Reactions of (μ_2-Carbyne)(μ-RS)Fe$_2$(CO)$_6$ Complexes: Isomerization and Acetylene Insertion[†]

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Bridging carbyne complexes of type (μ_2-EtOC)(μ-RS)Fe$_2$(CO)$_6$ undergo thermal or photochemical rearrangement to give bridging acyl complexes, (μ-EtC=O)(μ-RS)Fe$_2$(CO)$_6$. These μ_2-carbyne complexes, as well as those of type (μ_2-CH$_3$OCH=CHC)(μ-RS)Fe$_2$(CO)$_6$, react with activated acetylenes (HC≡CCO$_2$CH$_3$, CH$_3$O$_2$CC≡CCO$_2$CH$_3$, HC≡CC(O)CH$_3$, CH$_3$C≡CCO$_2$-CH$_3$) to give (μ-RS)Fe$_2$(CO)$_6$ complexes that contain a new ligand that is composed of the carbyne, the acetylene, and a CO ligand. Structure determinations of the new complexes were based on X-ray crystal structure and IR and ^{13}C NMR spectroscopic studies.

Introduction

In the course of our investigations of salts of the [(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]$^-$ anion we obtained complexes of type (μ_2-carbyne)(μ-RS)Fe$_2$(CO)$_6$ by two different routes. One route was a consequence of the ambident nature of the [(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]$^-$ anions (Scheme 1).[1,3] Reaction of such anions with most electrophiles involved attack at iron, but with hard electrophiles, such as triethyloxonium tetrafluoroborate, attack at the oxygen atom of the bridging CO ligand was observed (eq 1). For

$$Li^+[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^- + [Et_3O]BF_4 \longrightarrow$$

(1)

1 a, R = t-Bu
b, R = Ph
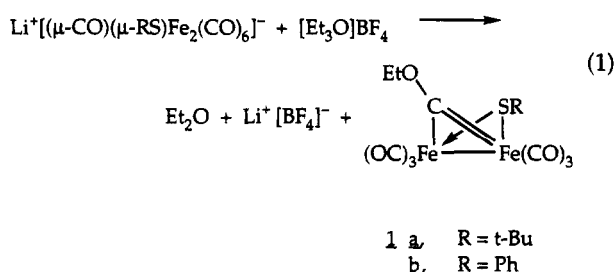
R = t-Bu, the ethoxycarbyne complex was isolated in the form of only one isomer, but for R = Ph, both possible isomers (R axial and equatorial) were formed as an inseparable mixture. Their identity as μ_2-carbyne complexes, **1**, was demonstrated by the low field resonances (380−388 ppm) observed in their ^{13}C NMR spectra. In all of these reactions the respective (μ-RS)$_2$-Fe$_2$(CO)$_6$ complex was a byproduct.

A second route to (μ_2-carbyne)(μ-RS)Fe$_2$(CO)$_6$ complexes was encountered when we studied the reactions of [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$] complexes with mercurials of type Hg(C≡CCH$_2$Z)$_2$ (Z = OMe, NMe$_2$), as reported in a recent paper.[2] These μ_2-carbyne complexes contained vinyl substituents on the carbyne carbon atom, **2** and **3**. Such complexes also resulted from the reactions of [Et$_3$NH][(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]

Scheme 1
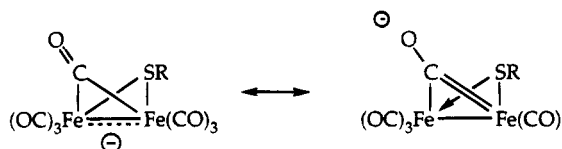
with BrC≡CCH$_2$OMe and BrC≡CCH$_2$NMe$_2$, respectively.[2] An X-ray crystal structure determination of **2a** confirmed the structure indicated. Furthermore, the ^{13}C NMR spectra of all complexes of types **2** and **3** showed far downfield resonances (~360 ppm), indicative of the bridging carbyne ligand.

We report here two reactions of such μ_2-carbyne Fe$_2$-(CO)$_6$ complexes: (1) the isomerization of complexes of type **1**, and (2) the insertion of activated acetylenes into complexes of type **1** and **2**.

