3834 *Organometallics* **1994,** *13,* 3834–3848

Reactions of Triethylammonium Salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ Anions with Alkynylmercury Compounds. Unexpected Products via Hydrogen Migration Processes[†]

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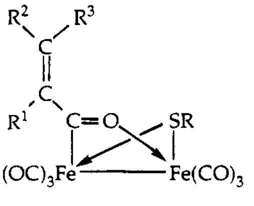
The reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ with bis(1-alkynyl)mercury compounds gave different products depending on the nature of the organomercurial. Bis(phenylethynyl)mercury and bis(1-hexynyl)mercury gave $\mu\text{-}\eta^1{:}\eta^2$-acetylide complexes, $(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}CR^1)(\mu\text{-RS})Fe_2(CO)_6$, while bis(3-methoxy-1-propynyl)mercury and bis(3-(dimethylamino)-1-propynyl)mercury formed doubly bridging vinylcarbyne products, $(\mu\text{-XCH}{=}CHC)(\mu\text{-RS})Fe_2(CO)_6$, where $X = OCH_3$, $N(CH_3)_2$. The vinylcarbyne products resulted from a net 1,2-hydrogen shift from the propargylic carbon atom to the β-carbon atom of the original acetylenic unit. In addition, the reaction with bis(3-methoxy-1-propynyl)mercury gave a tetrairon cluster, $[(\mu\text{-CH}_3OCH_2\text{-}CHC)(\mu\text{-RS})Fe_2(CO)_6]_2Hg$, composed of two butterfly diiron hexacarbonyl moieties (each of which possessed doubly bridging vinylidene and thiolate ligands) bridged by a mercury atom on the butterfly hinges. X-ray crystal structure determinations were carried out on the vinyl carbyne complex $(\mu\text{-CH}_3OCH{=}CHC)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ as well as the dimeric mercury product $[(\mu\text{-CH}_3OCH_2CH{=}C)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2Hg$. The reactions of propargylic substituted 1-bromoalkynes also were dependent on the nature of the acetylene. 3-Methoxy-1-bromopropyne formed the $\mu\text{-}\eta^1{:}\eta^2$-acetylide complex $(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}CCH_2OCH_3)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$, as well as the doubly bridging vinylcarbyne product, while 3-dimethylamino-1-bromopropyne gave only the vinylcarbyne complex. The vinylcarbyne complex $(\mu\text{-CH}_3OCH{=}CHC)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ was converted to the formyl-substituted $\mu\text{-}\eta^1{:}\eta^2$-vinyl complex $(\mu\text{-}\eta^1{:}\eta^2\text{-CH}{=}CHC(O)H)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ upon treatment with aqueous hydrochloric acid or trifluoroacetic acid.

Introduction

In an earlier paper,[1] we reported reactions of the triethylammonium salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions with alkyl-, aryl-, and vinylmercuric halides. With alkyl- and arylmercuric halides, products of the type $(\mu\text{-R}'C{=}O)(\mu\text{-RS})Fe_2(CO)_6$ (R′ = alkyl, aryl) were formed, most likely *via* the process shown in Scheme 1. However, with vinylic mercuric halides, two types of products, **1** and **2**, were formed, their yields depending on the substituents on the vinyl carbon atoms. Type **2** complexes were produced by decarbonylation of **1**, as was shown in separate experiments.



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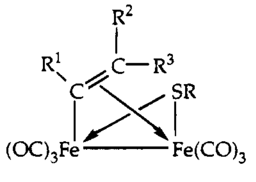

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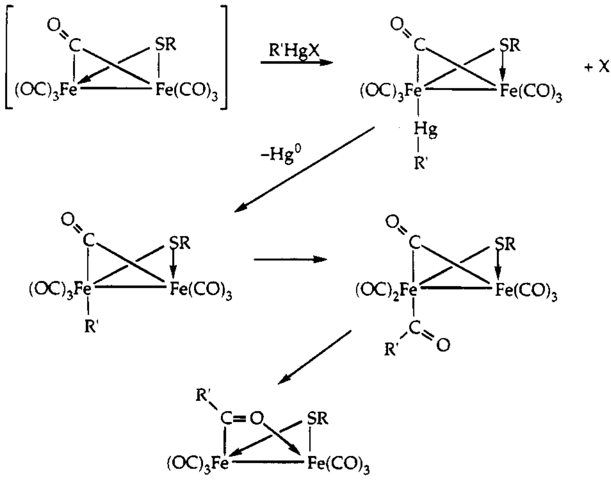
Scheme 1



In view of these findings, it was of interest to see how $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ complexes react with alkynylmercury compounds. In prior work[2] we had found that bromoalkynes react with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ complexes to give products of type $(\mu\text{-}\eta^1{:}\eta^2\text{-R}'C{\equiv}C)(\mu\text{-RS})Fe_2(CO)_6$ (**3**; eq 1); therefore, such

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[†] Dedicated to Professor Jacques Satgé, with all best wishes, on the occasion of his 65th birthday.

[®] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) Seyferth, D.; Archer, C. M.; Ruschke, D. P.; Cowie, M.; Hilts, R. W. *Organometallics* **1991,** *10,* 3363.

(2) Seyferth, D.; Hoke, J. B.; Wheeler, D. R. *J. Organomet. Chem.* **1988,** *341,* 421.

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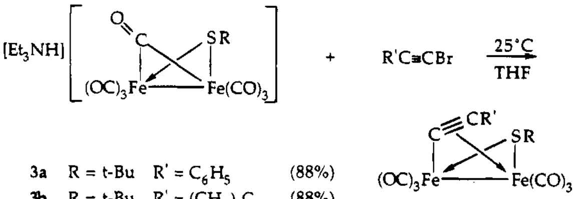
complexes might be expected to be formed in the reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with alkynylmercury compounds.



(1)

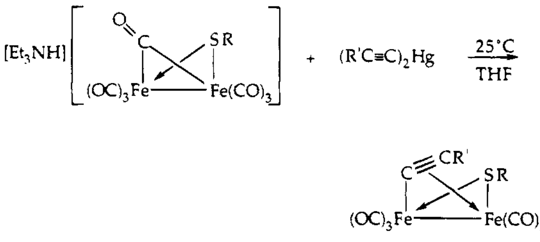
3

3a	R = t-Bu	R' = C_6H_5	(88%)
3b	R = t-Bu	R' = $(CH_3)_3C$	(88%)
3c	R = t-Bu	R' = $(CH_3)_3Si$	(93%)
3d	R = Et	R' = C_6H_5	(84%)
3e	R = Et	R' = $(CH_3)_3C$	(71%)
3f	R = Ph	R' = $(CH_3)_3C$	(66%)

This was found to be the case when simple alkynylmercurials, $(RC{\equiv}C)_2Hg$, were used, but with γ-substituted propynylmercury compounds $(ZCH_2C{\equiv}C)_2Hg$ (Z = CH_3O, $(CH_3)_2N$) more complicated chemistry was encountered.

Results and Discussion

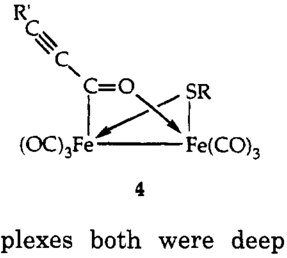
Reactions with Dialkynylmercury Compounds $(R'C{\equiv}C)_2Hg$ (R' = C_6H_5, *n*-C_4H_9). Since $RC{\equiv}C$ is a good anionic leaving group, these experiments were carried out with mercurials of type $(R'C{\equiv}C)_2Hg$, which are more stable than $R'C{\equiv}CHgX$. Reaction of $(PhC{\equiv}C)_2Hg$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ and of $(n\text{-}C_4H_9C{\equiv}C)_2Hg$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ gave the respective μ-η^1:η^2-alkynyl complexes $(\mu\text{-}\eta^1\text{:}\eta^2\text{-}R'C{\equiv}C)(\mu\text{-}RS)Fe_2(CO)_6$ (**3**; R = Et, R' = Ph; R = *t*-Bu, R' = *n*-C_4H_9) in moderate yields (eq 2), in addition to the respective $(\mu\text{-}RS)_2Fe_2(CO)_6$ complexes, which usually are byproducts in $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$/organomercurial reactions.[1] A black, powdery precipitate was indicative of the formation of elemental mercury.[1] We assume that in these reactions the initially formed product is the unstable $(\mu\text{-}R'C{\equiv}CC{=}O)(\mu\text{-}RS)Fe_2(CO)_6$ (**4**), which then undergoes decarbonylation. These μ-η^1:η^2-alkynyl complexes both were deep red oils and wereisolated as mixtures of two inseparable isomers due to an axial or equatorial orientation of the R substituent of the bridging thiolate ligand. Similar to the μ-η^1:η^2-vinyl complexes, the μ-η^1:η^2-alkynyl complexes showed fluxional behavior, very likely due to a flipping motion of the alkylnyl ligand across the face of the $Fe_2(CO)_6$ core (eq 3).



(2)

3

3g	R = Et	R' = C_6H_5	(47%)
3h	R = t-Bu	R' = n-C_4H_9	(57%)



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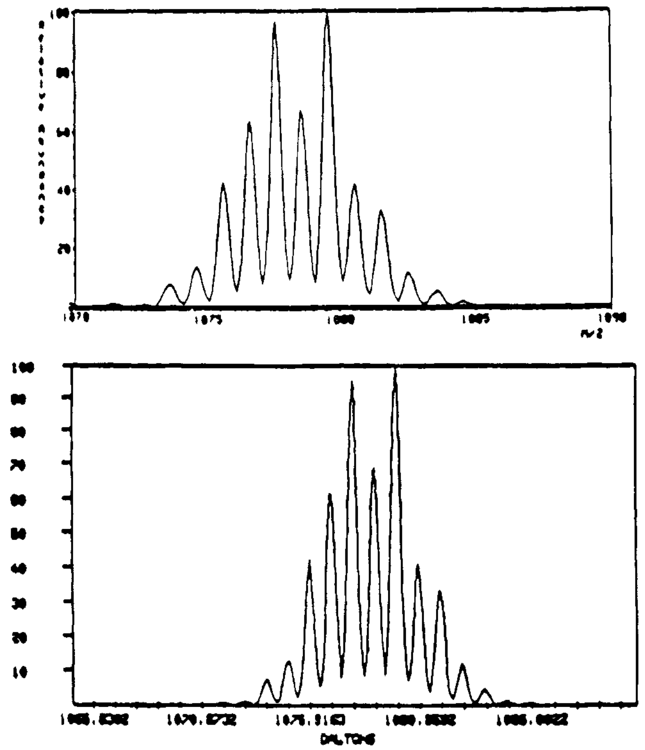
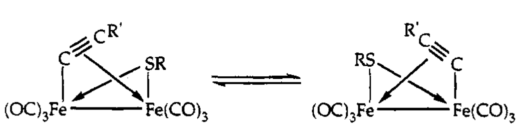


Figure 1. Experimental (top) and calculated (bottom) isotopic ratios for the parent ion (M^+) of $C_{28}H_{30}Fe_4HgO_{14}S_2$ (**6**).



(3)

Reactions with Functionally Substituted Dialkynylmercury Compounds $(R'C{\equiv}C)_2Hg$ (R' = CH_3OCH_2, $(CH_3)_2NCH_2$). Functionally substituted dialkynylmercurials $(ZCH_2C{\equiv}C)_2Hg$ (Z = CH_3O, $(CH_3)_2N$) reacted quite differently. When solid $(CH_3OCH_2C{\equiv}C)_2Hg$ was added to a brown-red solution of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ in THF (under nitrogen), brisk gas evolution ensued, and the color of the solution changed to deep red. After 30 min, TLC showed the presence of three products, two of which moved with pentane; the third did not. Removal of THF left a red oil. Filtration chromatography of the latter (elution with pentane) gave the known $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ (**5**; 20% yield) and an orange-red solid which was not, according to its NMR spectra, the expected $(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH_3OCH_2C{\equiv}C)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$. Further elution with CH_2Cl_2 led to isolation of the air-stable, red-black solid **6**, which contained mercury. The latter was difficult to purify; extended medium-pressure chromatography was required.

The field desorption mass spectrum of the mercury-containing product **6** established the formula $C_{28}H_{30}O_{14}S_2Fe_4Hg$. Figure 1 shows the excellent agreement between the observed parent ion (M^+) peak and that calculated for the parent ion of that formula. A possible and reasonable structure of **6** is that shown in Figure

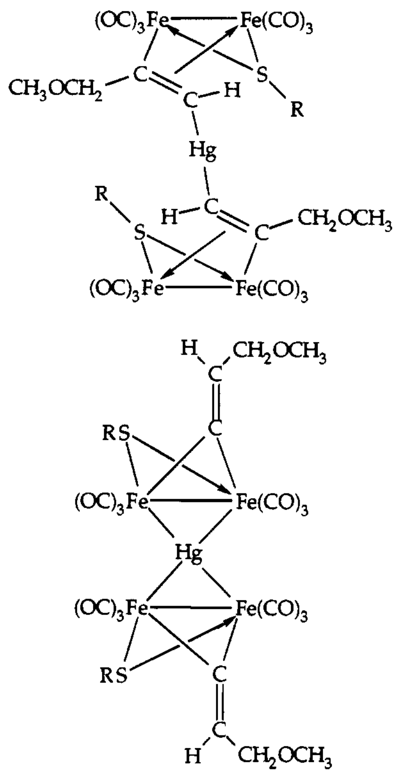


Figure 2. Complex **6**: (a, top) anticipated structure; (b, bottom) observed structure.

2a, i.e., the product of the addition of the $[(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]^-$ anion to the C≡C bond of $(CH_3OCH_2C{\equiv}C)_2Hg$. The extra (vinylic) proton would be derived by protonation of the anionic intermediates by $[Et_3NH]^+$, as was the case in reactions of simple acetylenes with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$.[3]

However, the NMR spectra of **6** were not in agreement with this structure. In the ^{1}H NMR spectrum two signals, a complex two-proton multiplet at 4.0 ppm and a one-proton triplet at 6.2 ppm (J = 6.3 Hz), were observed in addition to the *t*-BuS and CH_3O resonances. The ^{13}C NMR spectrum showed a triplet at 74 ppm, a doublet at 140 ppm, and a singlet at 221 ppm, in addition to signals due to the $(CH_3)_3CS$ ligand and five singlets in the terminal CO region (207–211 ppm).

