\mathrm{Fe_2(CO)_6}]$. A 250-mL three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet (gas adapter), glass stopper, stirbar, and rubber septum was charged with 1.51 g (3.00 mmol) of $\mathrm{Fe_3(CO)_{12}}$ and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged successively with 50 mL of THF, 3.00 mmol of the appropriate thiol, and 0.42 mL (3.00 mmol) of triethylamine by syringe. The mixture was stirred for 20 min, during which time slow gas evolution and a gradual color change from green to brown-red was observed. The resulting $[\mathrm{Et_3NH}][\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{RS})\mathrm{Fe_2(CO)_6}]$ reagent solution then was utilized in situ without further purification.

Reactions of $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}]$ with Acetylenes. The general procedure used was as follows. To the standard $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}]$ reagent solution (3.00 mmol), prepared as described above, was added 3.0 mmol of the acetylene, by syringe, at room temperature. An immediate reaction ensued, with brisk gas evolution and a gradual color change from brown-red to dark red. The reaction mixture was stirred under nitrogen or argon for 2 h at room temperature, and then the solvent was removed at reduced pressure. The residue, usually a red oil (sometimes a tar), was purified by filtration chromatography, by column chromatography if needed, and finally, if a solid, by recrystallization. The isolation and the characterization of the various products are described below for each acetylene used. The IR and EI mass spectra of the products are provided in the supplementary material. The IR spectra are characterized by strong bands in the terminal carbonyl region (~2100–1950 cm^{-1}) and the mass spectra usually by the occurrence of the molecular ion (M$^+$) and fragment ions corresponding to the successive loss of the CO ligands.

$\mathrm{EtOC{\equiv}CH}$. The product was purified by filtration chromatography. Pentane eluted a dark red-brown band from which $(\mu\text{-}\sigma,\pi\text{-}\mathrm{EtOC{=}CH_2})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6a**), a red solid with mp 48.0–51.0 °C (recrystallization from pentane) was isolated in 84% yield. Anal. Calcd for $\mathrm{C_{14}H_{16}Fe_2O_7S}$: C, 38.21; H, 3.66. Found: C, 38.20; H, 3.69. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.25 (t, J = 6.99 Hz, 3 H, OCH$_2$CH_3), 1.36 (s, 9 H, SC(CH$_3$)$_3$), 2.02 (d, J = 5.02 Hz, 1 H, C=CH$_2$ endo), 3.23 (d, J = 5.03 Hz, 1 H, C=CH$_2$ exo), 3.69 (m, 1 H, OCH_2CH$_3$ diastereotopic CH$_2$), 3.86 (m, 1 H, OCH_2CH$_3$ diastereotopic CH$_2$). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 14.30 (q, J = 127.1 Hz, OCH$_2$CH$_3$), 33.25 (q, J = 127.2 Hz, SC(CH$_3$)$_3$), 47.68 (s, SC(CH$_3$)$_3$), 50.94 (dd, J = 152.4 Hz, J = 163.4 Hz, C=CH$_2$), 67.30 (t, J = 144.0 Hz, OCH$_2$CH$_3$), 209.88 and 211.34 (both s, Fe—CO), 216.71 (s, EtOC=CH$_2$).

$\mathrm{MeO_2CC{\equiv}CCO_2Me}$. The product was purified by filtration chromatography. Pentane/CH$_2$Cl$_2$ (9:1 v/v) eluted two minor, pale orange bands, which were not collected. Pentane/CH$_2$Cl$_2$ (3:2 v/v) eluted a bright red band, which gave 1.22 g of a brown-orange solid identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 1.03 g (2.00 mmol, 67%) of $(\mu\text{-}\sigma,\pi\text{-}\mathrm{MeO_2CC{=}CHCO_2Me})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6b**) and 0.19 g (0.40 mmol, 13%) of $(\mu\text{-}\sigma,\pi\text{-}\mathrm{MeO_2CC{=}C(CO_2Me)C(O)S\text{-}})\mathrm{Fe_2(CO)_6}$ (**7a**).[3] Recrystallization from pentane/CH$_2$Cl$_2$ yielded analytically pure $(\mu\text{-}\sigma,\pi\text{-}\mathrm{MeO_2CC{=}CHCO_2Me})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6b**) as a brown-orange, air-stable solid, mp 114.0–116.0 °C. Anal. Calcd for $\mathrm{C_{16}H_{15}Fe_2O_{10}S}$: C, 37.53; H, 3.15. Found: C, 37.73; H, 3.24. ^{1}H NMR (CDCl$_3$; 90 MHz): δ 1.42 (s, 9 H, SC(CH$_3$)$_3$), 2.91 (s, 1 H, C=CHCO$_2$Me), 3.69 (s, 3 H, CO$_2$CH$_3$), 3.76 (s, 3 H, CO$_2$CH$_3$). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 32.99 (q, J = 127.8 Hz, SC(CH$_3$)$_3$), 51.88 (q, J = 146.8 Hz, CO$_2$CH$_3$), 52.42 (q, J = 147.4 Hz, CO$_2$CH$_3$), 67.99 (d, J = 168.7 Hz, C=CHCO$_2$Me), 169.05 (s, CO$_2$Me), 173.94 (s, CO$_2$Me), 176.55 (s, C=CHCO$_2$Me), 206.55 (s, Fe—CO), 208.05 (broad s, Fe—CO).

Characterization data for the second product, **7a** (formed in a different reaction), have been given in ref 3.

$\mathrm{CH_3C{\equiv}CCO_2Me}$. The cherry red tar obtained was purified by filtration chromatography. Pentane eluted a minor pale orange band. Pentane/CH$_2$Cl$_2$ (9:1 v/v) eluted a dark red band from which $(\mu\text{-}\sigma,\pi\text{-}\mathrm{CH_3C{=}CHCO_2Me})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6c**), a dark red solid with mp 65.0–68.0 °C (recrystallization from pentane) was isolated in 60% yield. Anal. Calcd for $\mathrm{C_{15}H_{16}Fe_2O_8S}$: C, 38.49; H, 3.44. Found: C, 38.60; H, 3.46. ^{1}H NMR (CDCl$_3$; 90 MHz): δ 1.40 (s, 9 H, SC(CH$_3$)$_3$), 2.91 (s, 1 H, C=CHCO$_2$Me), 3.00 (s, 3 H, CH_3C=CHCO$_2$Me), 3.69 (s, 3 H, CO$_2$CH$_3$). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 33.12 (q, J = 127.3 Hz, SC(CH$_3$)$_3$), 38.09 (q, J = 128.4 Hz, CH$_3$C=CHCO$_2$Me), 49.14 (s, SC(CH$_3$)$_3$), 51.57 (q, J = 146.8 Hz, CO$_2$CH$_3$), 77.03 (d, J = 165.5 Hz, C=CHCO$_2$Me), 169.50 (s, CO$_2$Me), 190.36 (s, MeC=CHCO$_2$Me), 208.54 and 209.39 (both s, Fe—CO).

$\mathrm{HC{\equiv}CCO_2Me}$. The red oil obtained was purified by filtration chromatography. Pentane eluted a minor pale orange band, and then 9:1 v/v pentane/CH$_2$Cl$_2$ eluted the product $(\mu\text{-}\sigma,\pi\text{-}\mathrm{HC{=}CHCO_2Me})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6d**), a slightly air-sensitive red oil, in 61% yield. Anal. Calcd for $\mathrm{C_{14}H_{14}Fe_2O_8S}$: C, 37.04; H, 3.11. Found: C, 36.57; H, 3.17. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.37 (s, 9 H, SC(CH$_3$)$_3$), 3.45 (d, J = 12.20 Hz, 1 H, HC=CHCO$_2$Me), 3.70 (s, 3 H, CO$_2$CH$_3$), 8.83 (d, J = 12.20 Hz, 1 H, HC=CHCO$_2$Me). ^{13}C NMR (CD$_2$Cl$_2$; 67.9 MHz): δ 33.4 (q, J = 127 Hz, SC(CH$_3$)$_3$), 49.0 (s, SC(CH$_3$)$_3$), 52.1 (q, J = 144 Hz, CO$_2$CH$_3$), 76.0 (d, J = 166 Hz, C=CHCO$_2$Me), 161.3 (d, J = 154 Hz, HC=CHCO$_2$Me), 169.7 (s, CO$_2$Me), 208.7 (s, Fe—CO).