2 a, R = t-Bu
b, R = Et

3 a, R = t-Bu
b, R = Et
c, R = Ph
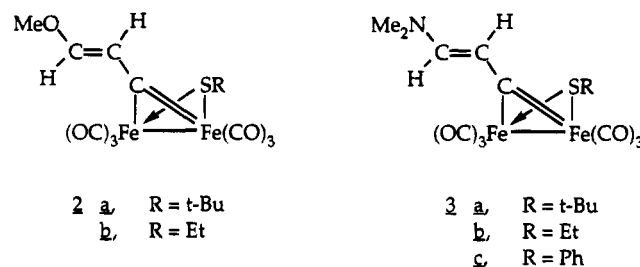
Results and Discussion

1. Isomerization of (μ_2-EtOC)(μ-RS)Fe$_2$(CO)$_6$ Complexes. When a solution of (μ_2-EtOC)(μ-t-BuS)-Fe$_2$(CO)$_6$ or (μ_2-EtOC)(μ-PhS)Fe$_2$(CO)$_6$ in toluene was heated at reflux for 4 h, a darkening of the initially orange color to red was observed, but thin layer chromatography (TLC) detected no change. However, removal of the solvent and filtration chromatography of the residue gave red oils whose spectroscopic properties indicated that the isomerization shown in eq 2 had

(2)

1 a, R = t-Bu
b, R = Ph

4 a, R = t-Bu
b, R = Ph
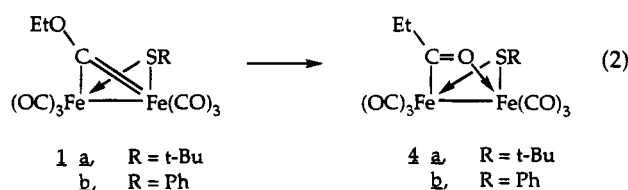
† Dedicated, with all best wishes, to Professor Gerhard Fritz on the occasion of his 75th birthday.

⊛ Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

(2) Seyferth, D.; Ruschke, D. P.; Davis, W. M. *Organometallics* **1989**, *8*, 836.

(3) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430.

taken place. The infrared spectra of the products, formed in essentially quantitative yield, showed C=O stretching frequencies at 1512 and 1518 cm⁻¹, respectively, characteristic of type **4**.[1] In addition, the ^{13}C NMR spectra of the products now showed signals in the range 300–302 ppm (characteristic of such μ-acyl complexes[3]), rather than the resonances in the 380–388 ppm range observed for the μ_2-ethoxycarbyne complexes. In the case of both products a mixture of isomers, **5ax** and **5eq**, was present. This isomerization

5ax   **5eq**
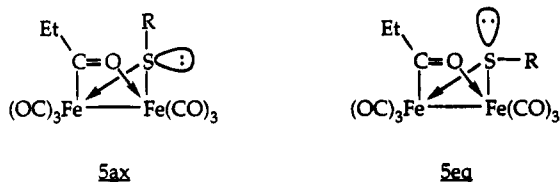
also could be induced photochemically, two days of UV irradiation in toluene serving to give an essentially quantitative yield. A mechanism for this isomerization may be suggested in which the carbyne ligand is transformed as shown in eq 3, proceeding via a C–OEt type bridge with subsequent (or concomitant) migration of the ethyl group from oxygen to carbon.


$$(3)$$
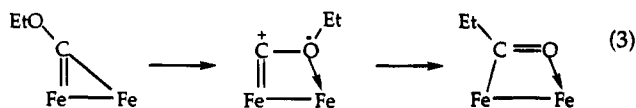
A similar thermal isomerization of $(\mu_2\text{-ROC})(\mu\text{-Ph}_2\text{P})$-Fe$_2(CO)_6$ (R = Me and Et) had been observed by Osterloh,[4] but, under comparable conditions (several hours at 100 °C in toluene), the yields of isomerized product were only around 35%.