In order to unambiguously determine the structure of the Hg-containing product of the $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]/(CH_3OCH_2C{\equiv}C)_2Hg$ reaction, an X-ray diffraction study was carried out. The complex crystallized in the space group $P2_1/c$ (No. 14) with some disorder in the outer regions of the molecule. An ORTEP plot showing 40% probability ellipsoids is given in Figure 3. The structure is not an expected one. The complex **6** contains two $Fe_2(CO)_6$ units, each of which is bridged by a *t*-BuS ligand and a $CH_3OCH_2CH{=}C$ vinylidene ligand, and the two $Fe_2(CO)_6$ units also are bridged by the mercury atom. The line drawing shown in Figure 2b makes this clear. The two $[(\mu\text{-}CH_3OCH_2CH{=}C)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ units are virtually identical (see Table 1 for bond distances and angles). The molecule contains two Fe—Fe single bonds (average d(Fe—Fe) = 2.646 Å), symmetrical *t*-BuS bridges (average d(Fe—S) = 2.260 Å), and symmetrical vinylidene bridges (average d(Fe—C) = 1.97 Å). The C═C distance of the vinylidene ligands (average d(C═C) = 1.32 Å) is in the range normally associated with C═C bonds in olefins, 1.34 Å.[4] Each of the $[(\mu\text{-}CH_3OCH_2CH{=}C)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ units can be regarded as essentially monoanionic, with each Fe atom having a formal electron count of 18. Thus, the mercury would have a formal charge of 2+, making the overall complex neutral. The geometry of the mercury atom in **6** is between square planar and tetrahedral, with a dihedral angle of 35.5° between the two planes formed by Fe(1)—Fe(3)—Hg and Fe(2)—Fe(4)—Hg. Thus, in the solid state, this complex is not completely symmetrical about a plane that bisects the two Fe—Fe bonds and contains the Hg atom. It could be that these distortions in the solid state result from packing (intermolecular forces). The ^{1}H and ^{13}C NMR solution spectra of **6** in any case

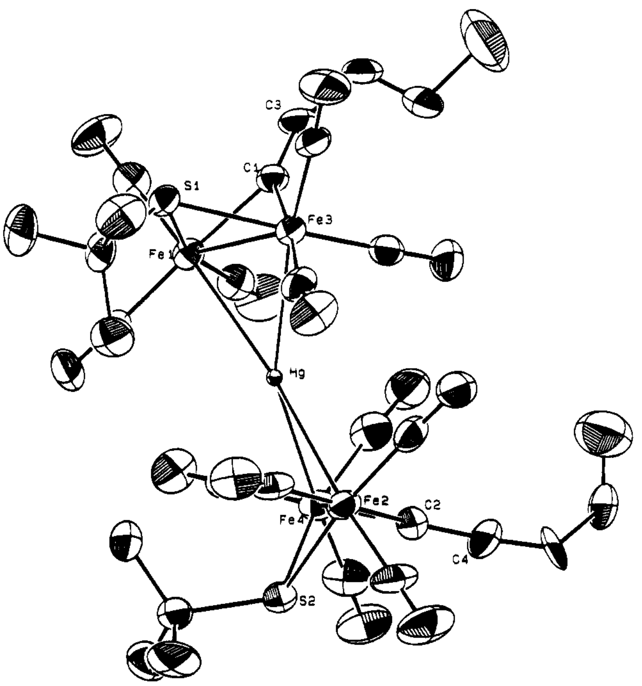


Figure 3. ORTEP plot of $[(\mu\text{-}CH_3OCH_2CH{=}C)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2Hg$ (**6**), showing 40% probability ellipsoids.

Table 1. Relevant Bond Distances (Å) and Angles (deg) for $[(\mu\text{-}CH_3OCH_2CH{=}C)(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2Hg$ (6)[a]

Fe(1)—Hg	2.774(2)	Fe(3)—Hg	2.761(2)
Fe(2)—Hg	2.778(2)	Fe(4)—Hg	2.772(2)
Fe(1)—Fe(3)	2.645(2)	Fe(2)—Fe(4)	2.647(3)
Fe(1)—S(1)	2.260(4)	Fe(2)—S(2)	2.254(4)
Fe(3)—S(1)	2.260(3)	Fe(4)—S(2)	2.266(4)
Fe(1)—C(1)	1.98(1)	Fe(2)—C(2)	1.99(1)
Fe(3)—C(1)	1.96(1)	Fe(4)—C(2)	1.96(1)
C(1)—C(3)	1.32(2)	C(2)—C(4)	1.31(1)
Fe(3)—Hg—Fe(4)	155.23(6)	Fe(4)—Hg—Fe(1)	126.03(6)
Fe(3)—Hg—Fe(1)	57.08(5)	Fe(4)—Hg—Fe(2)	56.97(6)
Fe(3)—Hg—Fe(2)	123.80(6)	Fe(1)—Hg—Fe(2)	172.43(5)
Fe(3)—Fe(1)—C(1)	47.6(3)	Fe(4)—Fe(2)—C(2)	47.4(4)
Fe(1)—Fe(3)—C(1)	48.2(3)	Fe(2)—Fe(4)—C(2)	48.4(4)
Fe(1)—C(1)—Fe(3)	84.2(5)	Fe(4)—C(2)—Fe(2)	84.2(5)
Fe(3)—Fe(1)—S(1)	54.2(1)	Fe(4)—Fe(2)—S(2)	54.4(1)
Fe(1)—Fe(3)—S(1)	54.2(1)	Fe(2)—Fe(4)—S(2)	54.0(1)
Fe(1)—S(1)—Fe(3)	71.6(1)	Fe(2)—S(2)—Fe(4)	71.7(1)
Fe(3)—S(1)—C(101)	120.0(4)	Fe(4)—S(2)—C(201)	121.1(4)
Fe(1)—S(1)—C(101)	120.1(5)	Fe(2)—S(2)—C(201)	119.2(4)

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

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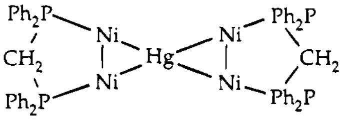
[3] Seyferth, D.; Hoke, J. B.; Womack, G. M. *Organometallics* **1990**, *9*, 2662.

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

show equivalent proton and carbon signals. On the basis of the determined structure, the yield of **6** produced in the [Et$_3$NH][(μ-CO)(μ-*t*-BuS)Fe$_2$(CO)$_6$]/(CH$_3$OCH$_2$C≡C)$_2$Hg reaction was 36%. An analogous mercury product was obtained in 40% yield in the reaction of [Et$_3$NH][(μ-CO)(μ-EtS)Fe$_2$(CO)$_6$] with (CH$_3$OCH$_2$C≡C)$_2$Hg.

Transition-metal clusters in which four metal atoms are spiro-bridged by a mercury atom are known.[5] Most of these cluster complexes contain more than four metal atoms, e.g., [(μ-C$_2$-*t*-Bu)Ru$_3$(CO)$_9$]$_2$Hg.[6] In these the mercury occupies a metal–metal edge-bridging position; hence, only two metal atoms of each polymetal unit of the cluster are involved. One complex containing a M$_2$HgM$_2$ system has been isolated, [{Ni$_2$(μ-CNCH$_3$)(CNCH$_3$)$_4$(Ph$_2$PCH$_2$PPh$_2$)}$_2$Hg][NiCl$_4$], in which the [HgNi$_4$(Ph$_2$PCH$_2$PPh$_2$)$_2$] core has the structure **7**.[7] The similarity to **6** is striking in that the dihedral angle between the two Ni$_2$Hg planes is 34.6(1)°. This suggests that the asymmetry above is not merely a solid-state effect. Complex **8** has been suggested as the product of the disproportionation of complexes of type (μ-CO)(μ-R$_2$P)(μ-MHg)Fe$_2$(CO)$_6$ (MHg = CpW(CO)$_3$Hg, (OC)$_5$MnHg, (OC)$_4$CoHg, CpFe(CO)$_6$Hg), but it was not isolated and only a ^{31}P NMR signal at +10 ppm (vs (MeO)$_3$P) in THF was cited as evidence for its presence.[8]



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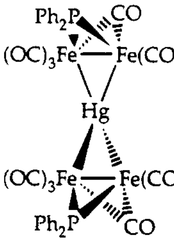

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The orange-red product from the [Et$_3$NH][(μ-CO)(μ-*t*-BuS)Fe$_2$(CO)$_6$]/(CH$_3$OCH$_2$C≡C)$_2$Hg reaction which was eluted by pentane does not contain mercury. It contains a bridging *t*-BuS ligand, and according to the ^{1}H NMR spectrum, only one isomer is present. As noted above, the organic ligand is not the μ-η^1:η^2-CH$_3$OCH$_2$C≡C group, but according to the elemental analysis of the complex, it is isomeric with this group. An X-ray diffraction study of this complex showed it to be **9**. The complex crystallized in the space group $P\bar{1}$ (No. 2) with two independent molecules per asymmetric unit. An ORTEP plot of molecule 1 is shown in Figure 4; its atom-labeling scheme is used in our discussion of the structure. Relevant bond distances and angles are given in Table 2.

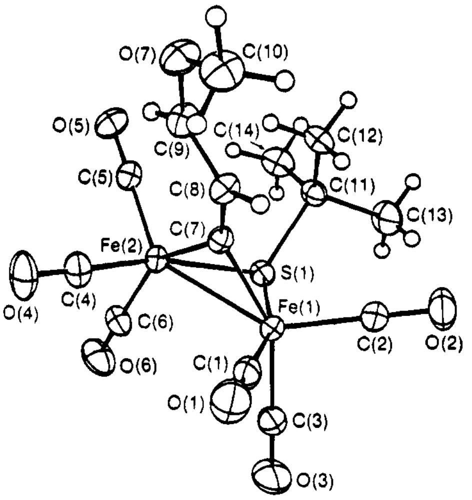
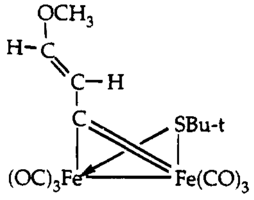


Figure 4. ORTEP plot of molecule 1 of (μ-CH$_3$OCH=CHC)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (**9**), showing 20% probability ellipsoids.

Table 2. Relevant Bond Distances (Å) and Angles (deg) for (μ-CH$_3$OCH=CHC)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (9)[a]

molecule 1		molecule 2	
Fe(1)–Fe(2)	2.5214(6)	Fe(21)–Fe(22)	2.5035(7)
Fe(1)–S(1)	2.265(1)	Fe(21)–S(21)	2.257(1)
Fe(2)–S(1)	2.263(1)	Fe(22)–S(21)	2.261(1)
Fe(1)–C(7)	1.860(3)	Fe(21)–C(27)	1.843(3)
Fe(2)–C(7)	1.881(3)	Fe(22)–C(27)	1.879(4)
C(7)–C(8)	1.416(5)	C(27)–C(28)	1.468(6)
C(8)–C(9)	1.317(5)	C(28)–C(29)	1.241(7)
C(9)–O(7)	1.335(5)	C(29)–O(27)	1.406(6)
O(7)–C(10)	1.411(5)	O(27)–C(30)	1.394(7)
Fe(1)–Fe(2)–C(7)	47.28(9)	Fe(21)–Fe(22)–C(27)	47.1(1)
Fe(2)–Fe(1)–C(7)	48.0(1)	Fe(22)–Fe(21)–C(27)	48.4(1)
Fe(1)–C(7)–Fe(2)	84.7(1)	Fe(21)–C(27)–Fe(22)	84.5(2)
Fe(1)–C(7)–C(8)	134.5(2)	Fe(21)–C(27)–C(28)	130.0(3)
Fe(2)–C(7)–C(8)	139.5(2)	Fe(22)–C(27)–C(28)	143.9(3)
C(7)–C(8)–C(9)	122.7(3)	C(27)–C(28)–C(29)	117.3(5)
C(8)–C(9)–O(7)	129.3(3)	C(28)–C(29)–O(27)	124.4(6)
C(9)–O(7)–C(10)	117.1(3)	C(29)–O(27)–C(30)	122.1(4)
Fe(1)–S(1)–Fe(2)	67.67(3)	Fe(21)–S(21)–Fe(22)	67.29(3)
Fe(1)–S(1)–C(11)	116.7(1)	Fe(21)–S(21)–C(31)	118.8(1)
Fe(2)–S(1)–C(11)	115.3(1)	Fe(22)–S(21)–C(31)	116.6(1)

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



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Complex **9** contains an Fe–Fe single bond (average *d*(Fe(1)–Fe(2)) 2.513(7) Å) and a symmetrically bridging 2-methyl-2-propanethiolate ligand (average *d*(Fe(1)–S(1)) = 2.261(1) Å and *d*(Fe(2)–S(1)) = 2.262(1) Å). The bridging *t*-BuS ligand has the *t*-Bu group in an axial orientation. The carbyne carbon atom bridges the Fe$_2$(CO)$_6$ core slightly asymmetrically (average *d*(Fe(1)–C(7)) = 1.852(3) Å; *d*(Fe(2)–C(7)) = 1.880(4) Å). These bond distances are both shorter than those in related iron complexes containing bridging carbene or carbene-like systems.[9] The observed asymmetry would appear to result from nonbonded interactions between Fe(2)/Fe(22) and the vinyl moiety, which is bent toward this metal atom. It is noteworthy that the two independent

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[5] Gade, L. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 24.

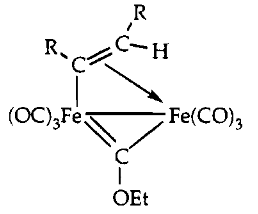
[6] Ermer, S.; King, K.; Hardcastle, K. I.; Rosenberg, E.; Manotti-Lanfredi, A. M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Inorg. Chem.* **1983**, *22*, 1339.

[7] Gong, J.; Huang, J.; Fanwick, P. E.; Kubiak, C. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 396.

[8] Geina, R.; Rossell, O.; Seco, M. *J. Organomet. Chem.* **1990**, *398*, 285.

molecules of **9** display significantly different parameters for the bridging vinylcarbyne ligand. These differences appear to be real, since parameters involving the rest of the two molecules are in excellent agreement.

The solution ^{13}C NMR spectrum of complex **9** was in agreement with the bridging carbyne structure. In particular, the carbyne carbon atom resonance at δ_C 360.47 is far downfield, as expected.[10] Note that a related $Fe_2(CO)_6$ complex, **10**, reported by Ros et al.[11]



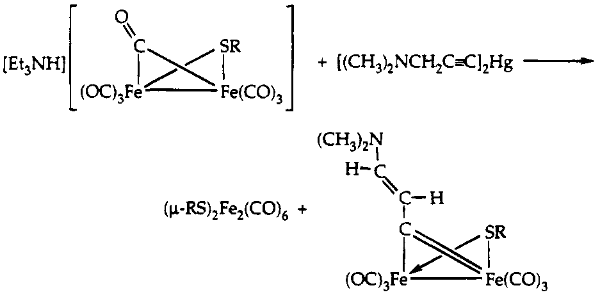
10

showed the bridging carbyne carbon atom resonance at δ_C 383.8. The vinyl carbon resonances in the spectrum of **9** were observed as doublets at δ_C 132.72 and 165.85. In its ^1H NMR spectrum the vinyl proton resonance, an AB quartet (J = 11.52 Hz) at δ 8.08, gave no clear indication whether the vinyl hydrogens were in a *trans* or *cis* arrangement.

A similar complex with the same bridging vinylcarbyne ligand, but with an ethanethiolate bridge (both axial and equatorial isomers), was obtained in the reaction of $(CH_3OCH_2C{\equiv}C)_2Hg$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$.