$\mathrm{HC{\equiv}CC(O)CH_3}$. The brown-red tar obtained was purified by filtration chromatography. Pentane eluted a pale orange band, which gave 0.09 g (14%, based on S) of the known $(\mu\text{-}{}^t\mathrm{BuS})_2\mathrm{Fe_2(CO)_6}$, identified by its melting point and ^{1}H NMR spectrum.[17] Subsequently, 6:4 v/v pentane/CH$_2$Cl$_2$ eluted a red solid (0.69 g) that was a mixture, as shown by proton NMR spectroscopy, of **7b** (25%) and $(\mu\text{-}\sigma,\pi\text{-}\mathrm{HC{=}CC(O)CH_3})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6e**; 28%). The latter was obtained pure by recrystallization from pentane and isolated as a magenta solid, mp 53.5–57.5 °C. Anal. Calcd for $\mathrm{C_{14}H_{14}Fe_2O_7S}$: C, 38.39; H, 3.22. Found: C, 38.72; H, 3.37. ^{1}H NMR (CDCl$_3$; 90 MHz): δ 1.39 (s, 9 H, SC(CH$_3$)$_3$), 2.26 (s, 3 H, C(O)CH$_3$), 3.63 (d, J = 12.21 Hz, 1 H, HC=CHC(O)Me), 8.88 (d, J = 11.72 Hz, 1 H, HC=CHC(O)Me). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 29.41 (q, J = 127.4 Hz, C(O)CH$_3$), 33.57 (q, J = 129.3 Hz, SC(CH$_3$)$_3$), 48.59 (s, SC(CH$_3$)$_3$), 82.12 (d, J = 161.0 Hz, C=CHC(O)Me), 160.42 (d, J = 153.2 Hz, HC=CHC(O)Me), 198.98 (s, C(O)Me), 207.89 and 208.69 (both s, Fe—CO).

$\mathrm{PhC{\equiv}CPh}$. In this case the reaction mixture had to be heated at reflux for 45 min in order to effect the usual color change. The red tar obtained was purified by filtration chromatography. Pentane eluted the usual minor pale orange band, and then 20:1 v/v pentane/CH$_2$Cl$_2$ eluted a bright red band, which gave $(\mu\text{-}\sigma,\pi\text{-}\mathrm{PhC{=}CHPh})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6f**), a magenta solid with mp 141.0–143.0 °C (recrystallization from pentane), in 42% yield. Anal. Calcd for $\mathrm{C_{24}H_{20}Fe_2O_6S}$: C, 52.59; H, 3.68. Found: C, 52.62; H, 3.70. ^{1}H NMR (CD$_2$Cl$_2$; 90 MHz): δ 1.49 (s, 9 H, SC(CH$_3$)$_3$), 4.12 (s, 1 H, C=CHPh), 6.62–7.53 (m, 10 H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 33.13 (q, J = 127.1 Hz, SC(CH$_3$)$_3$), 48.81 (s, SC(CH$_3$)$_3$), 90.25 (d, J = 154.6 Hz, C=CHPh), 125.13–129.80 (m, C$_6$H$_5$), 140.02 (s, ipso C$_6$H$_5$), 154.97 (s, ipso C$_6$H$_5$), 176.58 (s, PhC=CHPh), 210.40 (broad S, Fe—CO).

$\mathrm{HC{\equiv}CH}$. In this reaction gaseous acetylene was bubbled through the refluxing $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}]$ solution in THF for 1 h and then at room temperature for 1 h. The crude product, a red oil, was dissolved in 4:1 v/v pentane/CH$_2$Cl$_2$ and filtered through a narrow pad of silicic acid. Removal of the solvent at reduced pressure left a red oil, which was further purified by filtration chromatography. Pentane eluted a red band, from which the product, $(\mu\text{-}\sigma,\pi\text{-}\mathrm{HC{=}CH_2})(\mu\text{-}{}^t\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**6g**), a slightly air-sensitive red oil, was isolated in 20% yield. Anal.

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[17] De Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757.

Calcd for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05. Found: C, 36.57; H, 3.13. ^1H NMR (C_6D_6; 250 MHz): δ 1.07 (s, 9 H, $SC(CH_3)_3$), 3.08 (d, J = 13.9 Hz, 1 H, $C{=}CH_2$ endo), 3.35 (d, J = 9.2 Hz, 1 H, $C{=}CH_2$ exo), 7.77 (dd, J = 13.9 Hz, J = 9.2 Hz, 1 H, $HC{=}CH_2$). ^{13}C NMR (C_6D_6; 67.9 MHz): δ 33.0 (q, J = 126 Hz, $SC(CH_3)_3$), 47.8 (s, $SC(CH_3)_3$), 74.8 (dd, J = 163 Hz, J = 157 Hz, $C{=}CH_2$), 154.8 (d, J = 151 Hz, $HC{=}CH_2$), 209 (s, Fe—CO), 209–211 (broad s, Fe—CO).

PhC≡CH. In this case, the reaction mixture was stirred at reflux for 1 h and then at room temperature for 4 h. After removal of the solvent, the crude product, a red oil, was dissolved in pentane/CH_2Cl_2 (1:1 v/v) and filtered through a narrow pad of silicic acid. Removal of the solvent left a red oil, which was purified by filtration chromatography. Pentane eluted a pale yellow band, which was not collected. Pentane then eluted a red band, which gave, as an inseparable mixture, 0.69 g (49%) of $(\mu\text{-}\sigma,\pi\text{-}PhC{=}CH_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**6h**) and $(\mu\text{-}\sigma,\pi\text{-}HC{=}CHPh)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**6h′**) as an air-stable red solid with mp 85.0–90.0 °C after recrystallization from pentane. Anal. Calcd for $C_{18}H_{16}Fe_2O_6S$: C, 45.78; H, 3.42. Found: C, 45.69; H, 3.51. ^1H NMR ($CDCl_3$; 250 MHz): δ 1.40 (s, 9 H, $SC(CH_3)_3$), 1.43 (s, 9 H, $SC(CH_3)_3$), 2.79 (d, J = 2.5 Hz, $C{=}CH_2$ endo), 3.58 (d, J = 2.5 Hz, $C{=}CH_2$ exo), 4.46 (d, J = 13.7 Hz, $C{=}CHPh$), 7.20–7.30 (m, 10 H, C_6H_5 both isomers), 8.30 (d, J = 13.7 Hz, $HC{=}CHPh$). **6h**/**6h′** = 1.4/1.0. ^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 33.0 (q, J = 128 Hz, $SC(CH_3)_3$), 33.3 (q, J = 128 Hz, $SC(CH_3)_3$), 48.1 (s, $SC(CH_3)_3$), 48.3 (s, $SC(CH_3)_3$), 68.8 (dd, J = 155 Hz, J = 163 Hz, $C{=}CH_2$), 96.6 (d, J = 158 Hz, $C{=}CHPh$), 124.8–130.5 (m, C_6H_5), 139.3 (s, ipso C_6H_5), 141.5 (d, J = 145 Hz, $HC{=}CHPh$), 156.9 (s, ipso C_6H_5), 185.0 (s, $PhC{=}CH_2$) 208.1, 210.0, and 212.2 (all s, Fe—CO).