2. Reactions of (μ_2-Carbyne)(μ-RS)Fe$_2$(CO)$_6$ with Activated Acetylenes. The reactivity of transition metal carbene and carbyne complexes with organic molecules has been an area of extensive study in recent years and includes neutral, cationic, and anionic transition metal species.[5] In order to compare the reactivity of our neutral, doubly bridging carbyne species with other systems reported in the literature, we investigated the reactivity of the vinylcarbyne complexes **2** and **3** and of the ethoxycarbyne complexes **1** with acetylenes.

Initially, the vinylcarbyne complex (μ_2-CH$_3$OCH= CHC)(μ-t-BuS)Fe$_2$(CO)$_6$, **2a**, was treated with activated acetylenes (HC≡CCO$_2$CH$_3$, CH$_3$O$_2$CC≡CCO$_2$CH$_3$, HC≡ CC(O)CH$_3$, CH$_3$C≡CCO$_2$CH$_3$) at room temperature. An immediate reaction was not apparent. However, longer reaction times (on average, approximately 24 h) produced a color change from orange-red to brown-black and TLC analysis of the reaction mixtures showed the presence of new brown-black products that moved more slowly on the TLC slides. After chromatographic work-up, these products were isolated as air-stable, brown-black, oily solids and were recrystallized from pentane/

(4) Osterloh, W. T. Ph.D. Dissertation, Univ. of Texas at Austin, 1982.
(5) (a) Dyke, A. F.; Finnimore, S. R.; Knox, S.A.R.; Naish, P. J.; Orpen, A. G.; Riding, G. H.; Taylor, G. E. in *Reactivity of Metal–Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series 155; American Chemical Society: Washington, D.C., 1981, p 259 and references therein. (b) Summer, C. E.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (c) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2099, and references therein.
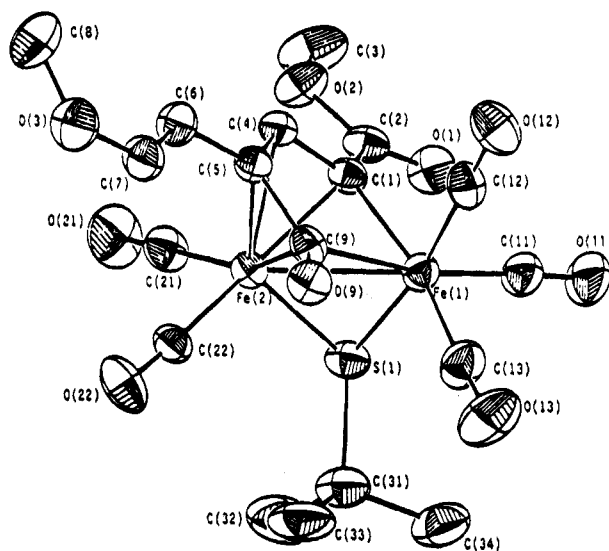
Figure 1. ORTEP plot of **6a** showing the atom numbering scheme with the hydrogen atoms omitted for clarity.

CH$_2$Cl$_2$ at -20 °C. The yields of the new insertion products depended on the extent of electron-withdrawal from the C≡C bond: CH$_3$O$_2$CC≡CCO$_2$CH$_3$, 76%; HC≡ CCO$_2$CH$_3$, 43%; HC≡CC(O)CH$_3$, 32%; CH$_3$C≡CCO$_2$-CH$_3$, 35%.

The identity of these new products was not immediately apparent. Their mass spectra showed molecular ions equivalent to the sum of the mole masses of the two reactants, the vinylcarbyne complex **2a** and the activated acetylene, as well as successive loss of six carbonyl fragments. Carbon and hydrogen combustion analyses also indicated that the products contained the sum of the mole masses of the two reactants. Their infrared spectra showed strong bands at approximately 1630 cm⁻¹ which could not be assigned to the carbonyl stretches of the ketone and ester substituents of the originally acetylenic carbon atoms, but might indicate the presence of some sort of bridging carbonyl ligand. Their ^{1}H NMR spectra showed the expected resonances for the protons of the activated acetylenes as well as the methoxy-substituted vinyl ligand. The vinyl protons appeared as two distinct doublets resonating at 5.0 and 7.5 ppm. The ^{13}C NMR spectra of these new products were markedly different from that of the starting vinylcarbyne complex. Thus, the carbyne carbon resonance of the vinylcarbyne complex **2a** which had appeared at 360.47 ppm had disappeared and three new signals appeared in the vinyl region at approximately 70, 115, and 125 ppm. In addition, five distinct singlets in the terminal carbonyl region were observed as well as a singlet at approximately 235 ppm for each of the new products.