The yields of the vinylcarbyne-bridged $Fe_2(CO)_6$ complexes are low: 27% in the case of **9** and 9% in the case of the μ-EtS analog. As noted above, $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ was an additional product (20% yield) in the case of $(CH_3OCH_2C{\equiv}C)_2Hg/[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reaction. In the reaction of $(CH_3OCH_2C{\equiv}C)_2Hg$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$, a 44% yield of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ was obtained. The possible origin of $(\mu\text{-}RS)_2Fe_2(CO)_6$ byproducts obtained in nearly all reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes with organomercury compounds in ligand exchange processes was discussed in our earlier paper.[1]

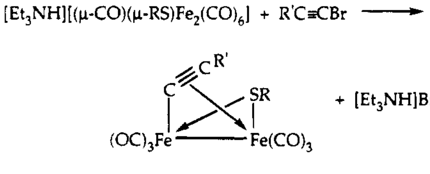
Similar reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (R = *t*-Bu, Et, Ph) complexes were carried out with $[(CH_3)_2NCH_2C{\equiv}C]_2Hg$. In these reactions no mercury-containing product was isolated. (This does not mean that they were not formed; if they were, then they were much less tractable than the $(CH_3OCH_2C{\equiv}C)_2Hg$-derived mercury products.) The soluble products that were isolated in each case were the respective $(\mu\text{-}RS)_2Fe_2(CO)_6$ species and the bridging vinylcarbyne complex **11** (eq 4),which establishes at least a limited generality, whose limits remain to be explored. The ^{13}C NMR spectra of these products were indicative of the structure shown in eq 4. All showed typical bridging carbyne carbon atom signals (major, minor isomer): **11a**, δ_C 375.32, 364.57; **11b**, δ_C 367.53 (both isomers); **11c**, δ_C 376.85, 362.97.



(4)

11, **a** R = t-Bu (29%)
b Et (30%)
c Ph (22%)

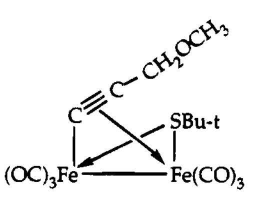
In an earlier paper we described the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes with bromoacetylenes (eq 5).[2] In view of the results obtained with



(5)

(R = t-Bu, Me$_3$Si, Ph)

$(CH_3OCH_2C{\equiv}C)_2Hg$ and $[(CH_3)_2NCH_2C{\equiv}C]_2Hg$, it was of interest to study the reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes with the corresponding bromoacetylenes. Three products were formed in the reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with $CH_3OCH_2C{\equiv}CBr$: $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ (15%), the $\mu\text{-}\eta^1{:}\eta^2$-alkynyl complex **12** (43%), and the μ-vinylcarbyne



12

complex **9** (24%). Similar reaction of $(CH_3)_2NCH_2C{\equiv}CBr$ with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (R = *t*-Bu, Et, Ph) gave only the μ-vinylcarbyne complexes **11a** (49%), **11b** (33%), and **11c** (28%) in addition to the respective $(\mu\text{-}RS)_2Fe_2(CO)_6$. In none of these reactions could a $(\mu\text{-}\eta^1{:}\eta^2\text{-}(CH_3)_2NCH_2C{\equiv}C)(\mu\text{-}RS)Fe_2(CO)_6$-type product be isolated. TLC examination of the reaction mixture gave no hint of their formation.

It is of interest to consider how the organomercury product **6** and the μ-vinylcarbyne complex **9** had been formed. The first reaction to take place, very likely, is nucleophilic displacement of an acetylide anion from mercury by the iron nucleophile (eq 6). The intermediate

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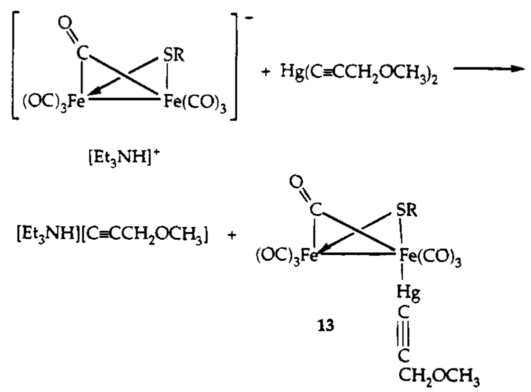
(9) Hoke, J. B.; Dewan, J. C.; Seyferth, D. *Organometallics* **1987**, *6*, 1816.

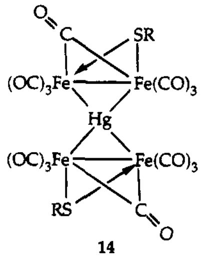
(10) (a) Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, *51* (μ-$COCH_3$, neutral, δ_C 361.3; μ_3-$COCH_3$, δ_C 342.6). (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621 (μ_3-$COCH_3$, anionic, δ_C 357.0, 362.9). (c) Keister, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 214 (μ-$COCH_3$, neutral, δ_C 360). (d) Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572 (μ-$COCH_3$, neutral, δ_C 383.3). (e) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620 (μ-CR, cationic, δ_C 448.27, 443.65, 432.7). (f) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134 (μ-CH, cationic, δ_C 490.2). (g) Casey, C. P.; Konings, M. S.; Marder, S. R. *Polyhedron* **1988**, *7*, 881 (μ-vinylcarbyne, cationic, δ_C 395.2–472.7). (h) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411 (μ-vinylcarbyne, cationic, δ_C 440.2, 444.6, 451.1). (i) Casey, C. P.; Konings, M. S.; Marder, S. R.; Takezawa, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5296 (μ-vinylcarbyne, cationic, δ_C 439.9).

(11) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087.

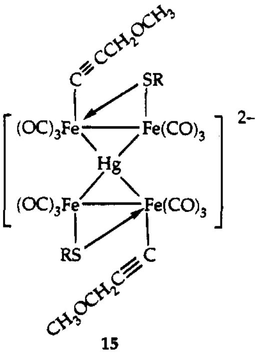


(6)

13, containing a displaceable $C{\equiv}CCH_2OCH_3$ substituent, could react with another $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anion to give **14**. Reaction of the two molar equivalents of $C{\equiv}CCH_2OCH_3^-$ anion generated in these steps with **14** could then introduce the μ-η^1:η^2-$C{\equiv}CCH_2OCH_3$ with loss of CO, giving **15**. The latter then could be protonated by Et_3NH^+ to give the observed **6**. In support of the last reaction, it is known that vinylidene–metal complexes can be prepared by protonation of σ-alkynyl–metal complexes.[12] The different reaction course that results when $Hg(C{\equiv}CPh)_2$ and $Hg(C{\equiv}C\text{-}n\text{-}C_4H_9)_2$ react with $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ may be due to a lesser stability of the initial intermediate (analogous to **13** in the case of $Hg(C{\equiv}CCH_2OCH_3)_2$) relative to extrusion of Hg and migration of the alkynyl group to the carbon atom of a CO ligand. It should be emphasized that this postulated reaction course is speculative; it has no experimental support, but it seems a reasonable one to us.



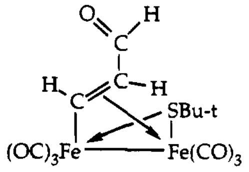
14



15

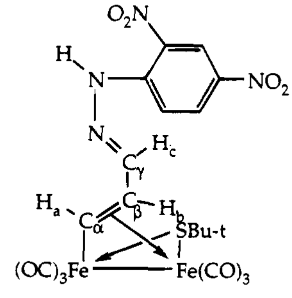
The formation of the μ-carbyne complex **9** possibly could occur via a deprotonation (by the Et_3N released in the reaction course above)/reprotonation sequence of $(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CCH_2OCH_3)(\mu\text{-RS})Fe_2(CO)_6$ as shown in Scheme 2. This reaction course also is speculative.

Hydrolysis of the Vinylcarbyne Complex 9. The μ-vinylcarbyne complexes obtained in these reactions are vinyl ethers, and as such they might be expected to undergo acid hydrolysis. This was found to be the case. When a THF solution of **9** was treated with an equimolar amount of aqueous hydrochloric acid, or even with water alone, an immediate color change from deep red to light orange occurred. Removal of THF *in vacuo*, extraction of the residue with diethyl ether, and subsequent evaporation of the extracts gave a nearly quantitative yield of an air-stable orange solid. The latter was identified as the μ-η^1:η^2-α,β-unsaturated aldehyde complex **16**.



16

Complex **16** showed a $\nu_{C=O}$ stretching frequency in its infrared spectrum at 1692 cm^{-1} which corresponded to the carbonyl of the aldehyde functionality. This stretching frequency fell in the region normally associated with conjugated aldehydes (1710–1685 cm^{-1}).[13] Its ^1H NMR spectrum showed three resonances for the vinyl and aldehydic protons. The proton attached to the α-carbon atom of the bridging vinyl ligand resonated downfield at 8.84 ppm and, as expected, was coupled to the proton bonded to the β-carbon atom (J = 12.21 Hz). The proton attached to the β-carbon atom appeared upfield at 3.80 ppm as a doublet of doublets, being coupled to the proton on the α-carbon atom as well as to the aldehydic proton (^3J = 5.37 Hz). The aldehydic proton gave a doublet far downfield at 9.10 ppm (^3J = 5.38 Hz), coupled to the proton bonded to the β-carbon atom of the vinyl ligand. The downfield shift of the proton on the α-carbon atom and the upfield shift of the proton on the β-carbon atom were consistent with those for other μ-η^1:η^2-vinyl complexes as discussed in ref 1. The ^{13}C NMR spectrum of **16** also supported the α,β-unsaturated aldehyde structure. The α-carbon atom signal was a doublet (J_{CH} = 152.5 Hz) at 163.03 ppm, and the aldehydic carbon atom signal was a doublet (J_{CH} = 171.8 Hz) at 193.95 ppm. The β-carbon atom gave a doublet of doublets at 84.71 ppm, coupled not only to the attached proton (J_{CH} = 163.2 Hz) but also to the aldehydic proton ($^2J_{CH}$ = 26.8 Hz). Again, the downfield shift of the α-carbon atom and the upfield shift on the β-carbon atom were consistent with those for previously discussed μ-η^1:η^2-vinyl complexes.[1] Mass spectral and carbon and hydrogen combustion analysis data also supported the composition of **16**. Chemical evidence for the presence of the formyl substituent in **16** was given by the preparation of the 2,4-dinitrophenyl hydrazone derivative **17**.



17

Independent preparation of a μ-η^1:η^2 unsaturated aldehyde complex was effected by the reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]$ with phenylpropargylaldehyde (eq 7). The IR and ^1H and ^{13}C NMR spectra of the product confirmed its structure as written.

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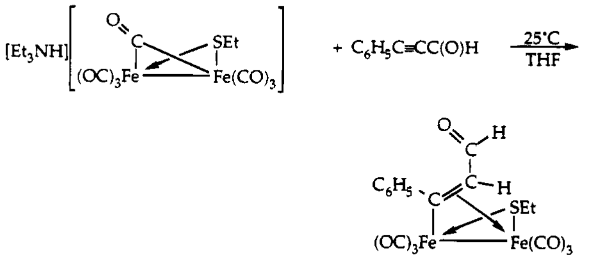
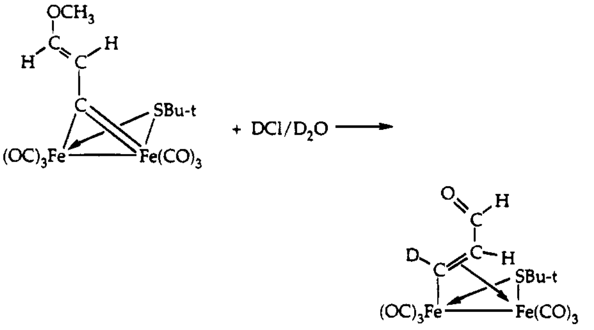
[12] Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.



(7)

18

Reaction of complex **9** with DCl/D$_2$O solution provided information bearing on the mechanism of the hydrolysis reaction. The product that was isolated in 80% yield again was a formyl-substituted μ-η^1:η^2-vinyl complex; in this case, however, a deuterium instead of a proton was bonded exclusively to the α-carbon atom of the bridging vinyl ligand (eq 8). This was confirmed by a comparison of the IR, ^{1}H NMR, and ^{13}C NMR spectral data of the product, **19**, with those of its protio counterpart, **16** (Table 3).



(8)

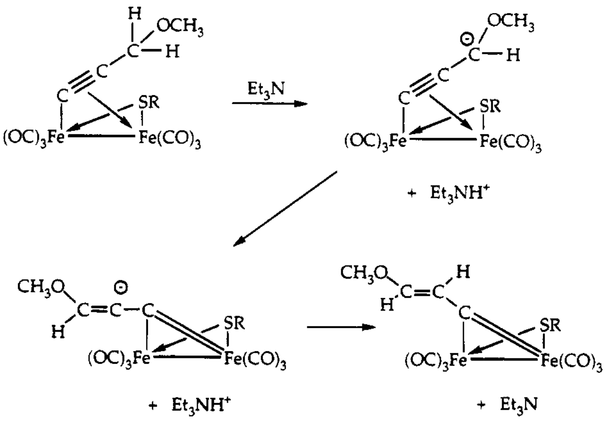
19

The deuterated complex **19** showed no downfield resonance in its ^{1}H NMR spectrum for the substituent bonded to the α-carbon atom. Also, the signal at 3.80 ppm due to H_b in **16** had now collapsed from a doublet of doublets to only a doublet, as H_b in **19** was no longer coupled to H_a and H_c but only to H_c. The ^{13}C NMR spectrum of **19** also showed a collapsed signal for C_α at approximately 163 ppm. The J_{CH} coupling seen in **16** (a doublet, $J_{CH} = 152.5$ Hz) was now replaced by a triplet with peaks of equal intensity ($J_{CD} = 18.0$ Hz) due to coupling with the attached deuterium. This corresponded well with the expected diminution of coupling when a proton is replaced by a deuteron. Since ^{2}H has a spin of 1 and a magnetic moment 15% that of ^{1}H, proton to deuterium exchange would be expected to produce a triplet with peaks of equal intensity and a carbon–deuterium coupling constant 15% of the corresponding carbon–proton coupling constant.[14] In addition, the β-carbon atom appeared as a doublet of doublets as before, showing coupling to the attached proton H_b as well as two-bond coupling to the aldehydic proton H_c. The suggested course of this hydrolysis is shown in Scheme 3.

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. Triiron dodecacarbonyl,[15] 3-methoxy-1-bromopropyne,[16] and 3-(dimethylamino)-1-bromopropyne[16] were prepared by literature procedures. *n*-Butyllithium (Alfa), mercuric chloride (Alfa), potassium iodide (Mallinckrodt), and sodium hydroxide (Mallinckrodt) were used as received. Phenylacetylene, 1-hexyne, methyl propargyl ether, 3-(dimethylamino)-1-propyne, propargyl alcohol, and (trimethylsilyl)acetylene were purchased from Aldrich, vacuum-distilled at room temperature when necessary, and purged with nitrogen prior to use.

Scheme 2



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 using Sigma S-0507 230–400 mesh silica gel. In addition, preparative thin-layer chromatography plates (EM Science 60 F$_{254}$, silica gel, 20 × 20 × 0.025 cm) were used as needed. 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 using 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. Electron impact mass spectra were obtained using a Finnigan 3200 mass spectrometer operating at 70 eV. Field desorption mass spectra were obtained using a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isotopes: ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{32}S, ^{56}Fe, and ^{201}Hg. 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 in Herlev, Denmark.