A similar reaction was carried out between PhC≡CH and $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ to give an inseparable 1:2 mixture of $(\mu\text{-}\sigma,\pi\text{-}PhC{=}CH_2)(\mu\text{-}EtS)Fe_2(CO)_6$ and $(\mu\text{-}\sigma,\pi\text{-}HC{=}CHPh)(\mu\text{-}EtS)Fe_2(CO)_6$ as an air-stable, red solid with mp 80–82 °C after crystallization from pentane, in 65% yield. Anal. Calcd for $C_{16}H_{12}Fe_2O_6S$: C, 43.28; H, 2.72. Found: C, 43.35; H, 2.80. ^1H NMR (CD_2Cl_2; 250 MHz): δ 1.38 (4 lines, overlapping triplets, J = 7.4 Hz, CH_3), 2.41 (q, J = 7.4 Hz, CH_2), 2.42 (d, J = 2.5 Hz, $=CH_2$), 3.60 (d, J = 2.5 Hz, $=CH_2$), 4.40 (d, J = 13.7 Hz, $=CHPh$), 7.2–7.4 (complex m, Ph), 8.50 (d, J = 13.7 Hz, Fe_2CH). ^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 17.9 (q, J = 129 Hz, CH_3), 33.7 (t, J = 143 Hz, SCH_2), 34.6 (t, J = 137 Hz, SCH_2), 67.1 (dd, J = 156 Hz, J = 162 Hz, $=CH_2$), 95.2 (d, J = 159 Hz, $=CH$), 124.6–130.7 (Ph), 139.4 (s, ipso Ph), 144.2 (d, J = 149 Hz, Fe_2CH), 156.4 (s, ipso Ph), 187.4 (s, Fe_2CPh), 209.4 (s, CO).

$Me_3SiC{\equiv}CH$. The reaction mixture was stirred at room temperature for 1 h and at reflux for 2 h. The red tar that was obtained was purified by filtration chromatography. Pentane eluted an orange band, which gave, as an inseparable mixture, 0.48 g (34%) of $(\mu\text{-}\sigma,\pi\text{-}Me_3SiC{=}CH_2)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**6i**) and $(\mu\text{-}\sigma,\pi\text{-}HC{=}CHSiMe_3)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ (**6i′**) as a slightly air-sensitive red oil. Anal. Calcd for $C_{15}H_{20}Fe_2O_6S$: C, 38.48; H, 4.30. Found: C, 38.45; H, 4.41. ^1H NMR ($CDCl_3$; 250 MHz): δ 0.11 (s, 9 H, $Si(CH_3)_3$), 0.25 (s, 9 H, $Si(CH_3)_3$), 1.36 (s, 9 H, $SC(CH_3)_3$), 1.40 (s, 9 H, $SC(CH_3)_3$), 3.30 (d, J = 3.57 Hz, $C{=}CH_2$ endo), 3.47 (d, J = 15.19 Hz, $HC{=}CHSiMe_3$), 4.05 (d, J = 3.53 Hz, $C{=}CH_2$ exo), 8.25 (d, J = 15.10 Hz, $HC{=}CHSiMe_3$). **6i**/**6i′** = 1.0. ^{13}C NMR ($CDCl_3$; 67.9 MHz): δ −0.56 (q, J = 119.4 Hz, $Si(CH_3)_3$), 2.24 (q, J = 119.0 Hz, $Si(CH_3)_3$), 33.30 (q, J = 126.4 Hz, $SC(CH_3)_3$), 32.89 (q, J = 127.3 Hz, $SC(CH_3)_3$), 48.04 (s, $SC(CH_3)_3$), 48.54 (s, $SC(CH_3)_3$), 78.19 (t, J = 158.2 Hz, $C{=}CH_2$), 91.40 (d, J = 141.1 Hz, $C{=}CHSiMe_3$), 159.71 (d, J = 147.8 Hz, $HC{=}CHSiMe_3$), 181.19 (s, $Me_3SiC{=}CH_2$), 207.96 (s, Fe—CO), 209.82 (broad s, Fe—CO), 212.06 (s, Fe—CO). Mass spectrum (FAB): m/z 468 (M^+).

$n\text{-}C_3H_7C{\equiv}C\text{-}n\text{-}C_3H_7$. The reaction mixture was stirred at reflux for 35 min. The product, a red oil, was dissolved in pentane/CH_2Cl_2 (4:1, v/v) and the solution filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil, which was purified by medium-pressure chromatography. Pentane eluted three red bands. The first two contiguous bands were difficult to separate and were collected together. Removal of the solvent on a rotary evaporator left a red oil, which was subjected to repeated medium-pressure chromatography. Ultimately, the first band yielded 0.45 g (1.00 mmol, 31%) of $(\mu\text{-}\sigma,\pi\text{-}{}^nPrC{=}CH^nPr)(\mu\text{-}EtS)Fe_2(CO)_6$ (**9a**) as a slightly air-sensitive red oil. Anal. Calcd for $C_{16}H_{20}Fe_2O_6S$: C, 42.51; H, 4.46. Found: C, 42.94; H, 4.57. ^1H NMR ($CDCl_3$; 250 MHz): δ 0.96 (t, J = 7.40 Hz, 3 H, $CH_2CH_2CH_3$), 1.02 (t, J = 7.25 Hz, 3 H, SCH_2CH_3), 1.54, 1.75, 2.02, 2.37 (all very broad s, 8 H, CH_2), 2.63 (t, J = 7.74 Hz, 2 H, $CH_3CH_2CH_2C{=}CH^nPr$), 2.91 (t, J = 6.01 Hz, 1 H, $C{=}CHCH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2; 75.4 MHz): δ 14.55 (q, J = 124.3 Hz, $CH_2CH_2CH_3$), 14.99 (q, J = 126.6 Hz, $CH_2CH_2CH_3$), 18.36 (q, J = 127.6 Hz, SCH_2CH_3), 24.37 (t, J = 125.7 Hz, $CH_2CH_2CH_3$), 28.93 (t, J = 127.5 Hz, $CH_2CH_2CH_3$), 34.90 (t, J = 137.7 Hz, SCH_2CH_3), 36.18 (t, J = 125.6 Hz, $CH_2CH_2CH_3$), 52.53 (t, J = 125.4 Hz, $CH_2CH_2CH_3$), 96.94 (d, J = 154.0 Hz, $C{=}CH^nPr$), 187.27 (s, $^nPrC{=}CH^nPr$), 209.16 and 211.76 (both s, Fe—CO).

The second band yielded 0.06 g (0.16 mmol, 10% based on S) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$,[18] identified by its ^1H NMR spectrum. The third red band eluting in pentane gave 0.40 g (0.83 mmol, 26%) of $(\mu\text{-}{}^nPrCH{=}C(^nPr)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$ (**10a**; an inseparable mixture of two isomers), as a slightly air-sensitive red oil. Analytically pure **10a** for carbon/hydrogen combustion analysis could not be obtained because of its limited thermal stability. ^1H NMR ($CDCl_3$; 250 MHz): δ 0.68 (t, J = 7.23 Hz, 3 H, $CH_2CH_2CH_3$ major isomer), 0.74 (t, J = 6.64 Hz, 3 H, $CH_2CH_2CH_3$ minor isomer), 0.95 (t, J = 7.34 Hz, 3 H, $CH_2CH_2CH_3$ major isomer), 0.97 (t, J = 7.39 Hz, 3 H, $CH_2CH_2CH_3$ minor isomer), 1.29 (t, J = 7.42 Hz, 2 H, $CH_3CH_2CH_2C{=}CH^nPr$ minor isomer), 1.30 (t, J = 7.36 Hz, 3 H, SCH_2CH_3 minor isomer), 1.51 (t, J = 7.48 Hz, 3 H, SCH_2CH_3 major isomer), 1.54 (t, J = 7.58 Hz, 2 H, $CH_3CH_2CH_2C{=}CH^nPr$ major isomer), 1.77, 2.06, 2.22 (all m, 12 H, CH_2 both isomers), 2.41 and 2.59 (both m, 4 H, SCH_2CH_3 both isomers), 6.54 (t, J = 7.36 Hz, 1 H, $C{=}CHCH_2CH_2CH_3$ major isomer), 6.71 (t, J = 7.34 Hz, 1 H, $C{=}CHCH_2CH_2CH_3$ minor isomer). major/minor = 3.8/1.0. ^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 13.72 (q, J = 123.6 Hz, $CH_2CH_2CH_3$ both isomers), 17.71 (q, J = 128.0 Hz, SCH_2CH_3 minor isomer), 18.26 (q, J = 127.5 Hz, SCH_2CH_3 major isomer), 22.04 (t, J = 126.1 Hz, CH_2), 26.10 (t, J = 125.2 Hz, CH_2), 27.38 (t, J = 126.4 Hz, CH_2), 27.56 (t, J = 125.7 Hz, CH_2), 29.65 (t, J = 124.9 Hz, CH_2), 31.20 (t, J = 124.8 Hz, CH_2), 32.93 (t, J = 140.9 Hz, SCH_2CH_3 both isomers), 150.26 (s, $^nPrC{=}CH^nPr$ minor isomer), 150.85 (s, $^nPrC{=}CH^nPr$ major isomer), 153.08 (d, J = 150.0 Hz, $C{=}CH^nPr$ major isomer), 154.68 (d, J = 151.4 Hz, $C{=}CH^nPr$ minor isomer), 208.2, 208.80, 209.63, 209.75, 210.82, 211.37, 212.12, and 212.69 (all s, Fe—CO), 287.14 (s, acyl C=O major isomer), 288.64 (s, acyl C=O minor isomer).