Even though the spectroscopic and analytical data for these new products were all very similar, their structural assignment was not obvious. In order to determine unambiguously the identity of these products, an X-ray diffraction study was performed on the crystalline product obtained in the reaction of the vinylcarbyne complex (μ_2-CH$_3$OCH=CHC)(μ-t-BuS)Fe$_2$(CO)$_6$, **2a**, with HC≡CCO$_2$CH$_3$.

An ORTEP plot of the structure of this product, **6a**, is shown in Figure 1 which gives the atom numbering scheme. Hydrogen atoms are omitted for clarity. Relevant bond distances and angles are listed in Table 1.

Table 1. Relevant Bond Distances (Å) and Bond Angles (deg) for 6a

Fe(1)–Fe(2)	2.498(2)	C(9)–Fe(2)	2.138(6)
Fe(1)–C(1)	1.983(6)	C(9)–O(9)	1.221(6)
C(1)–C(4)	1.405(7)	C(6)–C(7)	1.302(9)
C(4)–C(5)	1.407(7)	C(7)–O(3)	1.349(7)
C(5)–C(9)	1.463(8)	Fe(1)–S(1)	2.291(2)
C(9)–Fe(1)	2.180(6)	Fe(2)–S(1)	2.189(2)

Fe(1)–C(1)–C(4)	116.8(4)
C(1)–C(4)–C(5)	118.1(5)
C(4)–C(5)–C(9)	113.7(5)
C(5)–C(9)–Fe(1)	110.6(4)
C(9)–Fe(1)–C(1)	79.3(2)

The structure shown in Figure 1 shows that not only the activated acetylene but also one of the terminal carbonyl ligands has been inserted in the Fe–carbyne bond. The inserted CO ligand now triply bridges both of the iron centers as well as the original carbyne carbon atom. As a result, a five-membered metallacycle has been formed that is comprised of the two acetylenic carbon atoms, the original carbyne carbon atom, the carbon atom of the inserted carbonyl ligand, and one of the iron atoms. This metallacyle then in turn is coordinated unsymmetrically to the second iron atom (which possesses only two terminal carbonyl ligands) in a pseudo-ferrole manner. The complex **6a** contains an Fe–Fe single bond (Fe(1)–Fe(2) = 2.498(2) Å) with three terminal carbonyl ligands on Fe(1) and two on Fe(2), with an average Fe–C bond distance of 1.801 Å and an average C–O bond distance of 1.135 Å for the terminal carbonyl ligands. The thiolate ligand bridges the Fe₂ unit unsymmetrically, being slightly more tightly bonded to Fe(2) than Fe(1), Fe(1)–S(1) = 2.291-(2) Å versus Fe(2)–S(1) = 2.189(2) Å.