X-ray Crystallography. Structure of [(μ-CH$_3$OCH$_2$CH=C)(μ-*t*-BuS)Fe$_2$(CO)$_6$]$_2$Hg. A red rod of [(μ-CH$_3$OCH$_2$-

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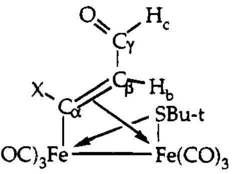
(13) *Spectrometric Identification of Organic Compounds*; Silverstein, R. M., Bassler, G. C., Morrill, T. C., Eds.; Wiley: New York, 1981; pp 119–120.

(14) Reference 13, p 257.

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

(16) *Synthesis of Acetylenes, Allenes, and Cumulenes*; Brandsma, L., Verkuijsse, H. D., Eds.; Elsevier: New York, 1981; p 98.

Table 3. Comparison of Relevant IR, ^{1}H NMR, and ^{13}C NMR Spectral Data for $(\mu\text{-}\eta^1\text{:}\eta^2\text{-CH=CHC(O)H})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ (16) and $(\mu\text{-}\eta^1\text{:}\eta^2\text{-CD=CHC(O)H})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ (19)[a]



complex	X	$\nu_{C=O}$	δ_X	δ_{H_b}	δ_{H_c}	δ_{C_α}
16	H_a	1692	8.84 (d), $J = 12.21$	3.80 (dd), $J = 12.21$, $^3J = 5.37$	9.10 (d), $^3J = 5.38$	163.10 (d), $J_{CH} = 152.5$
19	D	1694		3.80 (d), $^3J = 4.99$	9.10 (d), $^3J = 4.29$	162.59 (t), $J_{CD} = 18.0$

[a] ν values are in cm^{-1}, δ values in ppm, and J values in Hz.

Scheme 3. Proposed Reaction Course for the Aqueous Acid Hydrolysis of $(\mu\text{-CH}_3\text{OCH=CHC})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ (9) To Form $(\mu\text{-}\eta^1\text{:}\eta^2\text{-CH=CHC(O)H})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ (16)

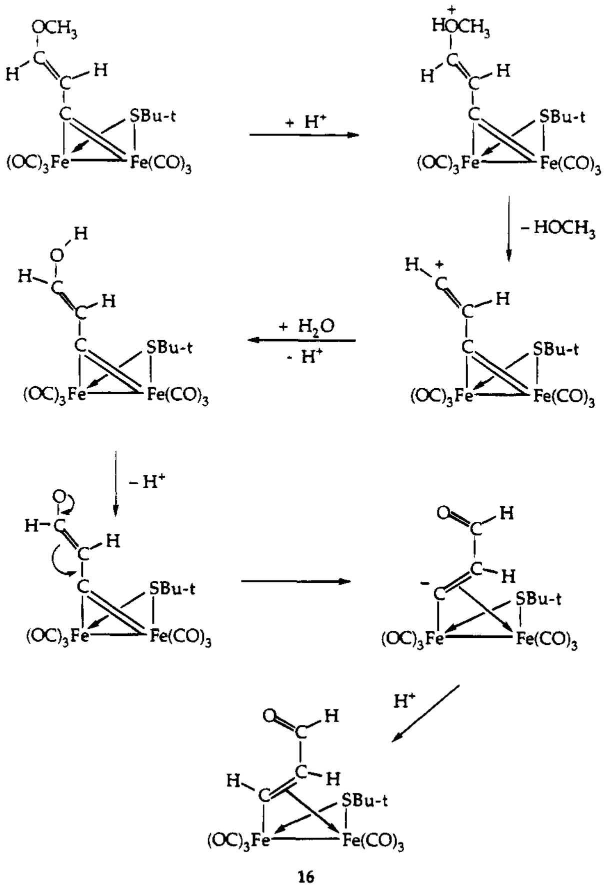


Table 4. Crystal Data for $[(\mu\text{-CH}_3\text{OCH}_2\text{CH=C})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2Hg$ (6)

empirical formula	$C_{28}H_{30}O_{14}S_2Fe_4Hg$
fw	1078.63
cryst color, habit	red, rod
cryst dimens (mm)	0.156 × 0.240 × 0.360
cryst syst	monoclinic
no. of rflns used for unit cell determination (2θ range, deg)	25 (25.0–32.0)
ω-scan peak width at half-height	0.37
lattice params	$a = 15.554(4)$ Å $b = 12.496(3)$ Å $c = 19.752(5)$ Å $\beta = 99.26(2)°$ $V = 3789(2)$ Å^3
space group	$P2_1/c$ (No. 14)
Z	4
D_{calc}	1.891 g/cm^3
F_{000}	2104
μ(Mo Kα)	56.98 cm^{-1}

CH=C)(μ-t-BuS)Fe$_2$(CO)$_6$]$_2$Hg (which had been grown in pentane/CH$_2$Cl$_2$) having approximate dimensions of 0.156 × 0.240 × 0.360 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25.00° < 2\theta < 32.00°$, corresponded to a monoclinic cell with dimensions given in Table 4. For $Z = 4$ and fw = 1078.63, the calculated density is 1.891 g/cm^3. On the basis of the systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.37° with a takeoff angle of 6.0°. Scans of $(1.42 + 0.35 \tan\theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of eight rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 31 cm.

Of the 9429 reflections which were collected, 9103 were unique ($R_{int} = 0.090$). The intensities of 3 representative reflections which were measured after every 150 reflections declined by −9.30%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient for Mo Kα is 57.0 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.76 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of the Patterson method and direct methods.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d(C–H) = 0.95 Å) and were assigned isotropic thermal parameters which were 20% greater than the B_{equiv} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement[18] was based on 3418 observed reflections ($I > 3.00\sigma$-

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

(18) Least-squares: function minimized $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and $p = p$ factor.

Table 5. Final Positional Parameters for [(μ-$CH_3OCH_2CH{=}C$)(μ-*t*-BuS)$Fe_2(CO)_6$]$_2$Hg (6)

atom	*x*	*y*	*z*	*B*(eq) (Å^2)	atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Hg	0.26358(3)	0.02942(4)	0.12525(2)	3.32(2)	C(42)	0.336(1)	−0.249(1)	0.2722(7)	5.6(7)
Fe(1)	0.3723(1)	0.2036(1)	0.11777(8)	3.66(8)	C(43)	0.297(1)	−0.045(1)	0.2704(8)	5.8(8)
Fe(2)	0.1585(1)	−0.1514(1)	0.1153(1)	4.03(8)	C(6′)	0.062(2)	−0.214(3)	0.286(2)	9(2)
Fe(3)	0.2018(1)	0.2336(1)	0.09414(9)	3.83(8)	C(101)	0.2886(9)	0.206(1)	−0.0629(6)	4.7(6)
Fe(4)	0.3016(1)	−0.1489(1)	0.20812(9)	4.17(8)	C(102)	0.208(1)	0.253(1)	−0.1072(8)	7(1)
S(1)	0.2954(2)	0.2765(3)	0.0220(2)	3.9(1)	C(103)	0.372(1)	0.236(1)	−0.0874(7)	7(1)
S(2)	0.2639(2)	−0.2770(2)	0.1276(2)	3.9(1)	C(104)	0.281(1)	0.086(1)	−0.0562(7)	6.4(8)
O(1)	0.226(2)	0.464(3)	0.278(1)	10(2)	C(201)	0.3290(8)	−0.299(1)	0.0561(7)	4.6(6)
O(2)	0.040(3)	−0.161(5)	0.347(3)	12(3)	C(202)	0.272(1)	−0.364(1)	0.0040(8)	8(1)
O(1′)	0.184(2)	0.414(2)	0.242(2)	8(2)	C(203)	0.361(1)	−0.198(1)	0.0259(7)	5.6(7)
O(11)	0.5017(7)	0.3725(9)	0.1203(6)	8.2(7)	C(204)	0.408(1)	−0.363(1)	0.0916(8)	6.6(9)
O(12)	0.4834(7)	0.0442(9)	0.0645(5)	6.9(6)	H(1)	0.3698	0.4011	0.2203	7.2
O(13)	0.4353(7)	0.144(1)	0.2605(5)	7.5(6)	H(2)	0.0681	−0.1998	0.2447	11.9
O(2′)	0.085(3)	−0.155(4)	0.366(2)	9(2)	H(3)	0.1902	0.4415	0.1863	12.1
O(21)	0.0294(6)	0.0079(8)	0.1416(6)	6.6(6)	H(4)	0.2586	0.5314	0.2055	12.1
O(22)	0.1385(7)	−0.1142(9)	−0.0334(5)	6.7(6)	H(5)	0.2020	−0.2005	0.3437	6.3
O(23)	0.0285(7)	−0.321(1)	0.0982(7)	9.5(7)	H(6)	0.1292	−0.2866	0.3352	6.3
O(31)	0.1109(8)	0.434(1)	0.0586(8)	10.2(8)	H(7)	0.1243	0.5726	0.2598	16.5
O(32)	0.1302(7)	0.1908(9)	0.2204(5)	7.2(6)	H(8)	0.0912	0.4555	0.2516	16.5
O(33)	0.0669(6)	0.1155(9)	0.0023(5)	6.6(6)	H(9)	0.1201	0.5029	0.3242	16.5
O(41)	0.4813(7)	−0.097(1)	0.1907(5)	6.8(6)	H(10)	0.1321	−0.0101	0.3679	15.1
O(42)	0.3572(7)	−0.312(1)	0.3108(5)	7.7(6)	H(11)	0.0474	−0.0332	0.3169	15.1
O(43)	0.2931(9)	0.014(1)	0.3125(6)	8.3(7)	H(12)	0.0441	−0.0213	0.3946	15.1
C(1)	0.2956(8)	0.308(1)	0.1544(6)	3.7(5)	H(13)	0.2137	0.3293	−0.1103	8.6
C(2)	0.1798(8)	−0.176(1)	0.2162(6)	4.4(6)	H(14)	0.1986	0.2236	−0.1517	8.6
C(3)	0.308(1)	0.388(1)	0.1982(7)	5.7(7)	H(15)	0.1560	0.2399	−0.0866	8.6
C(4)	0.133(2)	−0.199(1)	0.264(1)	10(1)	H(16)	0.4217	0.2145	−0.0555	8.2
C(5)	0.242(2)	0.459(1)	0.219(1)	10(1)	H(17)	0.3759	0.2060	−0.1311	8.2
C(6)	0.142(2)	−0.210(2)	0.327(2)	5(2)	H(18)	0.3755	0.3137	−0.0921	8.2
C(7)	0.138(2)	0.500(2)	0.278(1)	16(2)	H(19)	0.2311	0.0661	−0.0330	7.7
C(8)	0.078(2)	−0.053(2)	0.363(1)	13(2)	H(20)	0.2730	0.0493	−0.0984	7.7
C(11)	0.4507(9)	0.307(1)	0.1181(7)	4.9(7)	H(21)	0.3315	0.0563	−0.0271	7.7
C(12)	0.4360(8)	0.102(1)	0.0818(6)	4.4(6)	H(22)	0.2210	−0.3239	−0.0164	9.3
C(13)	0.4086(8)	0.166(1)	0.2065(7)	4.6(6)	H(23)	0.3021	−0.3838	−0.0338	9.3
C(21)	0.0821(9)	−0.053(1)	0.1313(7)	4.9(7)	H(24)	0.2533	−0.4275	0.0230	9.3
C(22)	0.1535(8)	−0.125(1)	0.0243(8)	4.8(6)	H(25)	0.3928	−0.1540	0.0622	6.5
C(23)	0.078(1)	−0.255(1)	0.1045(9)	6.2(8)	H(26)	0.3987	−0.2130	−0.0060	6.5
C(31)	0.145(1)	0.357(1)	0.073(1)	7.0(9)	H(27)	0.3131	−0.1558	0.0038	6.5
C(32)	0.1588(8)	0.205(1)	0.1722(7)	4.3(6)	H(28)	0.3882	−0.4276	0.1104	7.6
C(33)	0.1253(9)	0.157(1)	0.0362(7)	4.8(7)	H(29)	0.4460	−0.3814	0.0603	7.6
C(41)	0.411(1)	−0.116(1)	0.1922(6)	4.6(6)	H(30)	0.4399	−0.3225	0.1285	7.6

(*I*)) and 469 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of $R = 0.036$ and $R_w = 0.047$.

The standard deviation of an observation of unit weight[19] was 1.14. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.77 and −0.63 e/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_c;[21] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[22] All calculations were performed using the TEXSAN[23] crystallographic software package of Molecular Structure Corp.

Structure of (μ-$CH_3OCH{=}CHC$)(μ-*t*-BuS)$Fe_2(CO)_6$. A suitable quality, irregularly shaped red-black crystal of (μ-$CH_3OCH{=}CHC$)(μ-*t*-BuS)$Fe_2(CO)_6$ which had been grown in pentane was mounted on a glass fiber using epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 reflections in the range 22.0° ≤ 2θ ≤ 25.8°, which were accurately centered at 22 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The $\bar{1}$ diffraction symmetry and the lack of systematic absences were consistent with the space groups $P1$ and $P\bar{1}$, the latter of which was ultimately established as the probable one on the basis of the successful refinement of the model and on the location of all hydrogen atoms. A cell reduction[24] failed to show the presence of a higher symmetry cell.

Table 6. Crystal Data for (μ-$CH_3OCH{=}CHC$)(μ-*t*-BuS)$Fe_2(CO)_6$ (9)

empirical formula	$C_{14}H_{14}Fe_2O_7S$
fw	438.0
cryst color, habit	red-brown, irregular
cryst dimens (mm)	0.25 × 0.44 × 0.53
cryst syst	triclinic
lattice params	$a = 15.064(3)$ Å
	$b = 15.154(4)$ Å
	$c = 8.479(1)$ Å
	$\alpha = 100.11(2)°$
	$\beta = 99.30(1)°$
	$\gamma = 83.62(2)°$
	$V = 1873.7$ Å^3
space group	$P\bar{1}$ (No. 2)
Z	4
D_{calc}	1.553 g/cm^3
μ(Mo Kα)	16.831 cm^{-1}

Intensity data in the range 1.0° ≤ 2θ ≤ 53° were collected at 22 °C on the CAD4 diffractometer in the bisecting mode

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

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

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

(22) Cromer, D. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

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

(24) The cell reduction was performed using a modification of Tracer II by S. L. Lawson. See: Lawson, S. L.; Jacobson, R. A. In *The Reduced Cell and Its Crystallographic Applications*; Ames Laboratory Reports I5-1141; USAEC: Iowa State University, Ames, IA, April 1965.