$C_2H_5C{\equiv}CC_2H_5$. A reaction with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ for 30 min at reflux gave a red oil that was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil, which was purified by filtration chromatography. Pentane eluted an orange band, which gave 0.54 g (43%) of $(\mu\text{-}\sigma,\pi\text{-}EtC{=}CHEt)(\mu\text{-}EtS)Fe_2(CO)_6$ (**9b**) as an air-stable, red solid with mp 58.0–60.0 °C after recrystallization from pentane. Anal. Calcd for $C_{14}H_{16}Fe_2O_6S$: C, 39.66; H, 3.80. Found: C, 39.64; H, 3.85. ^1H NMR ($CDCl_3$; 250 MHz): δ 1.14 (t, J = 7.4 Hz, 3 H, CH_3), 1.28 (t, J = 7.4 Hz, 3 H, CH_3), 1.33 (t, J = 7.4 Hz, 3 H, SCH_2CH_3), 1.88, 2.13, 2.40, and 2.68 (all m, 6 H, CH_2), 2.84 (t, J = 6.0 Hz, 1 H, $C{=}CHEt$). ^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 14.7 (q, J = 131 Hz, CH_3), 17.9 (q, J = 128 Hz, CH_3), 18.6 (q, J = 131 Hz, CH_3), 26.2 (t, J = 128 Hz, CH_2), 34.2 (t, J = 141 Hz, SCH_2CH_3), 42.5 (t, J = 127 Hz, CH_2), 97.7 (d, J = 161 Hz, $EtC{=}CHEt$), 183.3 (s, $EtC{=}CHEt$), 210.8 (broad s, Fe—CO).

Further elution with pentane yielded a second orange band, which gave 0.42 g (31%) of $(\mu\text{-}EtCH{=}C(Et)C{=}O)(\mu\text{-}EtS)Fe_2(CO)_6$ (**10b**; an inseparable mixture of two isomers) as an air-stable, red solid with mp 57.0–58.0 °C after recrystallization from pentane. Anal. Calcd for $C_{15}H_{16}Fe_2O_7S$: C, 39.86; H, 3.57. Found: C, 39.97; H, 3.61. ^1H NMR (acetone-d_6; 250 MHz): δ 0.62 (t, J = 7.42 Hz, 3 H, CH_3 major isomer), 0.70 (t, J = 7.42 Hz, CH_3 minor isomer), 1.12 (t, J = 7.50 Hz, 3 H, CH_3 major isomer), 1.28 (t, J = 7.42 Hz, 3 H, 6 H, CH_3 and SCH_2CH_3 minor isomers), 1.50 (t, J = 7.43 Hz, 3 H, SCH_2CH_3 major isomer), 1.86 (q, J = 7.33 Hz, 2 H, CH_2 major isomer), 1.87 (q, J = 7.48 Hz, 2 H, CH_2 minor isomer), 2.33

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[18] (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (b) Dahl, L. F.; Wei, C.-H. *Inorg. Chem.* **1963**, *2*, 328.

and 2.72 (both m, 6 H, CH$_2$ minor isomer), 2.33 and 2.72 (both m, 6 H, CH$_2$ both isomers), 2.52 (q, *J* = 7.31 Hz, 2 H, SC*H*$_2$CH$_3$ minor isomer), 6.64 (t, *J* = 7.40 Hz, 1 H, C=C*H*CH$_2$CH$_3$ major isomer), 6.78 (t, *J* = 7.42 Hz, 2 H, C=C*H*CH$_2$CH$_3$ minor isomer). major/minor = 3.7/1.0. ^{13}C NMR (CDCl$_3$; 75.4 MHz): δ 13.10 (q, *J* = 127.8 Hz, CH$_3$ both isomers), 13.61 (q, *J* = 127.0 Hz, CH$_3$ both isomers), 18.21 (q, *J* = 123.9 Hz, SCH$_2$*C*H$_3$ both isomers), 19.04 (t, *J* = 122.4 Hz, CH$_2$ both isomers), 22.30 (t, *J* = 126.7 Hz, CH$_2$ both isomers), 32.91 (t, 141.1 Hz, S*C*H$_2$CH$_3$ major isomer), 151.21 (s, Et*C*=CHEt minor isomer), 151.69 (s, Et*C*=CHEt major isomer), 153.98 (d, *J* = 153.0 Hz, EtC=*C*HEt major isomer), 155.56 (d, *J* = 154.2 Hz, EtC=*C*HEt minor isomer), 208.10, 208.85, 209.14, 209.73, 212.09, 212.28, and 212.66 (all s, Fe—CO both isomers), 287.20 (s, acyl C=O major isomer), 287.31 (s, acyl C=O minor isomer).

A similar reaction was carried out between 3-hexyne and [Et$_3$NH][μ-CO)(μ-^{t}BuS)Fe$_2$(CO)$_6$]. The product, a red oil, was chromatographed with use of a column (300 × 25 mm) of silicic acid. Pentane eluted three bands. The first yielded 0.47 g (35% yield) of (μ-EtC=CHEt)(μ-^{t}BuS)Fe$_2$(CO)$_6$ as a red, air-stable solid with mp 65–67 °C after crystallization from ethanol. Anal. Calcd for C$_{16}$H$_{20}$Fe$_2$O$_6$S: C, 42.51; H, 4.46. Found: C, 42.63; H, 4.57. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.13 (t, *J* = 7.4 Hz, 3 H, CH$_3$), 1.26 (t, *J* = 7.4 Hz, 3 H, CH$_3$), 1.38 (s, 9 H, *tert*-butyl), 1.87 (br), 2.13 (br), 2.61 (br) (4 H, CH$_2$ groups), 3.19 (t, *J* = 6.0 Hz, vinyl). ^{13}C NMR (CD$_2$Cl$_2$; 67.9 MHz): δ 15.1 (q, *J* = 126 Hz, CH$_3$), 18.8 (q, *J* = 127 Hz, CH$_3$), 26.2 (t, *J* = 126 Hz, CH$_2$), 33.4 (q, *J* = 132 Hz, *tert*-butyl CH$_3$), 43.4 (t, *J* = 128 Hz, CH$_2$), 48.7 (s, *C*Me$_3$), 100.1 (d, *J* = 156 Hz, EtC=*C*HEt), 180.8 (s, Et*C*=CHEt), 210.7 and 212.9 (both broad, CO).