The organic ligand framework, as discussed above, consists of a five-membered metallacycle, comprised of the two acetylenic carbon atoms (C(1) and C(4)), the original carbyne carbon atom (C(5)), the inserted carbonyl carbon atom (C(9)), and one iron atom (Fe(1)). The ring containing these five atoms is slightly puckered with the mean deviation from planarity equal to 0.0609 Å. The carbon atoms C(1) and C(9) are slightly above the plane while the carbon atoms C(4) and C(5) are slightly below the plane. The sum of the interior bond angles of the five-membered metallacycle is 538.5°, very nearly the value expected (540.0°) for a completely planar structure. The atoms C(1), C(4), and C(5), the two acetylenic carbon atoms and the original carbyne carbon atom, form a μ-σ,π-allyl unit which bridges the Fe₂ core unsymmetrically. The bond lengths C(1)–C(4) = 1.405(7) Å and C(4)–C(5) = 1.407(7) Å are identical and lie between the values reported for carbon–carbon single and double bonds.[6] The C(5)–C(9) bond distance of 1.463(8) Å is closer to that of a C–C single bond. In addition, the C(1)–C(4)–C(5) angle of 118.1-(5)° very nearly equals the ideal value of 120.0°. The metallacycle also contains a triply bridging carbonyl ligand which originally was a terminal carbonyl ligand on Fe(2). This carbonyl group bridges not only both of the iron atoms but also the former carbyne carbon atom. As expected for a triply bridging carbonyl ligand, the C(9)–O(9) bond distance (1.221(6) Å) is significantly longer than a terminal FeC–O bond (mean = 1.135 Å). This elongation is indicative of electron density π-dona-
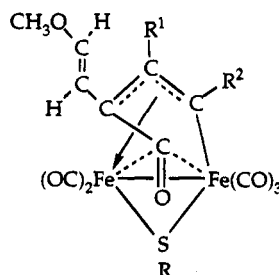
Figure 2. Line drawing of complexes **6**.

tion from the C=O bond of the inserted carbonyl ligand to one or both iron centers. The Fe(1)–C(9)–Fe(2) portion of the molecule thus could be regarded as a delocalized 3-center, 2-electron bond system. In terms of a line drawing, complexes of type **6** may then be represented as shown in Figure 2.

With respect to the above crystallographic conclusions, the spectroscopic ambiguities now were resolved. The strong bands in the infrared spectra of complexes **6a–d** at approximately 1630 cm^{-1} are assigned to the ν$_{C=O}$ stretches of the triply bridging carbonyl ligands. These values fall in the region normally assigned to such functionality (1675–1600 cm^{-1}).[7] In the ^{13}C NMR spectra, the five singlets in the terminal carbonyl region correspond to the three terminal carbonyl ligands on one iron atom and the two terminal carbonyl ligands on the other iron atom, while the singlets at approximately 235 ppm are assigned to the carbon atom of the inserted carbonyl ligand. In addition, the three signals in the vinyl region at approximately 70, 115, and 125 ppm represent the three carbon atoms of the unsymmetrical bridging allyl unit of the five-membered metallacycle. These relevant spectroscopic data are summarized in Tables 2 and 3.

The reactivity of the dimethylamino-substituted vinylcarbyne complex (μ2-(CH3)2NCH=CHC)(μ-t-BuS)Fe2-(CO)6, **3a**, with an activated acetylene, methyl propiolate, also was investigated. Unlike the methoxy-substituted vinylcarbyne complex **2a**, complex **3a** did not react with this activated acetylene in THF solution during 2 days at room temperature. Subsequent heating of the reaction mixture at reflux for 7 h produced only immobile brown decomposition products with destruction of starting material.

Reactions of the vinylcarbyne complex (μ2-CH3-OCH=CHC)(μ-t-BuS)Fe2(CO)6, **2a**, with nonactivated acetylenes also were pursued. However, **2a** proved to be unreactive toward these substrates in terms of forming new insertion products. The reaction of phenylacetylene and (trimethylsilyl)acetylene with **2a** at room temperature gave no color change to brown-black as had reactions of **2a** with activated acetylenes. Instead, after 4 and 7 days of reaction, respectively, the starting material had disappeared and the product isolated from the reaction mixture was the formyl-

(6) *International Tables for X-ray Crystallography*; Macgillavry, C. H.; Rieck, G. D., Eds.; Kynoch Press: Birmingham, 1974; Vol. III, p 276.

(7) *Principles and Applications of Organotransition Metal Chemistry*; Collman, J. P., Hegedus, L. S., Eds.; University Science Books: Mill Valley, CA, 1987; p 116.