Table 7. Final Positional Parameters for (μ-CH_3OCH=CHC)(μ-*t*-BuS)$Fe_2(CO)_6$ (9; Molecule 1)

atom	*x*	*y*	*z*	*B*(eq) (Å^2)[a]
Fe(1)	−0.50417(4)	0.30032(3)	0.00104(6)	3.94(1)
Fe(2)	−0.62357(3)	0.29438(3)	−0.24514(5)	3.59(1)
S(1)	−0.64485(6)	0.25881(6)	−0.0064(1)	4.09(2)
O(1)	−0.3480(2)	0.3667(2)	−0.0879(4)	8.02(9)
O(2)	−0.3964(3)	0.1899(2)	0.2221(4)	8.06(9)
O(3)	−0.5486(3)	0.4684(2)	0.2223(4)	10.0(1)
O(4)	−0.5507(2)	0.3642(2)	−0.4929(4)	8.32(9)
O(5)	−0.7338(2)	0.1711(2)	−0.4760(4)	6.47(8)
O(6)	−0.7508(3)	0.4559(2)	−0.1713(5)	8.21(9)
O(7)	−0.4180(2)	0.0680(2)	−0.5250(3)	6.11(7)
C(1)	−0.4101(3)	0.3434(3)	−0.0509(5)	5.18(9)
C(2)	−0.4393(3)	0.2329(3)	0.1364(5)	5.03(9)
C(3)	−0.5329(3)	0.4037(3)	0.1387(5)	6.0(1)
C(4)	−0.5799(3)	0.3381(3)	−0.3964(5)	5.31(9)
C(5)	−0.6923(2)	0.2198(3)	−0.3838(4)	4.38(8)
C(6)	−0.7030(3)	0.3946(3)	−0.2013(5)	5.17(9)
C(7)	−0.5097(2)	0.2312(2)	−0.2041(4)	3.65(7)
C(8)	−0.4465(2)	0.1738(3)	−0.2893(4)	4.23(8)
C(9)	−0.4694(3)	0.1256(3)	−0.4325(5)	5.07(9)
C(10)	−0.3238(3)	0.0646(3)	−0.4758(6)	6.5(1)
C(11)	−0.6548(3)	0.1368(2)	−0.0074(4)	4.47(8)
C(12)	−0.5918(3)	0.0737(2)	−0.1054(5)	5.11(9)
C(13)	−0.6343(4)	0.1249(3)	−0.1709(5)	8.1(1)
C(14)	−0.7536(3)	0.1217(3)	−0.0749(6)	6.1(1)
H(1)C(12)	−0.606	0.082	−0.216	6.1*
H(2)C(12)	−0.531	0.087	−0.067	6.1*
H(3)C(12)	−0.599	0.013	−0.097	6.1*
H(1)C(13)	−0.573	0.134	0.209	9.1*
H(2)C(13)	−0.671	0.167	0.233	9.1*
H(3)C(13)	−0.645	0.066	0.181	9.1*
H(1)C(14)	−0.793	0.161	−0.012	7.1*
H(2)C(14)	−0.764	0.134	−0.183	7.1*
H(3)C(14)	−0.765	0.061	−0.075	7.1*
H(1)C(10)	−0.293	0.023	−0.551	7.5*
H(2)C(10)	−0.303	0.122	−0.467	7.5*
H(3)C(10)	−0.312	0.046	−0.373	7.5*
H(8)	−0.385	0.170	−0.242	5.2*
H(9)	−0.531	0.133	−0.476	6.0*

[a] Values labeled with asterisks are fixed isotropic thermal parameters, which were not refined.

Table 8. Final Positional Parameters for (μ-CH_3OCH=CHC)(μ-*t*-BuS)$Fe_2(CO)_6$ (9; Molecule 2)

atom	*x*	*y*	*z*	*B*(eq) (Å^2)[a]
Fe(21)	0.00419(3)	0.18988(3)	0.34460(6)	4.19(1)
Fe(22)	−0.06886(3)	0.21464(3)	0.06718(7)	4.23(1)
S(21)	0.06925(6)	0.25749(5)	0.1811(1)	3.62(2)
O(21)	0.1425(2)	0.0371(2)	0.2779(4)	7.09(9)
O(22)	0.0682(3)	0.2849(3)	0.6664(4)	9.9(1)
O(23)	−0.1146(3)	0.0812(3)	0.4527(5)	11.3(1)
O(24)	0.0284(2)	0.0752(2)	−0.1493(5)	9.2(1)
O(25)	−0.1344(3)	0.3473(3)	−0.1449(4)	9.3(1)
O(26)	−0.2358(2)	0.1259(3)	−0.0012(5)	9.4(1)
O(27)	−0.3064(2)	0.3969(3)	0.3576(5)	8.8(1)
C(21)	0.0909(3)	0.0954(3)	0.3091(5)	4.96(9)
C(22)	0.0441(3)	0.2473(3)	0.5406(5)	6.2(1)
C(23)	−0.0665(3)	0.1226(3)	0.4126(6)	6.9(1)
C(24)	−0.0092(3)	0.1288(3)	−0.0695(5)	5.8(1)
C(25)	−0.1076(3)	0.2956(3)	−0.0607(5)	6.0(1)
C(26)	−0.1691(3)	0.1594(3)	0.0249(6)	6.3(1)
C(27)	−0.0987(2)	0.2587(3)	0.2751(5)	4.70(0)
C(28)	−0.1714(3)	0.3038(3)	0.3640(7)	6.8(1)
C(29)	−0.2331(3)	0.3482(4)	0.2893(7)	7.7(1)
C(30)	−0.3205(4)	0.3930(4)	0.5146(6)	8.5(1)
C(31)	0.0801(3)	0.3808(2)	0.2331(5)	4.41(8)
C(32)	0.1026(3)	0.4069(3)	0.0803(5)	6.5(1)
C(33)	0.1613(3)	0.3903(3)	0.3666(6)	7.7(1)
C(34)	−0.0038(3)	0.4355(3)	0.2853(6)	6.3(1)
H(1)C(32)	0.051	0.402	0.000	7.5*
H(2)C(32)	0.118	0.467	0.102	7.5*
H(3)C(32)	0.152	0.369	0.043	7.5*
H(1)C(33)	0.211	0.354	0.328	8.6*
H(2)C(33)	0.175	0.451	0.393	8.6*
H(3)C(33)	0.149	0.371	0.461	8.6*
H(1)C(34)	−0.017	0.419	0.382	7.3*
H(2)C(34)	0.006	0.498	0.304	7.3*
H(3)C(34)	−0.053	0.425	0.202	7.3*
H(1)C(30)	−0.374	0.428	0.539	9.6*
H(2)C(30)	−0.325	0.332	0.525	9.6*
H(3)C(30)	−0.270	0.416	0.587	9.6*
H(28)	−0.171	0.299	0.474	7.5*
H(29)	−0.231	0.350	0.179	8.3*

[a] See footnote *a* in Table 7.

employing the $\omega-2\theta$ scan technique and using graphite-monochromated Mo Kα radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variations in the intensities of these standards were noted so no correction for decomposition was applied. A total of 6812 unique reflections ($h,\pm k,\pm l$) were measured and processed in the usual manner using a value of 0.04 for p.[25] Of these, 5338 ($F_o^2 \geq 3\sigma(F_o^2)$) were considered to be observed and were used in subsequent calculations (433 variables).

The structure was solved in the space group $P\bar{1}$. The iron positions were obtained from the Patterson map, and all other atoms were obtained by subsequent least-squares and difference-Fourier calculations. Atomic scattering factors for hydrogen[26] and the other atoms[20] were taken from the usual tabulations; anomalous dispersion terms[27] were included in the calculations. All hydrogen atoms were located and were input in the least-squares cycle as fixed contributions in their idealized positions using C—H distances of 0.95 Å. The hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than the equivalent isotropic B value of their attached carbon atom. All other atoms were refined anisotropically. Absorption corrections were applied to the data using Gaussian integration.

Refinement by full-matrix techniques converged at R = 0.038 and R_w = 0.053. On the final difference-Fourier map, the largest peak was 0.74 e/Å^3; this can be compared to peaks corresponding to carbon atoms on earlier Fourier maps that had intensities of 3.1−6.0 e/Å^3. The alternate space group $P1$ was rejected, owing to the satisfactory refinement in $P\bar{1}$. It should be noted that the crystal structure of (μ-CH_3OCH=CHC)(μ-*t*-BuS)$Fe_2(CO)_6$ contains two independent molecules per unit cell, denoted as molecules 1 and 2 in Table 2.

Supplementary material for this structure was submitted with our preliminary communication of a portion of these results[28] and was deposited.

Standard *in Situ* Preparation of [Et_3NH][(μ-CO)(μ-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 successively 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][(μ-CO)(μ-RS)$Fe_2(CO)_6$] reagent solution then was utilized *in situ* without further purification.

Standard *in Situ* Preparation of [Li][(μ-CO)(μ-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 and 3.00 mmol of the appropriate thiol and cooled to −78 °C in a dry ice/acetone cold bath. Once the flask had been cooled to

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

[26] Stewart, R. F.; Davidson, E. F.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[27] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[28] Seyferth, D.; Ruschke, D. P.; Davis, W. M. *Organometallics* **1989**, *8*, 836.

−78 °C, a hexane solution of *n*-butyllithium (3.00 mmol) was added slowly by syringe. The deep green reaction mixture was stirred at −78 °C for 30 min. The dry ice/acetone cold bath then was removed and the reaction mixture warmed to room temperature, during which time slow gas evolution and a gradual color change from green to brown-red were observed. The resulting $[\mathrm{Li}][(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{RS})\mathrm{Fe_2(CO)_6}]$ reagent solution was stirred for an additional 30 min at room temperature and utilized *in situ* without further purification.

Organomercurial Syntheses. Terminal acetylenes can be readily converted to bis(1-alkynyl)mercury compounds by Nessler's solution, an alkaline solution of the tetraiodomercurate(II) ion.[29] The general procedure is given in eq 9. Both gaseous and liquid terminal acetylenes can be used, although this synthetic method is not compatible with all substituted terminal acetylenes.

$$\mathrm{2R'C{\equiv}CH + K_2HgI_4 + 2NaOH \xrightarrow[H_2O/EtOH]{0\ ^\circ C} (R'C{\equiv}C)_2Hg + 2KI + 2NaI + 2H_2O} \tag{9}$$

Bis(1-hexynyl)mercury. A dried and degassed 500-mL three-necked round-bottomed flask equipped with an overhead stirrer, an addition funnel, and a gas adapter was cooled to 0 °C in an ice bath. Mercuric chloride (35.4 g, 0.131 mol) and potassium iodide (82.9 g, 0.499 mol) were added as solids against a positive flow of nitrogen. The solids were dissolved in 50 mL of degassed water, which produced a clear yellow solution of aqueous $\mathrm{K_2HgI_4}$. Sodium hydroxide (10% w/v solution in water, 0.163 mol) then was added. 1-Hexyne, $n\text{-}\mathrm{C_4H_9C{\equiv}CH}$ (8.22 g, 0.100 mol in 100 mL of ethanol), was added dropwise over the course of 1 h. A white-gray precipitate formed as the reaction mixture was stirred at 0 °C for an additional 2 h. The crude product was filtered, washed with three 50-mL portions of water/ethanol (1/1 v/v), and recrystallized from boiling ethanol to give 13.4 g (74% based on 1-hexyne) of $(n\text{-}\mathrm{C_4H_9C{\equiv}C})_2\mathrm{Hg}$ as a white, flaky powder, mp 96.0−97.0 °C. Anal. Calcd for $\mathrm{C_{12}H_{18}Hg}$: C, 39.72; H, 5.00. Found: C, 39.81; H, 5.24. ^{13}C NMR ($\mathrm{CDCl_3}$, 100.5 MHz): δ_C 13.55 (q, J_CH = 124.6 Hz, $\mathrm{C{\equiv}CCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 19.41 (t, J_CH = 130.2 Hz, $\mathrm{C{\equiv}CCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 22.04 (t, J_CH = 124.6 Hz, $\mathrm{C{\equiv}CCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 30.90 (t, J_CH = 128.8 Hz, $\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 109.11 (s, $\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2CH_2CH_2CH_3}$), 110.90 (s, $\mathit{C}\mathrm{{\equiv}CCH_2CH_2CH_2CH_3}$).

Prepared in similar manner from the respective terminal acetylene were the following bis(1-alkynyl)mercurials.

Bis(3-(dimethylamino)-1-propynyl)mercury: $(\mathrm{Me_2NCH_2C{\equiv}C})_2\mathrm{Hg}$; 46% yield; white powder (difficult to recrystallize from boiling ethanol, long-term light sensitivity); poorly soluble in organic solvents; mp 105.0−130.0 °C dec (with formation of elemental Hg). Anal. Calcd for $\mathrm{C_{10}H_{16}HgN_2}$: C, 32.92; H, 4.42. Found: C, 32.78; H, 4.54. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz): δ_H 2.27 (s, 3H, $\mathrm{C{\equiv}CCCH_2N(C}\mathit{H}\mathrm{_3)_2}$), 3.30 (s, 1H, $\mathrm{C{\equiv}CC}\mathit{H}\mathrm{_2N(CH_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.4 MHz): δ_C 44.01 (q, J_CH = 133.0 Hz, $\mathrm{C{\equiv}CCH_2N(}\mathit{C}\mathrm{H_3)_2}$), 48.46 (t, J_CH = 138.2 Hz, $\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2N(CH_3)_2}$), 101.20 (s, $\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2N(CH_3)_2}$), 115.41 (s, $\mathit{C}\mathrm{{\equiv}CCH_2N(CH_3)_2}$).

Bis(3-methoxy-1-propynyl)mercury: $(\mathrm{CH_3OCH_2C{\equiv}C})_2\mathrm{Hg}$; 74% yield; white powder; mp 106.0−107.0 °C (from boiling ethanol). Anal. Calcd for $\mathrm{C_8H_{10}HgO_2}$: C, 28.36; H, 2.98. Found: C, 28.37; H, 3.23. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): δ_H 3.36 (s, 3H, $\mathrm{C{\equiv}CCH_2OC}\mathit{H}\mathrm{_3}$), 4.14 (s, 2H, $\mathrm{C{\equiv}CC}\mathit{H}\mathrm{_2OCH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 100.5 MHz): δ_C 57.58 (q, J_CH = 141.7 Hz, $\mathrm{C{\equiv}CCH_2O}\mathit{C}\mathrm{H_3}$), 60.16 (t, J_CH = 146.8 Hz, $\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2OCH_3}$), 102.78 (s, $\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2OCH_3}$), 116.98 (s, $\mathit{C}\mathrm{{\equiv}CCH_2OCH_3}$).

Bis(phenylethynyl)mercury: mp 124.5−125.5 °C (lit.[28] mp 125.0−126.0 °C); 31% yield.

Reaction of $[\mathbf{Et_3NH}][(\mu\text{-}\mathbf{CO})(\mu\text{-}\mathbf{EtS})\mathbf{Fe_2(CO)_6}]$ with Bis(phenylethynyl)mercury. The standard $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{EtS})\mathrm{Fe_2(CO)_6}]$ reagent solution (2.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $(\mathrm{C_6H_5C{\equiv}C})_2\mathrm{Hg}$ (1.24 g, 3.07 mmol) was added as a solid. An immediate reaction ensued with gas evolution and a color change to deep red. After 1 h at room temperature, TLC analysis of the reaction mixture indicated the formation of two major orange-red products. The solvent was removed *in vacuo* to give a red oily residue which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.52 g (1.29 mmol, 42% based on S) of $(\mathrm{EtS})_2\mathrm{Fe_2(CO)_6}$, identified by comparison of its ^{1}H NMR spectrum with that given in the literature.[30] Further elution with pentane/$\mathrm{CH_2Cl_2}$ (9/1 v/v) gave 0.62 g (1.40 mmol, 47%) of $(\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{C{\equiv}CC_6H_5})(\mu\text{-}\mathrm{EtS})\mathrm{Fe_2(CO)_6}$ (**3g**; a mixture of two inseparable isomers) as a slightly air-sensitive, deep red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[2] Further elution with $\mathrm{CH_2Cl_2}$ and acetone gave two very faint green-brown products whose instability and small yield precluded further characterization.