The second band eluted from the column with pentane and gave 0.11 g (0.24 mmol, 8% yield) of (μ-^{t}BuS)$_2$Fe$_2$(CO)$_6$, identified by its ^{1}H NMR spectrum. The third band was eluted from the column with use of a pentane/CH$_2$Cl$_2$ (9:1, v/v) mixture. Removal of the solvent gave 0.36 g (0.75 mmol, 25% yield) of (μ-EtCH=C(Et)C=O)(μ-^{t}BuS)Fe$_2$(CO)$_6$ as a slightly air-sensitive red oil. This oil was determined to be a 1.2/1 mixture of two isomers on the basis of the integration of the vinyl proton signals in the ^{1}H NMR spectrum. Anal. Calcd for C$_{17}$H$_{20}$Fe$_2$O$_7$S: C, 42.53; H, 4.20. Found: C, 42.44; H, 4.28. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 0.62 (t, *J* = 7.4 Hz, 3 H, CH$_3$ of major isomer), 0.67 (t, *J* = 7.5 Hz, 3 H, CH$_3$ of minor isomer), 1.12 (four lines, overlapping triplets, CH$_3$), 1.23 (*tert*-butyl of minor isomer), 1.5 (*tert*-butyl of major isomer), 1.80 (m, CH$_2$), 2.24 (m, CH$_2$), 6.51 (t, *J* = 7.3 Hz, vinyl proton of major isomer), 6.78 (t, *J* = 7.5 Hz, vinyl proton of minor isomer). ^{13}C NMR (C$_6$D$_6$; 67.9 MHz): δ 13.0 (q, *J* = 126 Hz, CH$_3$), 13.7 (q, *J* = 128 Hz, CH$_3$), 13.8 (q, *J* = 128 Hz, CH$_3$), 19.1 (t, *J* = 129 Hz, CH$_2$), 19.2 (t, *J* = 129 Hz, CH$_2$), 22.4 (t, *J* = 131 Hz, CH$_2$), 22.5 (t, *J* = 131 Hz, CH$_2$), 34.2 (q, *J* = 126 Hz, *tert*-butyl CH$_3$ of major isomer), 34.8 (q, *J* = 124 Hz, *tert*-butyl CH$_3$ of minor isomer), 47.8 (s, *C*Me$_3$), 49.5 (s, *C*Me$_3$), 150.8 (s, Et*C*=CHEt of minor isomer), 151.8 (s, Et*C*=CHEt of major isomer), 154.7 (d, *J* = 156 Hz, EtC=*C*HEt of major isomer), 155.6 (d, *J* = 157 Hz, EtC=*C*HEt of minor isomer), 207.8, 210.3, 211.3, 211.7, 212.6, and 213.6 (all s, CO).

CH$_3$C≡CC$_2$H$_5$ (Reaction with [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] at Reflux for 45 min). The red oil that was isolated was dissolved in pentane and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a red oil, which was purified by medium-pressure chromatography. Pentane eluted three red bands. The first two contiguous bands were difficult to separate and were collected together. Removal of the solvent on a rotary evaporator left a red oil, which was subject to repeated medium-pressure chromatography. Ultimately, the first band yielded, as an inseparable mixture, 0.26 g (20%) of (μ-σ,π-EtC=CHMe)(μ-EtS)Fe$_2$(CO)$_6$ (**9c′**) and (μ-σ,π-MeC=CHEt)(μ-EtS)Fe$_2$(CO)$_6$ (**9c**) as a slightly air-sensitive red oil. Anal. Calcd for C$_{13}$H$_{14}$Fe$_2$O$_6$S: C, 38.08; H, 3.44. Found: C, 38.58; H, 3.54. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.12 (t, *J* = 7.74 Hz, 3 H, CH$_2$C*H*$_3$), 1.25 (t, *J* = 7.24 Hz, 3 H, CH$_2$C*H*$_3$), 1.32 (t, *J* = 7.65 Hz, 3 H, SCH$_2$C*H*$_3$), 1.68 (d, *J* = 5.65 Hz, 3 H, EtC=CHCH$_3$), 1.95 (m, 2 H, MeC=CHC*H*$_2$CH$_3$), 2.34 (q, *J* = 7.29 Hz, 4 H, S*C*H$_2$CH$_3$ both isomers), 2.56 (s, 3 H, C*H*$_3$C=CHEt), 2.73 (q, *J* = 7.04 Hz, 2 H, CH$_3$C*H*$_2$C=CHMe), 2.93 (q, *J* = 5.58 Hz, 1 H, EtC=C*H*CH$_3$), 2.94 (t, *J* = 5.58 Hz, 1 H, MeC=C*H*CH$_2$CH$_3$). **9c**/**9c′** = 1.45/1.0. ^{13}C NMR (CD$_2$Cl$_2$; 67.9 MHz): δ 14.69 (q, *J* = 127.4 Hz, CH$_3$), 18.29 (q, *J* = 129.1 Hz, CH$_3$), 18.49 (q, *J* = 128.6 Hz, CH$_3$), 27.42 (t, *J* = 126.8 Hz, MeC=CH*C*H$_2$CH$_3$), 34.52 (t, *J* = 140.2 Hz, S*C*H$_2$CH$_3$), 34.64 (t, *J* = 140.5 Hz, S*C*H$_2$CH$_3$), 35.45 (q, *J* = 126.2 Hz, *C*H$_3$C=CHEt), 42.81 (t, *J* = 130.2 Hz, CH$_3$*C*H$_2$C=CHMe), 89.06 (d, *J* = 155.5 Hz, C=*C*HMe), 97.76 (d, *J* = 148.4 Hz, C=*C*HEt), 176.20 (s, Me*C*=CHEt), 184.40 (s, Et*C*=CHMe), 211.22 (s, Fe—CO both isomers).

The second band gave 0.07 g (11% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$, identified by its ^{1}H NMR spectrum.[18] The third band gave, as an inseparable mixture, 0.32 g (24%) of (μ-EtCH=C(Me)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10c**; also an inseparable mixture of two isomers) and (μ-MeCH=C(Et)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10c′**; two isomers) as a slightly air-sensitive red oil. Analytically pure **10c**/**10c′** could not be obtained for a carbon/hydrogen combustion analysis. ^{1}H NMR (CDCl$_3$; 300 MHz): δ 0.61 (t, *J* = 7.61 Hz, 3 H, CH$_2$C*H*$_3$ major isomer), 0.66 (t, *J* = 8.03 Hz, 3 H, CH$_2$C*H*$_3$ minor isomer), 1.09 (t, *J* = 7.62 Hz, 3 H, CH$_2$C*H*$_3$ major isomer), 1.10 (t, *J* = 7.45 Hz, 3 H, CH$_2$C*H*$_3$ minor isomer), 1.30 (t, *J* = 7.33 Hz, 3 H, SCH$_2$C*H*$_3$ minor isomer), 1.33 (s, 3 H, C*H*$_3$C=CHEt major isomer), 1.35 (t, *J* = 7.22 Hz, 3 H, SCH$_2$C*H*$_3$ minor isomer), 1.40 (s, 3 H, C*H*$_3$C=CHEt minor isomer), 1.48 (t, *J* = 7.24 Hz, 6 H, SCH$_2$C*H*$_3$ major isomers **c** and **c′**), 1.87 (d, *J* = 6.62 Hz, 3 H, EtC=CHC*H*$_3$ major isomer), 1.92 (d, *J* = 7.54 Hz, 3 H, EtC=CHC*H*$_3$ minor isomer), 1.85, 2.05, and 2.21 (all m, 8 H, C*H*$_2$CH$_3$ major and minor isomers **c** and **c′**), 2.41 and 2.59 (both m, 8 H, SC*H*$_2$CH$_3$ major and minor isomers **c** and **c′**), 6.55 (m, 2 H, MeC=C*H*Et minor isomer and EtC=C*H*Me major isomer), 6.62 (t, *J* = 6.85 Hz, 1 H, MeC=C*H*CH$_2$CH$_3$ major isomer), 6.76 (q, *J* = 7.33 Hz, 1 H, EtC=C*H*CH$_3$ minor isomer). **10c′**/**10c** = 1.1/1.0. **10c**(major)/**10c**(minor) = 2.0/1.0. **10c′**(major)/**10c′**(minor) = 2.5/1.0. ^{13}C{^{1}H} NMR (CDCl$_3$; 67.9 MHz): δ 11.01, 11.30, 12.81, 13.22, 14.17, 14.80, 17.91, 18.44, 18.81, 22.74, 26.48, 29.78, 31.31, 31.94, and 33.20 (CH$_2$ and CH$_3$), 145.33, 147.32, and 148.61 (R^1*C*=CHR^2), 153.49 and 154.53 (R^{1}C=*C*HR^2), 208.16, 209.76, 210.82, 211.12, 212.11, and 212.72 (Fe—CO), 286.42, 286.74, and 288.21 (acyl C=O).