Table 2. Summary of the Relevant IR and ^{1}H NMR Spectral Data for 6a–d
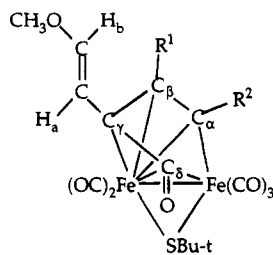
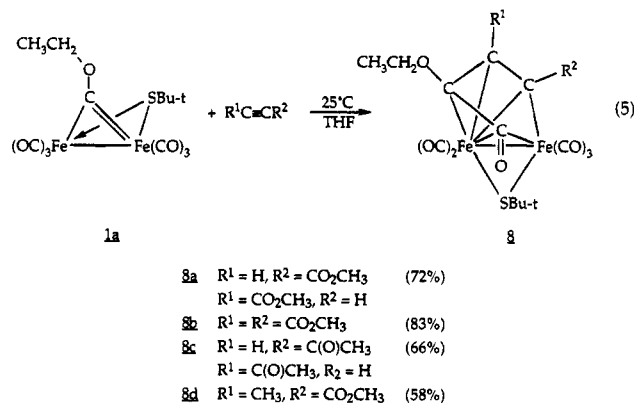| complex	R^1	R^2	$\nu_{C=O}$	δ_{H_a}	δ_{H_b}
6a	H	CO$_2$CH$_3$	1628 cm^{-1}	5.66 (d), J = 12.21 Hz	7.67 (d), J = 21.24 Hz
6b	CO$_2$CH$_3$	CO$_2$CH$_3$	1640, 1630 cm^{-1}	5.09 (d), J = 12.15 Hz	7.61 (d), J = 12.17 Hz
6c	H	C(O)CH$_3$	1629 cm^{-1}	5.22 (d), J = 12.21 Hz	7.59 (d), J = 12.20 Hz
6d	CH$_3$	CO$_2$CH$_3$	1636, 1624 cm^{-1}	5.13 (d), J = 12.37 Hz	7.56 (d), J = 12.38 Hz

Table 3. Summary of the Relevant ^{13}C NMR Spectral Data for 6a–d
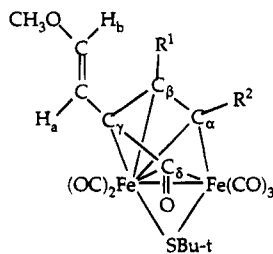
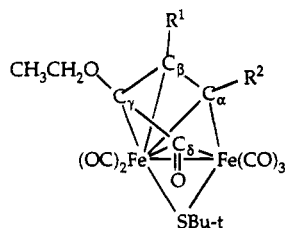| complex	R^1	R^2	δ_{C_α}	δ_{C_β}	δ_{C_γ}	δ_{C_δ}
6a	H	CO$_2$CH$_3$	118.51 (s)	117.67 (d), J_{CH} = 169.6 Hz	69.07 (s)	235.29 (s)
6b	CO$_2$CH$_3$	CO$_2$CH$_3$	125.88 (s)	108.44 (s)	71.45 (s)	233.60 (s)
6c	H	C(O)CH$_3$	131.40 (s)	113.19 (d), J_{CH} = 165.2 Hz	66.39 (s)	234.70 (s)
6d	CH$_3$	CO$_2$CH$_3$	126.38 (s)	118.20 (s)	70.00 (s)	235.34 (s)

substituted μ-σ,π-vinyl complex (μ-σ,π-CH=CHC(O)H)-(μ-t-BuS)Fe$_2$(CO)$_6$, 7 (eq 4). This conversion of 2a to 7 had been effected with water alone and with aqueous acid,[2] and, apparently, the terminal acetylenes reacted preferentially as weak acids to effect this conversion.

R = C$_6$H$_5$ (52%)