Reaction of $[\mathbf{Et_3NH}][(\mu\text{-}\mathbf{CO})(\mu\text{-}\boldsymbol{t}\text{-}\mathbf{BuS})\mathbf{Fe_2(CO)_6}]$ with Bis(1-hexynyl)mercury. To the $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}]$ reagent solution (2.98 mmol) was added $(\eta\text{-}\mathrm{C_4H_9C{\equiv}C})_2\mathrm{Hg}$ (1.20 g, 3.29 mmol). After the reaction mixture had been stirred at room temperature for 5.5 h, TLC analysis indicated the formation of two major orange-red products which moved very closely together in pentane. The solvent was removed *in vacuo* to yield a bright red oil which was purified by medium-pressure chromatography. Pentane eluted a large red band which gave 0.76 g (1.70 mmol, 57%) of $(\mu\text{-}\eta^1{:}\eta^2\text{-}n\text{-}\mathrm{C_4H_9C{\equiv}C})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}$ (**3h**; a mixture of two inseparable isomers) as a slightly air-sensitive red oil. Anal. Calcd for $\mathrm{C_{16}H_{18}Fe_2O_6S}$: C, 42.70; H, 4.03. Found: C, 42.80; H, 4.14. ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz): δ_H 0.89 (t, J = 7.00 Hz, 2.1H, $\mathrm{C{\equiv}CCH_2CH_2CH_2C}\mathit{H}\mathrm{_3}$, major isomer), 0.91 (t, J = 6.76 Hz, 0.9H, $\mathrm{C{\equiv}CCH_2CH_2CH_2C}\mathit{H}\mathrm{_3}$, minor isomer), 1.14 (s, 2.7H, $\mathrm{SC(C}\mathit{H}\mathrm{_3)_3}$, minor isomer), 1.2−1.44 (m, 2H, $\mathrm{C{\equiv}CCH_2CH_2C}\mathit{H}\mathrm{_2CH_3}$, both isomers), 1.30 (s, 6.3H, $\mathrm{SC(C}\mathit{H}\mathrm{_3)}$, major isomer), 1.49−1.64 (m, 2H, $\mathrm{C{\equiv}CCH_2C}\mathit{H}\mathrm{_2CH_2CH_3}$, both isomers), 2.38 (t, J = 7.14 Hz, 1.4H, $\mathrm{C{\equiv}CC}\mathit{H}\mathrm{_2CH_2CH_2CH_3}$, major isomer), 2.40 (t, J = 7.24 Hz, 0.6H, $\mathrm{C{\equiv}CC}\mathit{H}\mathrm{_2CH_2CH_2CH_3}$, minor isomer); isomer ratio (major/minor) 2.4/1.0. ^{13}C NMR ($\mathrm{CDCl_3}$, 75.4 MHz): δ_C 13.50 (q, J_CH = 124.5 Hz, $\mathrm{C{\equiv}CCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$, both isomers), 21.86 (t, J_CH = 128.6 Hz, $\mathrm{C{\equiv}CCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$, major isomer), 22.02 (t, J_CH = 127.7 Hz, $\mathrm{C{\equiv}CCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$, minor isomer), 24.04, (t, J_CH = 131.2 Hz, $\mathrm{C{\equiv}CCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$, major isomer), 24.32 (t, J_CH = 132.0 Hz, $\mathrm{C{\equiv}CCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$, minor isomer), 31.86 (t, J_CH = 134.2 Hz, $\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$, both isomers), 33.32 (q, J_CH = 127.3 Hz, $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$, major isomer), 34.49 (q, J_CH = 133.7 Hz, $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$, minor isomer), 47.40 (s, $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$, minor isomer), 48.18 (s, $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$, major isomer), 92.23 (s, $\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2CH_2CH_2CH_3}$, minor isomer), 96.69 (s, $\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2CH_2CH_2CH_3}$, major isomer), 100.22 (s, $\mathit{C}\mathrm{{\equiv}CCH_2CH_2CH_2CH_3}$, minor isomer), 102.16 (s, $\mathit{C}\mathrm{{\equiv}CCH_2CH_2CH_2CH_3}$, major isomer), 208.24 and 209.51 (both s, terminal *C*O's, both isomers).

Reaction of $[\mathbf{Et_3NH}][(\mu\text{-}\mathbf{CO})(\mu\text{-}\boldsymbol{t}\text{-}\mathbf{BuS})\mathbf{Fe_2(CO)_6}]$ with Bis(3-methoxy-1-propynyl)mercury. To the standard $[\mathrm{Et_3NH}][(\mu\text{-}\mathrm{CO})(\mu\text{-}t\text{-}\mathrm{BuS})\mathrm{Fe_2(CO)_6}]$ reagent solution (2.98 mmol) was added $(\mathrm{CH_3OCH_2C{\equiv}C})_2\mathrm{Hg}$ (1.05 g, 3.11 mmol). An immediate reaction ensued with brisk gas evolution and a color change from brown-red to deep red. After the reaction mixture had been stirred for 30 min at room temperature, TLC analysis indicated the formation of two orange-red products which moved in pentane and a deep red-black product at the origin. The solvent was removed *in vacuo* to yield a red oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.14 g (0.31 mmol, 20% based on S) of $(\mu\text{-}t\text{-}\mathrm{BuS})_2\mathrm{Fe_2(CO)_6}$, identified by comparison of its ^{1}H NMR

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(29) *Organometallic Synthesis*; King, R. B., Eisch, J. J., Eds.; Academic Press: New York, 1981; Vol. 2, p 114.

(30) (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.

spectrum with that of an authentic sample.[31] Further elution with pentane/CH_2Cl_2 (9/1 v/v) yielded a dark red band which gave 0.35 g (0.81 mmol, 27%) of (μ-$CH_3OCH{=}CHC$)(μ-*t*-BuS)$Fe_2(CO)_6$ (**9**) as an air-stable, orange-red solid after recrystallization from pentane; mp 85.0–87.0 °C. Anal. Calcd for $C_{14}H_{14}Fe_2O_7S$: C, 38.39; H, 3.22. Found: C. 38.65; H, 3.30. ^1H NMR ($CDCl_3$, 250 MHz): δ_H 0.90 (s, 9H, SC(CH_3)$_3$), 4.00 (s, 3H, OCH_3), 7.74 and 8.08 (AB quartet, $J = 11.52$ Hz, 2H, vinyl protons). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 32.92 (q, $J_{CH} = 127.4$ Hz, SC(CH_3)$_3$), 49.57 (s, S*C*(CH_3)$_3$), 59.91 (q, $J_{CH} = 148.5$ Hz, OCH_3), 132.72 (d, $J_{CH} = 159.5$ Hz, $CH_3OCH{=}CHC$), 165.85 (d, $J_{CH} = 181.5$ Hz, $CH_3OCH{=}CHC$), 209.92 and 211.12 (both s, terminal *C*O's), 360.47 (s, carbyne *C*).

Further elution with CH_2Cl_2/acetone (1/1 v/v) gave a faint green-brown band which was not collected. Finally, CH_2Cl_2 eluted a large deep red-black band which after removal of the solvent on a rotary evaporator yielded a red-black solid (0.90 g). This compound was purified using medium-pressure chromatography. Pentane/CH_2Cl_2 (1/4 v/v) eluted a large red-black band which gave 0.58 g (0.54 mmol, 36%) of [(μ-$CH_3OCH_2CH{=}C$)(μ-*t*-BuS)$Fe_2(CO)_6$]$_2$Hg (**6**) as an air-stable red-black solid after recrystallization from pentane/CH_2Cl_2; mp 159.0–163.0 °C. Anal. Calcd for $C_{28}H_{30}Fe_4HgO_{14}S_2$: C, 31.18; H, 2.80; Fe, 20.71; Hg, 18.60. Found: C, 31.81; H, 2.97; Fe, 20.06; Hg, 19.13. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 1.23 (s, 9H, SC(CH_3)$_3$), 3.28 (s, 3H, $CH_3OCH_2CH{=}C$), 3.94–4.07 (complex m, 2H, $CH_3OCH_2CH{=}C$), 6.13 (t, $^3J_{HH} = 6.32$ Hz, 1H, $CH_3OCH_2CH{=}C$). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ_C 31.46 (q, $J_{CH} = 126.7$ Hz, SC(CH_3)$_3$), 46.83 (s, S*C*(CH_3)$_3$), 57.25 (q, $J_{CH} = 142.6$ Hz, $CH_3OCH_2CH{=}C$), 74.61 (t, $J_{CH} = 138.9$ Hz, $CH_3OCH_2CH{=}C$), 140.89 (d, $J_{CH} = 157.2$ Hz, $CH_3OCH_2CH{=}C$), 207.05, 207.42, 210.14, 210.54, and 210.80 (all s, terminal *C*O's), 221.08 (s, $CH_3OCH_2CH{=}C$). Mass spectrum (FD): *m/z* 1079 (M^+).

Reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]$ with Bis(3-methoxy-1-propynyl)mercury. To the standard $[Et_3NH][(\mu\text{-CO})(\mu\text{-EtS})Fe_2(CO)_6]$ reagent solution (2.98 mmol) was added $(CH_3OCH_2C{\equiv}C)_2Hg$ (1.10 g, 3.24 mmol) as a solid. An immediate reaction with brisk gas evolution and a color change from brown-red to deep red were observed. After the reaction mixture had been stirred for 30 min at room temperature, TLC analysis indicated the formation of two orange-red products which moved in pentane and a deep red-black product at the origin. The solvent was removed *in vacuo* to yield a brown-red solid residue which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.28 g (0.69 mmol, 44% based on S) of (μ-EtS)$_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[30] Further elution with pentane/CH_2Cl_2 (9/1 v/v) yielded a dark red band which gave 0.11 g (0.28 mmol, 9%) of (μ-$CH_3OCH{=}CHC$)(μ-EtS)$Fe_2(CO)_6$ (a mixture of two inseparable isomers) as an air-stable, orange-red solid after recrystallization from pentane; mp 98.0–99.5 °C. Anal. Calcd for $C_{12}H_{10}Fe_2O_7S$: C, 35.16; H, 2.46. Found: C, 34.80; H, 2.53. ^1H NMR ($CDCl_3$, 250 MHz): δ_H 1.09 (t, $J = 7.54$ Hz, 1.1H, SCH_2CH_3, minor isomer), 1.41 (q, $J = 7.78$ Hz, 0.8 H, SCH_2CH_3, minor isomer), 1.50 (t, $J = 7.37$ Hz, 1.9 H, SCH_2CH_3, major isomer), 2.87 (q, $J = 7.37$ Hz, 1.2H, SCH_2CH_3, major isomer), 3.98 (s, 1.9H, $CH_3OCH{=}CHC$, major isomer), 4.04 (s, 1.1H, $CH_3OCH{=}CHC$, minor isomer), 7.53 and 8.02 (AB quartet, $J = 11.69$ Hz, 0.6H, vinyl protons, major isomer), 7.67 and 8.08 (AB quartet, $J = 11.91$ Hz, 0.4H, vinyl protons, minor isomer); isomer ratio (major/minor) 1.7/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 18.05 (q, $J_{CH} = 128.1$ Hz, SCH_2CH_3, both isomers), 30.44 (t, $J_{CH} = 125.4$ Hz, SCH_2CH_3, minor isomer), 35.52 (t, $J_{CH} = 137.7$ Hz, SCH_2CH_3, major isomer), 60.14 (q, $J_{CH} = 147.4$ Hz, $CH_3OCH{=}CHC$, minor isomer), 60.27 (q, $J_{CH} = 147.3$ Hz, $CH_3OCH{=}CHC$, major isomer), 131.65 (d, $J_{CH} = 160.4$ Hz, $CH_3OCH{=}CHC$, minor isomer), 133.78 (d, $J_{CH} = 160.3$ Hz, $CH_3OCH{=}CHC$, major isomer), 166.19 (d, $J_{CH} = 183.3$ Hz, $CH_3OCH{=}CHC$, major isomer), 167.01 (d, $J_{CH} = 179.5$ Hz, $CH_3OCH{=}CHC$, minor isomer), 210.02 and 210.80 (both s, terminal *C*O's, both isomers), 361.25 (s, carbyne *C*, major isomer), 374.09 (s, carbyne *C*, minor isomer).

Further elution with CH_2Cl_2/acetone (1/1 v/v) gave a large deep red-black band which after removal of the solvent on a rotary evaporator yielded a red-black solid (0.64 g). This compound was purified using medium-pressure chromatography. CH_2Cl_2 eluted a major red-black band which gave 0.61 g (0.60 mmol, 40%) of [(μ-$CH_3OCH_2CH{=}C$)(μ-EtS)$Fe_2(CO)_6$]$_2$Hg (a mixture of two inseparable isomers) as an air-stable, red-black solid after recrystallization from pentane/CH_2Cl_2; mp 185.0–187.0 °C. Anal. Calcd for $C_{24}H_{22}O_{14}S_2Fe_4Hg$: C, 28.19; H, 2.17; Fe, 21.85; Hg, 19.62. Found: C, 30.27; H, 2.75; Fe, 21.22; Hg, 18.89. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 1.22 (t, $J = 7.32$ Hz, 2.3H, SCH_2CH_3, major isomer), 1.26 (t, $J = 7.28$ Hz, 0.7H, SCH_2CH_3, minor isomer), 2.06 (q, $J = 7.31$ Hz, 1.5H, SCH_2CH_3, major isomer), 2.50 (q, $J = 7.31$ Hz, 0.5H, SCH_2CH_3, minor isomer), 3.27 (s, 2.3H, $CH_3OCH_2CH{=}C$, major isomer), 3.32 (s, 0.7H, $CH_3OCH_2CH{=}C$, minor isomer), 3.97–4.00 (complex m, 1.5H, $CH_3OCH_2CH{=}C$, major isomer), 4.04–4.07 (complex m, 0.5H, $CH_3OCH_2CH{=}C$, minor isomer), 6.12 (t, $^3J_{HH} = 6.38$ Hz, 0.8H, $CH_3OCH_2CH{=}C$, major isomer), 6.18 (t, $^3J_{HH} = 6.54$ Hz, 0.2H, $CH_3OCH_2CH{=}C$, minor isomer); isomer ratio (major/minor) 3.2/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 17.07 (q, $J_{CH} = 129.2$ Hz, SCH_2CH_3, major isomer), 17.28 (q, $J_{CH} = 127.8$ Hz, SCH_2CH_3, minor isomer), 41.03 (t, $J_{CH} = 138.8$ Hz, SCH_2CH_3, both isomers), 57.17 (q, $J_{CH} = 141.1$ Hz, $CH_3OCH_2CH{=}C$, major isomer), 57.45 (q, $J_{CH} = 141.6$ Hz, $CH_3OCH_2CH{=}C$, minor isomer), 74.32 (t, $J_{CH} = 141.6$ Hz, $CH_3OCH_2CH{=}C$, minor isomer), 74.47 (t, $J_{CH} = 141.4$ Hz, $CH_3OCH_2CH{=}C$, major isomer), 138.39 (d, $J_{CH} = 154.9$ Hz, $CH_3OCH_2CH{=}C$, minor isomer), 140.70 (d, $J_{CH} = 157.0$ Hz, $CH_3OCH_2CH{=}C$, major isomer), 205.21, 205.58, 206.51, 206.69, 208.34, 208.63, 210.11, 210.49, 211.26, and 212.15 (all s, terminal *C*O's, both isomers), 223.92 (s, $CH_3OCH_2CH{=}C$, major isomer), 231.74 (s, $CH_3OCH_2CH{=}C$, minor isomer). Mass spectrum (FD): *m/z* 1023 (M^+).