Decarbonylation Reactions. (a) (μ-^{n}PrCH=C(^{n}Pr)C=O)(μ-EtS)Fe$_2$(CO)$_6$. A 100-mL three-necked, round-bottomed flask equipped with a reflux condenser and nitrogen inlet (gas adapter), glass stopper, stirbar, and rubber septum was charged with 0.18 g (0.38 mmol) of (μ-^{n}PrCH=C(^{n}Pr)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10a**) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 mL of THF. After the reaction mixture had been stirred for 20 h at room temperature and then 4 h at reflux, the solvent was removed in vacuo to yield a dark red oil, which was purified by medium-pressure column chromatography. Pentane eluted two contiguous bands, which were collected together and which yielded a red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 0.03 g (0.07 mmol, 18%) of (μ-σ,π-^{n}PrC=CH^{n}Pr)(μ-EtS)Fe$_2$(CO)$_6$ (**9a**) and 0.03 g (0.07 mmol, 36% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$. Pentane then eluted two contiguous orange bands, which were collected together and which gave 0.06 g (0.13 mmol, 35%) of starting material (**10a**; a mixture of two inseparable isomers) identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

(b) (μ-EtCH=C(Et)C=O)(μ-EtS)Fe$_2$(CO)$_6$. In an experiment similar to the one above, a THF solution containing 0.16 g (0.34 mmol) of (μ-EtCH=C(Et)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10b**) was heated at reflux for 4 h. Subsequently, the solvent was removed in vacuo and the resulting brown-black oil was purified by medium-pressure column chromatography. Pentane eluted two contiguous orange bands, which were collected together and which yielded 0.05 g of a red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 0.02 g (0.05 mmol, 14%) of (μ-σ,π-EtC=CHEt)(μ-EtS)Fe$_2$(CO)$_6$ (**9b**) and 0.03 g (0.07 mmol, 42% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$. Pentane then eluted a third orange band, which gave 0.03 g (0.07 mmol, 21%) of starting material (**10b**; a mixture of two inseparable isomers) identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

(c) (μ-MeCH=C(Et)C=O)(μ-EtS)Fe$_2$(CO)$_6$ and (μ-EtCH=C(Me)C=O)(μ-EtS)Fe$_2$(CO)$_6$. In an experiment similar to the decarbonylation of **10a**, a THF solution containing 0.19 g (0.43 mmol) of (μ-EtCH=C(Me)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10c**) and (μ-MeCH=C(Et)C=O)(μ-EtS)Fe$_2$(CO)$_6$ (**10c′**) as an inseparable mixture was heated at reflux for 4 h. Subsequently, the solvent was removed in vacuo and the resulting brown-black oil was purified by medium-pressure column chromatography. Pentane eluted an orange band, which yielded 0.06 g of a red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 0.05 g (0.12 mmol, 27%) of (μ-σ,π-EtC=CHMe)(μ-EtS)Fe$_2$(CO)$_6$ (**9c′**) and (μ-σ,π-MeC=CHEt)(μ-EtS)Fe$_2$(CO)$_6$ (**9c**) and 0.02 g (0.04 mmol, 18% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$. Pentane then eluted a second orange band, which gave 0.06 g (0.13 mmol, 31%) of starting material (**10c**/**10c′**; mixture of four inseparable isomers) identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz).

Synthesis of (μ-CH$_2$=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$. To the standard [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (3.21 mmol) was added 0.26 mL (3.21 mmol) of acryloyl chloride by syringe at room temperature. An immediate reaction ensued with brisk gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et$_3$NH][Cl]). After the reaction mixture had been stirred for 1 h at room temperature, the solvent was removed in vacuo to yield a red oily solid, which was purified by filtration chromatography. Pentane eluted two orange bands. The first band gave a red oil that, when subjected to repeated purification by medium-pressure chromatography, yielded 0.53 g (1.44 mmol, 45%) of (μ-σ,π-HC=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$ (**16a**)[11a] and 0.04 g (0.10 mmol, 6% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$, both as slightly air-sensitive red oils, and both were identified by their respective ^{1}H NMR spectra. The second band gave 0.56 g of a slightly air-sensitive red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz) to be a mixture of 0.07 g (0.19 mmol, 6%) of the decarbonylation product (μ-σ,π-HC=CH$_2$)(μ-EtS)Fe$_2$(CO)$_6$ (**16a**)[11a] and 0.48 g (1.76 mmol, 38%) of (μ-CH$_2$=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15a**; itself a mixture of two inseparable isomers). Due to the facile loss of carbon monoxide, analytically pure (μ-CH$_2$=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15a**) could not be obtained. IR (CCl$_4$): ν(C=C) 1619 (wv), 1603 (w) cm^{-1}; ν (bridge C=O) 1462 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.33 (t, *J* = 7.23 Hz, 3 H, SCH$_2$C*H*$_3$ minor isomer), 1.49 (t, *J* = 7.44 Hz, 3 H, SCH$_2$C*H*$_3$ major isomer), 2.08, 2.26, and 2.67 (all m, 4 H, SC*H*$_2$CH$_3$ both isomers), 5.69–6.22 (m, 6 H, vinylic protons both isomers). major/minor = 2.5/1.0. ^{13}C NMR (CDCl$_3$; 100.5 MHz): δ 18.35 (q, *J* = 128.4 Hz, SCH$_2$*C*H$_3$ both isomers), 25.91 (t, *J* = 139.0 Hz, S*C*H$_2$CH$_3$ minor isomer), 32.97 (t, *J* = 138.0 Hz, S*C*H$_2$CH$_3$ major isomer), 128.34 (t, *J* = 159.0 Hz, HC=*C*H$_2$ major isomer), 129.40 (t, *J* = 159.8 Hz, HC=*C*H$_2$ minor isomer), 143.76 (d, *J* = 154.7 Hz, H*C*=CH$_2$ major isomer), 144.21 (d, *J* = 158.7 Hz, H*C*=CH$_2$ minor isomer), 207.54, 209.34, 209.80, 210.16, 211.01, and 211.66 (all s, Fe—CO both isomers), 289.39 (s, acyl C=O major isomer), 291.88 (s, acyl C=O minor isomer).

Synthesis of (μ-PhCH=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$. To the standard [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] reagent solution (3.02 mmol) was added by cannula 0.50 g (3.01 mmol) of cinnamoyl chloride dissolved under nitrogen in a separate flask in 30 mL of THF. An immediate reaction ensued with brisk gas evolution, a gradual color change to bright red, and formation of a white precipitate ([Et$_3$NH][Cl]). After the reaction mixture had been stirred for 45 min at room temperature, the solvent was removed in vacuo to yield a red oily solid, which was purified by filtration chromatography. Pentane eluted a very pale orange band, which was not collected. Pentane/CH$_2$Cl$_2$ (20:1 v/v) eluted an orange band, which gave 0.45 g (1.00 mmol, 33%) of (μ-σ,π-HC=CHPh)(μ-EtS)Fe$_2$(CO)$_6$ (**16b** (**5h′**)) as an air-stable red solid identified by its ^{1}H NMR spectrum (CDCl$_3$; 300 MHz). Pentane then eluted a red band, which gave 0.89 g of a slightly air-sensitive red oil identified by its ^{1}H NMR spectrum (CDCl$_3$; 250 MHz) to be a mixture of 0.06 g (0.15 mmol, 5%) of the decarbonylation product (μ-σ,π-HC=CHPh)(μ-EtS)Fe$_2$(CO)$_6$ (**16b** (**6h′**)) and 0.83 g (1.76 mmol, 59%) of (μ-PhCH=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15b**; itself an inseparable mixture of two isomers). Due to the facile loss of carbon monoxide, analytically pure (μ-PhCH=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15b**) could not be obtained. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.34 (t, *J* = 7.48 Hz, 3 H, SCH$_2$C*H*$_3$ minor isomer), 1.50 (t, *J* = 7.42 Hz, 3 H, SCH$_2$C*H*$_3$ major isomer), 2.13, 2.37, 2.63 (all m, 4 H, SC*H*$_2$CH$_3$ both isomers), 6.55 (d, 15.85 Hz, 1 H, *H*C=CHPh major isomer), 6.87 (d, *J* = 15.74 Hz, 1 H, *H*C=CHPh minor isomer), 7.10 (d, *J* = 15.82 Hz, 1 H, HC=C*H*Ph major isomer), 7.13 (d, *J* = 15.81 Hz, 1 H, HC=C*H*Ph minor isomer), 7.26–7.53 (m, 10 H, C$_6$H$_5$ both isomers). major/minor = 2.3/1.0. ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 17.80 (q, *J* = 129.7 Hz, SCH$_2$*C*H$_3$ major isomer), 25.95 (t, *J* = 139.8 Hz, S*C*H$_2$CH$_3$ minor isomer), 32.95 (t, *J* = 141.7 Hz, S*C*H$_2$CH$_3$ major isomer), 125.80 (d, *J* = 152.4 Hz, HC=*C*HPh minor isomer), 128.86 (d, *J* = 158.5 Hz, C$_6$H$_5$), 131.14 (d, *J* = 150.4 Hz, HC=*C*HPh major isomer), 134.07 (s, ipso C$_6$H$_5$), 134.36 (d, *J* = 158.6 Hz, C$_6$H$_5$), 134.72 (d, *J* = 158.6 Hz, C$_6$H$_5$), 142.48 (d, *J* = 154.8 Hz, H*C*=CHPh minor isomer), 143.50 (d, *J* = 154.1 Hz, H*C*=CHPh major isomer), 207.66, 209.42, 210.23, 210.59, 211.38, 212.04 (all s, Fe—CO both isomers), 284.31 (s, acyl C=O major isomer), 287.02 (s, acyl C=O minor isomer).

Synthesis of (μ-σ,π-HC=CHMe)(μ-EtS)Fe$_2$(CO)$_6$ and (μ-MeCH=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$. The same procedure as above was used in the reaction of 3.12 mmol of [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] with 3.12 mmol of crotonyl chloride. The product, a red oily solid, was purified by filtration chromatography. Pentane and pentane/CH$_2$Cl$_2$ (20:1 v/v) eluted two orange bands. The first gave a red oil, which when subjected to repeated purification by medium-pressure chromatography yielded 0.05 g (0.13 mmol, 8% based on S) of (μ-EtS)$_2$Fe$_2$(CO)$_6$ (a red oil identified by its ^{1}H NMR spectrum)[18] and 0.12 g (0.34 mmol, 10%) of (μ-σ,π-HC=CHMe)(μ-EtS)Fe$_2$(CO)$_6$ (**16c**; also a slightly air-sensitive red oil). Anal. Calcd for C$_{11}$H$_{10}$Fe$_2$O$_6$S: C, 34.59; H, 2.64. Found: C, 34.92; H, 2.72. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.28 (t, *J* = 7.39 Hz, 3 H, SCH$_2$C*H*$_3$), 1.72 (d, *J* = 5.82 Hz, 3 H, C=CHC*H*$_3$), 2.30 (q, *J* = 7.36 Hz, 2 H, SC*H*$_2$CH$_3$), 3.57 (m, 1 H, HC=C*H*CH$_3$), 7.56 (d, *J* = 13.06 Hz, 1 H, *H*C=CHMe). ^{13}C NMR (CDCl$_3$; 100.5 MHz): δ 17.95 (q, *J* = 128.6 Hz, SCH$_2$CH$_3$), 24.86 (q, *J* = 127.3 Hz, C=CH*C*H$_3$), 33.71 (t, *J* = 140.5 Hz, S*C*H$_2$CH$_3$), 93.49 (d, *J* = 158.7 Hz, C=*C*HMe), 151.47 (d, *J* = 146.5 Hz, H*C*=CHMe), 208.85 and 209.85 (both s, Fe—CO).

The second band gave, as an inseparable mixture of two isomers, 1.03 g (2.51 mmol, 80%) of (μ-MeCH=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15c**) as a slightly air-sensitive red oil. Due to its facile decarbonylation, analytically pure material could not be obtained. ^{1}H NMR (CDCl$_3$; 300 MHz): δ 1.34 (t, *J* = 7.24 Hz, 3 H, SCH$_2$C*H*$_3$ minor isomer), 1.49 (t, *J* = 7.76 Hz, 3 H, SCH$_2$C*H*$_3$ major isomer), 1.85 (m, C=CHC*H*$_3$ both isomers), 2.11, 2.32, and 2.64 (all m, 4 H, SC*H*$_2$CH$_3$ both isomers), 5.96 (dd, *J* = 15.49 Hz, *J* = 1.47 Hz, 1 H, *H*C=CHMe major isomer), 6.07 (dd, *J* = 14.95 Hz, *J* = 2.30 Hz, 1 H, *H*C=CHMe minor isomer), 6.57 (m, 2 H, HC=C*H*Me both isomers). major/minor = 2.0/1.0. ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 17.70 (q, *J* = 128.1 Hz, HC=CH*C*H$_3$ both isomers), 18.18 (q, *J* = 128.4 Hz, SCH$_2$*C*H$_3$ both isomers), 25.86 (t, *J* = 142.9 Hz, S*C*H$_2$CH$_3$ minor isomer), 32.87 (t, *J* = 141.8 Hz, S*C*H$_2$CH$_3$ major isomer), 140.83 (d, *J* = 158.8 Hz, HC=*C*HMe major isomer), 141.33 (d, *J* = 160.4 Hz, HC=*C*HMe minor isomer), 143.91 (d, *J* = 154.3 Hz, H*C*=CHMe minor isomer), 145.03 (d, *J* = 154.9 Hz, H*C*=CHMe major isomer), 207.65, 209.45, 209.81, 210.14, 211.36, and 212.02 (all s, Fe—CO), 284.94 (s, acyl C=O major isomer), 287.74 (s, acyl C=O minor isomer).

Synthesis of (μ-Me$_2$C=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$. The same procedure as above was used in the reaction of 2.98 mmol of Me$_2$C=CHC(O)Cl with 2.98 mmol of [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$]. The red oily solid that was isolated was purified by filtration chromatography. Pentane/CH$_2$Cl$_2$ (20:1 v/v) eluted a red band, which gave 1.18 g (2.77 mmol, 93%) of (μ-Me$_2$C=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$ (**15d**) as a red oil (two isomers by NMR). A satisfactory analysis could not be obtained due to its instability. ^{1}H NMR (CDCl$_3$; 250 MHz): δ 1.34 (t, J_{HH} = 7.3 Hz, e isomer, –SCH$_2$C*H*$_3$), 1.48 (t, J_{HH} = 7.3 Hz, a isomer, –SCH$_2$C*H*$_3$), 1.60 (s, e isomer, *trans*-C*H*$_3$C=CH–), 1.67 (s, a isomer, *trans*-C*H*$_3$C=CH–), 1.70 (s, e isomer, *cis*-C*H*$_3$C=CH–), 1.73 (s, a isomer, *cis*C*H*$_3$C=CH–), 2.10–2.68 (m, 2 H, both isomers, –SC*H*$_2$CH$_3$), 6.30 (s, e isomer, (CH$_3$)$_2$C=C*H*–), 6.38 ns, a isomer, (CH$_3$)$_2$C=C*H*–). ^{13}C NMR (CDCl$_3$; 67.9 MHz): δ 17.9 (q, J_{CH} = 123.0 Hz, a isomer, –SCH$_2$C*H*$_3$), 18.4 (q, J_{CH} = 125.2 Hz, e isomer, –SCH$_2$C*H*$_3$), 21.5 (overlapping q's, J_{CH}'s could not be determined accurately, both isomers, *trans*-*C*H$_3$C=CH–), 26.8 (q, J_{CH} could not be determined accurately, a isomer, *trans*-*C*H$_3$C=CH–), 27.0 (q, J_{CH} = 124.9 Hz, e isomer, *cis*-*C*H$_3$C=CH–), 33.0 (t, J_{CH} = 141.0 Hz, –SC*H*$_2$CH$_3$), 136.4 (d, J_{CH} ; 158.0 Hz, e isomer, (CH$_3$)$_2$C=*C*H–), 136.6 (d, J_{CH} = 158.0 Hz, a isomer, (CH$_3$)$_2$C=*C*H–), 147.2 (s, both isomers [?], (CH$_3$)$_2$*C*=CH–), 207.8, 209.8, 210.4, 212.1 (s's, carbonyl C's), 283.8, 286.6 (s's, –C=CH*C*=O).