Reaction of $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ with Bis(3-(dimethylamino)-1-propynyl)mercury. The standard $[Et_3NH][(\mu\text{-CO})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]$ reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $((CH_3)_2NCH_2C{\equiv}C)_2Hg$ (0.92 g, 2.51 mmol) was added as a solid. Brisk gas evolution was observed along with a gradual color change to deep brown-red. After the reaction mixture had been stirred for 19 h at room temperature, TLC analysis indicated the formation of an orange and a rose product which moved in pentane and two orange products which moved closely together in pentane/CH_2Cl_2. The solvent was removed *in vacuo* to yield a brown oil which was purified by filtration chromatography. Pentane eluted an orange band which after removal of the solvent gave 0.10 g (0.22 mmol, 21% based on S) of (μ-*t*-BuS)$_2Fe_2(CO)_6$.[31] Further elution with pentane gave a faint rose band which was not collected. Pentane/CH_2Cl_2 (1/1 v/v) then eluted a dark red band which gave 0.26 g (0.58 mmol, 29%) of (μ-$(CH_3)_2NCH{=}CHC$)(μ-*t*-BuS)$Fe_2(CO)_6$ (**11a**; a mixture of two inseparable isomers) as an air-stable orange solid after recrystallization from pentane; mp 171.0–172.0 °C. Anal. Calcd for $C_{15}H_{17}Fe_2NO_6S$: C, 39.94; H, 3.80. Found: C, 39.67; H, 3.91. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 0.96 (s, 6.2H, SC(CH_3)$_3$, major isomer), 1.42 (s, 2.8H, SC(CH_3)$_3$, minor isomer), 3.11 (s, 0.9H, N(CH_3), minor isomer), 3.12 (s, 2.1H, N(CH_3), major isomer), 3.29 (s, 0.9H, N(CH_3), minor isomer), 3.33 (s, 2.1H, N(CH_3), major isomer), 7.28 and 7.54 (AB quartet, $J = 11.56$ Hz, 0.6H, vinyl protons, minor isomer), 7.48 and 7.64 (AB quartet, $J = 11.64$ Hz, 1.4H, vinyl protons, major isomer); isomer ratio (major/minor) 2.2/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 33.32 (q, $J_{CH} = 126.5$ Hz, SC(CH_3)$_3$, both isomers), 38.72 (q, $J_{CH} = 138.8$ Hz, N(CH_3), major isomer), 38.88 (q, $J_{CH} = 139.4$ Hz, N(CH_3), minor isomer), 46.57 (q, $J_{CH} = 138.5$ Hz, N(CH_3), major isomer), 46.67

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

(q, J_{CH} = 138.5 Hz, $N(CH_3)$, minor isomer), 48.81 (s, $SC(CH_3)_3$, both isomers), 129.09 (d, J_{CH} = 160.1 Hz, $(CH_3)_2NCH{=}CHC$, minor isomer), 129.27 (d, J_{CH} = 159.4 Hz, $(CH_3)_2NCH{=}CHC$, major isomer), 158.71 (d, J_{CH} = 170.5 Hz, $(CH_3)_2NCH{=}CHC$, major isomer), 160.36 (d, J_{CH} = 173.2 Hz, $(CH_3)_2NCH{=}CHC$, minor isomer), 211.77, 212.25, 213.20, and 213.45 (all s, terminal *C*O's, both isomers), 364.57 (s, carbyne *C*, minor isomer), 375.32 (s, carbyne *C*, major isomer).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with Bis-(3-(dimethylamino)-1-propynyl)mercury. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $((CH_3)_2NCH_2C{\equiv}C)_2Hg$ (1.28 g, 3.50 mmol) was added as a solid. Gas evolution was observed along with a gradual color change to brown-red. After the reaction mixture had been stirred for 1.5 h at room temperature, TLC analysis indicated an orange product which moved in pentane and green and orange-red products which moved in pentane/CH_2Cl_2. The solvent was removed *in vacuo* to yield a brown-red residue which was purified by filtration chromatography. Pentane eluted an orange band which after removal of the solvent gave 0.14 g (0.35 mmol, 35% based on S) of $(\mu\text{-}EtS)_2Fe_2(CO)_6$.[30] Further elution with pentane/CH_2Cl_2 (1/1 v/v) yielded a dark red band which was shown by TLC to be a mixture of two products. This residue was rechromatographed on a 450 × 25 mm medium-pressure column using Sigma 230–400 mesh silica gel. Pentane/CH_2Cl_2 (1/1 v/v) eluted a faint green band (0.074 g after removal of the solvent) which was not pursued due to its thermal instability and low yield. Pentane/CH_2Cl_2 (1/1 v/v) then eluted a dark red-orange band which gave 0.25 g (0.59 mmol, 30%) of $(\mu\text{-}(CH_3)_2NCH{=}CHC)(\mu\text{-}EtS)Fe_2(CO)_6$ (**11b**; a mixture of two inseparable isomers) as an air-stable red-brown solid after recrystallization from pentane; mp 103.0–104.5 °C. Anal. Calcd for $C_{13}H_{13}Fe_2NO_6S$: C, 36.91; H, 3.10. Found: C, 36.99; H, 3.12. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 1.06 (t, J = 7.24 Hz, 0.9H, SCH_2CH_3, minor isomer), 1.36 (t, J = 7.27 Hz, 2.1H, SCH_2CH_3, major isomer), 1.55 (q, J = 7.65 Hz, 0.6H, SCH_2CH_3, minor isomer), 2.58 (q, J = 7.40 Hz, 1.4H, SCH_2CH_3, major isomer), 3.11 (s, 2.1H, $N(CH_3)$, major isomer), 3.17 (s, 0.9H, $N(CH_3)$, minor isomer), 3.29 (s, 2.1H, $N(CH_3)$, major isomer), 3.35 (s, 0.9H, $N(CH_3)$, minor isomer), 7.31 and 7.58 (AB quartet, J = 11.20 Hz, 1.4H, vinyl protons, major isomer), 7.45 and 7.61 (AB quartet, J = 12.04 Hz, 0.6H, vinyl protons, minor isomer); isomer ratio (major/minor) 2.3/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 17.67 (q, J_{CH} = 127.2 Hz, SCH_2CH_3, minor isomer), 18.05 (q, J_{CH} = 127.4 Hz, SCH_2CH_3, major isomer), 32.48 (t, J_{CH} = 143.6 Hz, SCH_2CH_3, minor isomer), 35.14 (t, J_{CH} = 136.9 Hz, SCH_2CH_3, major isomer), 38.83 (q, J_{CH} = 138.1 Hz, $N(CH_3)$, both isomers), 46.62 (q, J_{CH} = 143.7 Hz, $N(CH_3)$, both isomers), 127.99 (d, J_{CH} 161.4 Hz, $(CH_3)_2NCH{=}CHC$, minor isomer), 129.49 (d, J_{CH} = 158.0 Hz, $(CH_3)_2NCH{=}CHC$, major isomer), 159.95 (d, J_{CH} = 167.6 Hz, $(CH_3)_2NCH{=}CHC$, major isomer), 160.32 (d, J_{CH} = 165.4 Hz, $(CH_3)_2NCH{=}CHC$, minor isomer), 212.07, 212.45, 212.82, and 213.06 (all s, terminal *C*O's, both isomers), 367.53 (s, carbyne *C*, both isomers).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with Bis-(3-(dimethylamino)-1-propynyl)mercury. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, $((CH_3)_2NCH_2C{\equiv}C)_2Hg$ (0.75 g, 2.06 mmol) was added as a solid. Gas evolution was observed along with a gradual color change to brown-red. After the reaction mixture had been stirred for 2 h at room temperature, TLC analysis indicated one orange product which moved in pentane and green and orange-red products which moved in pentane/CH_2Cl_2. The solvent was removed *in vacuo* to yield a brown oily residue which was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted an orange band which after removal of the solvent gave 0.22 g (0.44 mmol, 43% based on S) of $(\mu\text{-}PhS)_2Fe_2(CO)_6$.[32] Further elution with pentane/CH_2Cl_2 (1/1 v/v) yielded a dark red band which was shown by TLC to be a mixture of two products. This residue was rechromatographed on a 450 × 25 mm medium-pressure column using Sigma 230–400 mesh silica gel. Pentane/CH_2Cl_2 (1/1 v/v) eluted a faint green band which was not pursued due to its thermal instability and low yield. Pentane/CH_2Cl_2 (1/1 v/v) then eluted a dark red-orange band which gave 0.21 g (0.44 mmol, 22%) of $(\mu\text{-}(CH_3)_2NCH{=}CHC)(\mu\text{-}PhS)Fe_2(CO)_6$ (**11c**; a mixture of two inseparable isomers) as an air-stable red-brown solid (mp 128.0–130.0 °C) after recrystallization from pentane. ^1H NMR (acetone-d_6, 250 MHz): δ_H (3.23 (s, 0.9H, $N(CH_3)$, minor isomer), 3.36 (s, 2.1H, $N(CH_3)$, major isomer), 3.49 (s, 0.9H, $N(CH_3)$, minor isomer), 3.57 (s, 2.1H, $N(CH_3)$, major isomer), 7.06–7.82 (complex m, 7H, overlapping signals due to vinyl protons and C_6H_5, both isomers); isomer ratio (major/minor) 2.3/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 38.05 (q, J_{CH} = 139.7 Hz, $N(CH_3)$, major isomer), 38.87 (q, J_{CH} = 140.5 Hz, $N(CH_3)$, minor isomer), 45.98 (q, J_{CH} = 138.5 Hz, $N(CH_3)$, major isomer), 46.08 (q, J_{CH} = 136.9 Hz, $N(CH_3)$, minor isomer), 124.93–135.87 (complex m, C_6H_5 and $(CH_3)_2NCH{=}CHC$, both isomers), 159.82 (d, J_{CH} = 164.7 Hz, $(CH_3)_2NCH{=}CHC$, major isomer), 161.05 (d, J_{CH} = 163.8 Hz, $(CH_3)_2NCH{=}CHC$, minor isomer), 209.73, 210.11, 212.01, and 212.87 (all s, terminal *C*O's, both isomers), 362.97 (s, carbyne *C*, minor isomer), 376.85 (s, carbyne *C*, major isomer).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 3-Methoxy-1-bromopropyne. 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. $CH_3OCH_2C{\equiv}CBr$ (0.60 g, 4.05 mmol) was added by syringe. An immediate reaction ensued with brisk gas evolution and a color change from brown-red to bright red. After the reaction mixture had been stirred for 30 min at room temperature, TLC analysis indicated the formation of three orange-red products which moved in pentane. The solvent was removed *in vacuo* to yield a red oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.10 g (0.22 mmol, 15% 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.[31] Further elution with pentane/CH_2Cl_2 (9/1 v/v) yielded a dark red band which gave 0.32 g (0.72 mmol, 24%) of $(\mu\text{-}CH_3OCH{=}CHC)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ as an air-stable, orange-red solid, identified by comparison of its ^1H NMR spectrum with that of an authentic sample. Continued elution with pentane/CH_2Cl_2 (1/1 v/v) gave a dark red band which yielded 0.56 g (1.29 mmol, 43%) of $(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CCH_2OCH_3)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**12**; a mixture of two inseparable isomers) as a slightly air-sensitive red oil. Anal. Calcd for $C_{14}H_{14}Fe_2O_7S$: C, 38.39; H, 3.22. Found: C, 38.45; H, 3.30. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 1.13 (s, 2.6H, $SC(CH_3)_3$, minor isomer), 1.31 (s, 6.4H, $SC(CH_3)_3$, major isomer), 3.30 (s, 2.1H, $C{\equiv}CCH_2OCH_3$, major isomer), 3.35 (s, 0.9H, $C{\equiv}CH_2OCH_3$, minor isomer), 4.17 (s, 1.4H, $C{\equiv}CCH_2OCH_3$, major isomer), 4.21 (s, 0.6H, $C{\equiv}CCH_2OCH_3$, minor isomer); isomer ratio (major/minor) 2.4/1.0. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 33.24 (q, J_{CH} = 127.4 Hz, $SC(CH_3)_3$, major isomer), 34.50 (q, J_{CH} = 125.8 Hz, $SC(CH_3)_3$, minor isomer), 47.80 (s, $SC(CH_3)_3$, minor isomer), 48.44 (s, $SC(CH_3)_3$, major isomer), 57.47 (q, J_{CH} = 140.9 Hz, $C{\equiv}CCH_2OCH_3$, major isomer), 57.78 (q, J_{CH} = 139.0 Hz, $C{\equiv}CCH_2OCH_3$, minor isomer), 62.98 (t, J_{CH} = 146.4 Hz, $C{\equiv}CCH_2OCH_3$, major isomer), 63.35 (t, J_{CH} = 152.6 Hz, $C{\equiv}CCH_2OCH_3$, minor isomer), 86.56 (s, $C{\equiv}CCH_2OCH_3$, minor isomer), 91.42 (s, $C{\equiv}CCH_2OCH_3$, major isomer), 111.91 (s, $C{\equiv}CCH_2OCH_3$, ghvjbnm vbminor isomer), 114.28 (s, $C{\equiv}CCH_2OCH_3$, major isomer), 207.74 and 208.94 (both s, terminal *C*O's, both isomer).