Decarbonylation of the RCH=CHC(O)Cl/[Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] Reaction Products. (a) (μ-Me$_2$C=CHC=O)(μ-EtS)Fe$_2$(CO)$_6$. A 100-mL three-necked, round-bottomed flask equipped with a reflux condenser and nitrogen inlet (gas adapter), glass stopper, stirbar, and rubber septum was charged with 0.73 g (1.72 mmol) of (μ-Me_2C=CHC=O)(μ-EtS)$Fe_2(CO)_6$ (**15d**) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 mL of THF. After the reaction mixture had been stirred for 15 h at room temperature and then 4 h at reflux, the solvent was removed in vacuo to yield a red oil, which was dissolved in pentane/CH_2Cl_2 (4:1 v/v) and filtered through a thin pad of silicic acid. Removal of solvent left a red oil, which was purified by filtration chromatography. Pentane eluted two red bands. The first gave a red oil identified by its ^1H NMR spectrum to be a mixture of several products. The second band gave 0.13 g (0.30 mmol, 17%) of starting material, **15d**, identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz). Repurification of the first fraction by medium-pressure chromatography yielded two bands eluting in pentane. The first gave a red oil identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz) to be a mixture of 0.22 g (0.57 mmol, 33%) of (μ-σ,π-HC=CMe_2)(μ-EtS)$Fe_2(CO)_6$ (**16d**) and 0.12 g (0.31 mmol, 36% based on S) of (μ-EtS)$_2Fe_2(CO)_6$ (**11**).[18] The second gave 0.08 g (0.18 mmol, 11%) of starting material, **15d**, identified by its ^1H NMR spectrum ($CDCl_3$; 250 MHz). Analytically pure (μ-σ,π-HC=CMe_2)(μ-EtS)$Fe_2(CO)_6$ (**16d**; a slightly air-sensitive red oil) could be obtained by repeated medium-pressure chromatography of the first fraction (fractionation of the leading edge). Anal. Calcd for $C_{12}H_{12}Fe_2O_6S$: C, 36.40; H, 3.05. Found: C, 36.80; H, 3.14. ^1H NMR ($CDCl_3$; 250 MHz): δ 1.29 (t, J = 7.37 Hz, 3 H, SCH_2CH_3), 1.66 (s, 3 H, HC=$C(CH_3)_2$ endo), 1.77 (s, 3 H, HC=$C(CH_3)_2$ exo), 2.30 (q, J = 7.36 Hz, 2 H, SCH_2CH_3), 7.57 (s, 1 H, HC=CMe_2). ^{13}C NMR ($CDCl_3$; 100.5 MHz): δ 17.88 (q, J = 128.9 Hz, SCH_2CH_3), 24.76 (q, J = 128.1 Hz, HC=$C(CH_3)_2$ exo), 35.41 (t, J = 142.2 Hz, SCH_2CH_3), 36.10 (q, J = 128.6 Hz, HC=$C(CH_3)_2$ endo), 114.91 (s, HC=CMe_2), 153.31 (d, J = 143.5 Hz, HC=CMe_2), 208.86 and 210.09 (both s, Fe—CO).

(b) (μ-CH_2=CHC=O)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that above, a THF solution containing 0.39 g (0.99 mmol) of (μ-CH_2=CHC=O)(μ-EtS)$Fe_2(CO)_6$ (**15a**) was stirred for 48 h at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band, which gave 0.34 g (0.91 mmol, 92%) of (μ-σ,π-HC=CH_2)(μ-EtS)$Fe_2(CO)_6$ (**16a**),[11a] identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

(c) (μ-PhCH=CHC=O)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that above, a THF solution containing 0.09 g (0.20 mmol) of (μ-PhCH=CHC=O)(μ-EtS)$Fe_2(CO)_6$ (**15b**) was stirred for 40 h at room temperature and then 1.5 h at reflux. Subsequently, the solvent was removed in vacuo and the resulting red oil was purified by filtration chromatography. Pentane eluted a pale yellow band, which was not collected. Pentane then eluted a red band, which gave 0.07 g (0.16 mmol, 82%) of (μ-σ,π-HC=CHPh)(μ-EtS)$Fe_2(CO)_6$ (**16b** (**6h′**)), identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

(d) (μ-MeCH=CHC=O)(μ-EtS)$Fe_2(CO)_6$. In an experiment similar to that in (a), a THF solution containing 0.44 g (1.07 mmol) of (μ-MeCH=CHC=O)(μ-EtS)$Fe_2(CO)_6$ (**15c**) was stirred for 17 h at room temperature, 1.5 h at reflux, and then 4 h more at room temperature. Subsequently, the solvent was removed in vacuo, and the resulting red oil was purified by filtration chromatography. Pentane eluted an orange band, which gave 0.40 g (1.04 mmol, 98%) of (μ-σ,π-HC=CHMe)(μ-EtS)$Fe_2(CO)_6$ (**16c**), identified by its ^1H NMR spectrum ($CDCl_3$; 300 MHz).

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Supplementary Material Available: A table of IR and EI mass spectra of new compounds (13 pages). Ordering information is given on any current masthead page.

High-Resolution Solid-State ^{119}Sn and ^{13}C NMR Studies of Novel Organotin(IV) Coordination Polymers Involving R_3Sn and $M(CN)_m$ Fragments

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The room-temperature solid-state ^{119}Sn and ^{13}C CP/MAS NMR spectra of seven well-defined coordination polymers have been examined and satisfactorily interpreted: $[(Me_3Sn)_3Co^{III}(CN)_6]_\infty$ (**1**), $[(Et_3Sn)_3Co^{III}(CN)_6]_\infty$ (**2**), $[(Et_3Sn)Au^{I}(CN)_2]_\infty$ (**3**), $[(Me_3Sn)_4Fe^{II}(CN)_6]_\infty$ (**4**), $[(Me_3Sn)_4Ru^{II}(CN)_6]_\infty$ (**5**), $[(Me_3Sn)_4Fe^{II}(CN)_6 \cdot 2H_2O \cdot C_4H_8O_2]_\infty$ (**6**), and $[(Me_3Sn)_4Fe^{II}(CN)_6 \cdot nH_2O]_\infty$ (**7**). Owing to the appearance of relatively sharp NMR signals, the information to be deduced from the solid-state NMR spectra greatly exceeds that to be gained by other spectroscopic techniques applicable to powders (e.g. IR, Raman, and Mössbauer spectroscopy) and X-ray powder diffractometry. In particular, the NMR spectra of **1**, **6**, and **7** match well with the results of recent single-crystal X-ray studies. The ^{119}Sn NMR spectra of the isostructural homologues **4** and **5** may be interpreted in terms of trigonal bipyramidally configured $Me_3Sn(NC...)_2$ fragments (of the polymeric framework) as well as of quasi-mobile Me_3Sn^+ ions.

Introduction

Recently, high-resolution solid-state ^{119}Sn CP/MAS NMR spectroscopy has been shown to be one of the most effective tools for the detection of even subtle details in the structural and/or electronic properties of organotin compounds.[1] Thus, ^{119}Sn CP/MAS NMR spectra fre-

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