Reaction of $(\mu\text{-}CH_3OCH{=}CHC)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ with Aqueous Hydrochloric Acid. A 100-mL Schlenk flask

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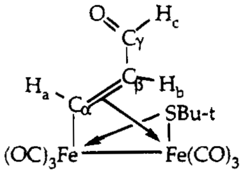
[32] (a) Kettle, S. F. A.; Orgel, L. E. *J. Chem. Soc.* **1960**, 3890. (b) Henslee, W.; Davis, R. E. *Cryst. Struct. Comm.* **1972**, *1*, 403.

equipped with a stirbar and a rubber septum was charged with (μ-CH$_3$OCH=CHC)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (0.31 g, 0.70 mmol) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 20 mL of THF. Aqueous hydrochloric acid (6.0 mL of a 0.12 M HCl solution in H$_2$O, 0.72 mmol) was added by syringe at room temperature. The dark red reaction mixture immediately turned light orange, and TLC indicated complete consumption of the starting material. The organic solvent was removed *in vacuo*, leaving an oily orange solid which was extracted with diethyl ether. Removal of the ether on a rotary evaporator gave 0.29 g (0.69 mmol, 97%) of (μ-η^1:η^2-CH=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (**16**) as an air-stable orange solid (mp 96.0–98.0 °C) after recrystallization from pentane. Anal. Calcd for C$_{13}$H$_{12}$Fe$_2$O$_7$S: C, 36.83; H, 2.85. Found: C, 36.79; H, 2.93. IR (CCl$_4$, cm^{-1}): 3010 (vw), 2960 (w), 2940 (sh), 2920 (w), 2895 (vw), 2860 (vw), 2815 (vw), 2780 (vw), 2720 (vw), 1692 (s, $\nu_{C=O}$ aldehyde), 1470 (vw), 1458 (w), 1408 (m), 1384 (vw), 1368 (m), 1180 (w), 1155 (m), 1069 (m), 905 (w), 685 (w), 622 (m), 609 (s, br), 595 (sh), 542 (m). IR for terminal carbonyl region (CCl$_4$, cm^{-1}): 2080 (s), 2050 (vs), 2015 (vs), 2000 (vs). ^{1}H NMR (CDCl$_3$, 300 MHz): δ_H 1.39 (s, 9H, SC(C*H*$_3$)$_3$), 3.80 (dd, $^3J_{H_aH_b}$ = 12.21 Hz, $^3J_{H_bH_c}$ = 5.37 Hz, 1H, CH=C*H*C(O)H), 8.84 (d, $^3J_{H_aH_b}$ = 12.21 Hz, 1H, C*H*=CHC(O)H), 9.10 (d, $^3J_{H_bH_c}$ = 5.38 Hz, 1H, CH=CHC(O)*H*). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ_C 33.03 (q, J_{CH} = 127.8 Hz, SC(*C*H$_3$)$_3$, 48.74 (s, S*C*(CH$_3$)$_3$), 84.71 (dd, J_{CH_b} = 163.2 Hz, $^2J_{CH_c}$ = 26.8 Hz, CH=*C*HC(O)HS*C*(CH$_3$)$_3$), 163.03 (d, J_{CH_a} = 152.5 Hz, *C*H=CHC(O)H), 193.95 (d, J_{CH_c} = 171.8 Hz, CH=CH*C*(O)H), 207.49 and 208.20 (both s, terminal *C*O's). Mass spectrum (EI): *m/z* (relative intensity) 424 (M$^+$, 3), 396 (M$^+$ − CO, 1), 368 (M$^+$ − 2CO, 15), 340 (M$^+$ − 3CO, 13), 312 (M$^+$ − 4CO, 17), 284 (M$^+$ − 5CO, 25), 256 (M$^+$ − 6CO, 45), 240 (unknown, 14), 201 (*t*-BuSFe$_2^+$ or H$_2$SFe$_2$CH=CHC(O)H$^+$, 16), 200 (HSFe$_2$CH=CHC(O)H$^+$, 100), 199 (SFe$_2$CH=CHC(O)H$^+$, 13), 198 (SFe$_2$CH=CC(O)H$^+$, 22), 172 (HSFe$_2$CH=CH$_2^+$, 18), 171 (HSFe$_2$CH=CH$^+$, 15), 170 (HSFe$_2$CH=C$^+$, 11), 169 (HSFe$_2$C=C$^+$, 17), 145 (HSFe$_2^+$, 58), 144 (SFe$_2^+$, 100), 86 (unknown, 11), 84 (unknown, 20), 57 (*t*-Bu$^+$, 49), 56 (*t*-Bu$^+$ − H or Fe$^+$, 18), 55 (CH=CHC(O)H$^+$, 13), 41 (C$_3$H$_5^+$, 44), 39 (C$_3$H$_3^+$, 15). A similar reaction with water required 30 min for consumption of starting material and gave **16** in 99% yield.



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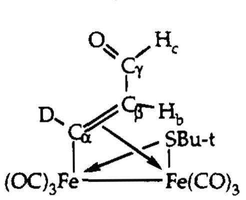
Reaction of (μ-CH$_3$OCH=CHC)(μ-*t*-BuS)Fe$_2$(CO)$_6$ with Deuterium Chloride in Deuterium Oxide. A 100-mL Schlenk flask equipped with a stirbar and a rubber septum was charged with (μ-CH$_3$OCH=CHC)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (0.15 g, 0.35 mmol) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 4 mL of THF. To the resulting deep red solution was added aqueous deuterium chloride (0.060 mL of a 5.91 M DCl solution in D$_2$O, 0.35 mmol) by syringe at room temperature. After 15 min of reaction, TLC analysis of the reaction mixture showed remaining starting material as well as a new product growing in. After 30 min, TLC indicated complete consumption of the starting material. The solvent was removed *in vacuo*, leaving a red solid which was extracted with diethyl ether. Removal of the ether on a rotary evaporator gave 0.12 g (0.28 mmol, 80%) of (μ-η^1:η^2-CD=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (**19**) as an air-stable red solid. Its identity was confirmed by comparison of its IR and ^{1}H and ^{13}C NMR spectra with those of its protio counterpart, (μ-η^1:η^2-CH=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$. IR (CCl$_4$, cm^{-1}): 3010 (vw), 2968 (w), 2940 (vw), 2925 (w), 2900 (w), 2860 (vw), 2815 (w), 2720 (vw), 1694 (s, $\nu_{C=O}$ aldehyde), 1475 (vw), 1460 (m), 1440 (vw), 1398 (m), 1368 (m), 1341 (m), 1320 (w), 1154 (m), 1114 (m), 1090 (m), 670 (w), 623 (m), 611 (s), 590 (s, br). IR for terminal carbonyl region (CCl$_4$, cm^{-1}): 2085 (s), 2055 (vs), 2020 (vs), 2005 (vs). ^{1}H NMR (CDCl$_3$, 300 MHz): δ_H 1.39 (s, 9H, SC(C*H*$_3$)$_3$), 3.80 (d, $^3J_{H_bH_c}$ = 4.99 Hz, 1H, CD=C*HC*(O)H), 9.10 (d, $^3J_{H_bH_c}$ = 4.29 Hz, 1H, CD=CHC(O)*H*). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ_C 32.98 (q, J_{CH} = 127.8 Hz, SC(*C*H$_3$)$_3$), 48.66 (s, S*C*(CH$_3$)$_3$), 84.80 (dd, J_{CH_b} = 174.0 Hz, $^2J_{CH_c}$ = 24.0 Hz, CD=*C*HC(O)H), 162.59 (t, J_{CD} = 18.0 Hz, *C*D=CHC(O)H), 194.09 (d, J_{CH_c} = 171.5 Hz, CD=CH*C*(O)H), 207.36 (s, terminal *C*O's).



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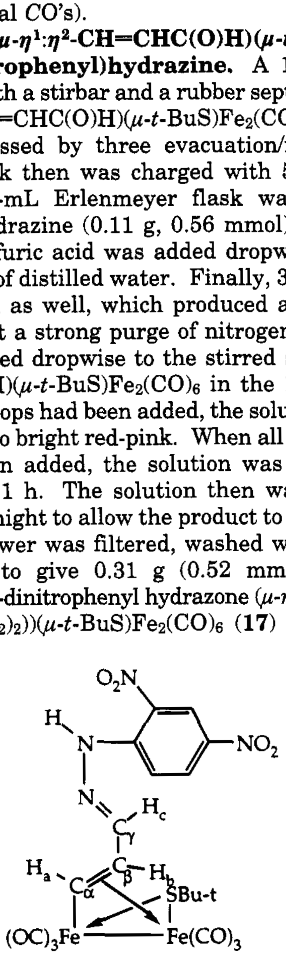
Reaction of (μ-η^1:η^2-CH=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$ with (2,4-Dinitrophenyl)hydrazine. A 100-mL Schlenk flask equipped with a stirbar and a rubber septum was charged with (μ-η^1:η^2-CH=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$ (0.22 g, 0.53 mmol) and degassed by three evacuation/nitrogen-backfill cycles. This flask then was charged with 5 mL of ethanol (95%). In a 50-mL Erlenmeyer flask was charged (2,4-dinitrophenyl)hydrazine (0.11 g, 0.56 mmol), and 0.5 mL of concentrated sulfuric acid was added dropwise by pipet followed by 1.0 mL of distilled water. Finally, 3.0 mL of ethanol (95%) was added as well, which produced an orange-yellow solution. Against a strong purge of nitrogen, the 2,4-DNPH solution was added dropwise to the stirred solution of (μ-η^1:η^2-CH=CHC(O)H)(μ-*t*-BuS)Fe$_2$(CO)$_6$ in the 100-mL Schlenk flask. After 20 drops had been added, the solution turned from deep red-orange to bright red-pink. When all of the 2,4-DNPH solution had been added, the solution was stirred at room temperature for 1 h. The solution then was placed in the refrigerator overnight to allow the product to precipitate. The bright orange power was filtered, washed with ethanol, and dried *in vacuo* to give 0.31 g (0.52 mmol, 98%) of the corresponding 2,4-dinitrophenyl hydrazone (μ-η^1:η^2-CH=CHCH(=NNHC$_6$H$_3$(NO$_2$)$_2$))(μ-*t*-BuS)Fe$_2$(CO)$_6$ (**17**) as an air-stable orange solid, mp 150.0 °C dec. The carbon and hydrogen combustion analysis gave a correct analysis for the dihydrate (confirmed by ν_{OH} at 3700 cm^{-1} (m, br) in the IR spectrum). Anal. Calcd for C$_{19}$H$_{20}$Fe$_2$N$_4$O$_{12}$S: C, 35.65; H, 3.15. Found: C, 35.75; H, 2.73. ^{1}H NMR (CDCl$_3$, 300 MHz): δ_H 1.42 (s, 9H, SC(C*H*$_3$)$_3$), 1.55 (s, br, ~4H, dihydrate), 4.37 (dd, $^3J_{H_aH_b}$ = 13.35 Hz, $^3J_{H_bH_c}$ = 7.70 Hz, 1H, CH=C*H*CH(=N)), 7.30 (d, $^3J_{H_bH_c}$ = 7.28 Hz, 1H, CH=CHC*H*(=N)), 7.94 (d, $^3J_{H_5H_6}$ = 9.01 Hz, 1H, C$_6$H$_3$H$_5$*H*$_6$(NO$_2$)$_2$), 8.20 (d, $^3J_{H_aH_b}$ = 13.34 Hz, 1H, C*H*=CHCH(=N)), 8.30 (dd, $^3J_{H_5H_6}$ = 9.54 Hz, $^4J_{H_3H_5}$ = 2.76 Hz, 1H, C$_6$H$_3$*H*$_5$H$_6$(NO$_2$)$_2$), 9.11 (d, $^4J_{H_3H_5}$ = 3.26 Hz, 1H, C$_6$*H*$_3$H$_5$H$_6$(NO$_2$)$_2$), 11.05 (s, br, 1H, N*H*). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ_C 33.26 (q, J_{CH} = 128.6 Hz, SC(*C*H$_3$)$_3$), 48.78 (s, S*C*(CH$_3$)$_3$), 87.56 (dd, J_{CH_b} = 165.6 Hz, $^2J_{CH_c}$ = 7.0 Hz, CH=*C*HCH(=N)), 116.80 (d, J_{CH} = 174.9 Hz, *C*$_6$), 123.39 (d, J_{CH} = 174.1 Hz, *C*$_3$),



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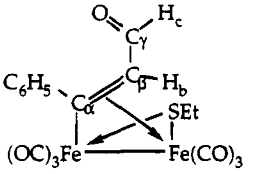
129.38 (s, C_2), 129.98 (d, J_{CH} = 170.5 Hz, C_5), 138.18 (s, C_4), 144.47 (s, C_1), 151.54 (d, J_{CH_c} = 154.0 Hz, CH=CH*C*H(=N)), 153.80 (d, J_{CH_a} = 150.9 Hz, *C*H=CHCH(=N)), 208.89 (s, terminal *C*O's).

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ with Phenylpropargylaldehyde. The standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}EtS)Fe_2(CO)_6]$ reagent solution (2.97 mmol) was generated at room temperature. Phenylpropargylaldehyde, $C_6H_5C{\equiv}CC(O)H$ (0.40 mL, 0.43 g, 3.27 mmol) was added by syringe. After 21 h, the reaction mixture was bright red and TLC analysis showed the formation of two orange-red products. The solvent was removed *in vacuo* to give a red-brown oily solid which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.072 g (0.18 mmol, 11% 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.[30] Further elution with pentane/CH_2Cl_2 (4/1 v/v) gave 0.78 g (1.65 mmol, 56%) of $(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_5C{=}CHC(O)H)(\mu\text{-}EtS)Fe_2(CO)_6$ (**18**) as an air-stable red-black solid, mp 118.0−119.0 °C, after recrystallization from pentane. Anal. Calcd for $C_{17}H_{12}Fe_2O_7S$: C, 43.26; H, 2.56. Found: C, 43.28; H, 2.73. IR (CCl_4, cm^{-1}): 3080 (vw), 3060 (vw), 2970 (w), 2935 (w), 2870 (vw), 2835 (w), 2780 (vw), 2720 (vw), 1682 (vs, $\nu_{C=O}$ aldehyde), 1483 (w), 1454 (w), 1442 (m), 1408 (w), 1380 (w), 1343 (m), 1313 (vw), 1257 (m), 1146 (s), 1090 (s), 1048 (vw), 1030 (vw), 996 (vw), 975 (vw), 890 (w), 850 (w), 712 (s), 693 (m), 646 (s), 619 (vs), 608 (vs), 551 (m). IR for terminal carbonyl region (CCl_4, cm^{-1}): 2080 (m), 2060 (vs), 2020 (vs), 2010 (vs), 2005 (vs), 1975 (sh). ^1H NMR (CD_2Cl_2, 300 MHz): δ_H 1.44 (t, J = 7.27 Hz, 3H, SCH_2CH_3), 2.43−2.63 (complex m, 2H, SCH_2CH_3), 3.14 (d, $^3J_{H_bH_c}$ = 7.59 Hz, 1H, $C_6H_5C{=}CHC(O)H$), 7.30 (s, 5H, $C_6H_5C{=}CHC(O)H$), 8.45 (d, $^3J_{H_bH_c}$ = 7.54 Hz, 1H, $C_6H_5C{=}CHC(O)H$). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ_C 17.50 (q, J_{CH} = 128.6 Hz, SCH_2CH_3), 34.37 (t, J_{CH} = 141.6 Hz, SCH_2CH_3), 81.70 (dd, J_{CH_b} = 162.2 Hz, $^2J_{CH_c}$ = 24.7 Hz, $C_6H_5C{=}CHC(O)H$), 125.55−132.84 (complex m, $C_6H_5C{=}CHC(O)H$), 152.82 (s, ipso $C_6H_5C{=}CHC(O)H$), 192.39 (d, J_{CH_c} = 177.2 Hz, $C_6H_5C{=}CHC(O)H$), 194.93 (s, $C_6H_5C{=}CHC(O)H$), 206.22 and 208.21 (both s, terminal *C*O's).



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Supplementary Material Available: Listings of IR and EI mass spectral data for the compounds in this paper and tables of *U* values, intramolecular distances involving the non-hydrogen atoms, intramolecular distances involving the hydrogen atoms, intramolecular bond angles involving the non-hydrogen atoms, intramolecular bond angles involving the hydrogen atoms, torsion or conformation angles, and intermolecular distances involving the non-hydrogen atoms for compound **6** (34 pages). Ordering information is given on any current masthead page.

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