R = Si(CH$_3$)$_3$ (39%)
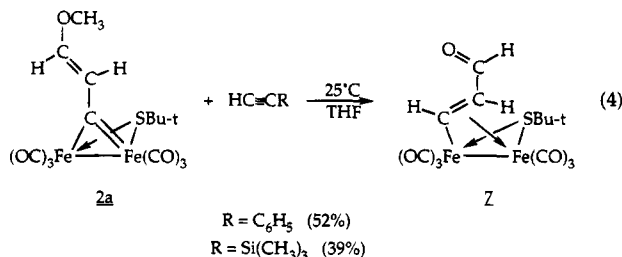
Reactions of the μ_2-ethoxycarbyne complexes, 1, with activated acetylenes also were investigated. Reactions of 1a with HC≡CCO$_2$CH$_3$, CH$_3$O$_2$CC≡CCO$_2$CH$_3$, HC≡CC(O)CH$_3$, and CH$_3$C≡CCO$_2$CH$_3$ proceeded similarly to those with the vinylcarbyne complex 2a, with a gradual color change from orange-red to brown over the course of 24 h at room temperature. Although TLC analysis of the reaction mixtures showed some remaining starting material, longer reaction times produced immobile, brown decomposition products. The products were isolated in good yield and were brown-black, oily solids which were recrystallized from pentane/CH$_2$Cl$_2$ (eq 5). In contrast to the vinylcarbyne complex 2a, reactions with activated acetylenes where only one isomer of addition for the unsymmetrical acetylenes was observed, the methyl propiolate and 3-butyn-2-one reactions with 1a gave both regioisomers. The major isomer was that in which the least bulky substituent of the acetylene was nearest the ethoxy ligand.

8a	R^1 = H, R^2 = CO$_2$CH$_3$	(72%)
	R^1 = CO$_2$CH$_3$, R^2 = H	
8b	R^1 = R^2 = CO$_2$CH$_3$	(83%)
8c	R^1 = H, R^2 = C(O)CH$_3$	(66%)
	R^1 = C(O)CH$_3$, R$_2$ = H	
8d	R^1 = CH$_3$, R^2 = CO$_2$CH$_3$	(58%)

Subsequent spectroscopic analysis showed that these new insertion products, 8, were entirely similar to the insertion products 6, obtained from the reaction of the vinylcarbyne complex 2a with activated acetylenes. The mass spectra of 8a–d all showed molecular ions corresponding to the sum of the mole masses of the reactants as well as successive loss of six carbonyl fragments. Their infrared spectra showed strong bands at approximately 1620 cm^{-1}. As before, these bands were assigned the $\nu_{C=O}$ stretch for the triply bridging carbonyl ligand. Their ^{1}H NMR spectra showed all of the expected resonances with the most notable feature being complex multiplets at approximately 4.3 ppm due to the methylene protons of the original ethoxycarbyne ligand. This results from the diastereotopic nature of these protons when attached to a chiral framework and has been observed previously in this work.[8] The ^{13}C NMR spectra of 8a–d were the most instructive in identifying their structures. As before, the carbyne carbon resonance of the ethoxycarbyne 1a which had

Table 4. Summary of the Relevant IR and ¹H NMR Spectral Data for 8a–d

complex	R¹	R²	$\nu_{C=O}$, cm⁻¹	δ_{CH_2}	$\delta_{R^1}{}^a$
8a	H	CO₂CH₃	1623	4.19–4.35 (m)	5.66 (s) maj
	CO₂CH₃	H			6.81 (s) min
8b	CO₂CH₃	CO₂CH₃	1625	4.24–4.39 (m)	–
8c	H	C(O)CH₃	1619	4.49–4.87 (m)	5.67 (s) maj
	C(O)CH₃	H			6.71 (s) min
8d	CH₃	CO₂CH₃	1617	4.21–4.42 (m)	–

*ᵃ* maj = major isomer, min = minor isomer.

appeared at 383.3 ppm had disappeared and three new signals appeared in the vinyl region at approximately 100, 105, and 125 ppm, corresponding to the two acetylenic carbon atoms and the original carbyne carbon atom which now comprised the unsymmetrical bridging allyl unit. In the terminal carbonyl region, five singlets again were observed as well as a singlet at 230 ppm due to the carbon atom of the triply bridging carbonyl ligand. In **8a** and **8c** where isomers of addition were observed, ten singlets in the terminal carbonyl region were identified, and, in addition to a peak at 230 ppm, a singlet at 245 ppm also was observed due to the triply bridging carbonyl carbon atom of the other positional isomer (the minor isomer). These relevant spectroscopic data are summarized in Tables 4 and 5. A comparison of the spectral data in Tables 4 and 5 with the spectral data in Tables 2 and 3 clearly shows the similarity between the complexes **8a–d** and the complexes **6a–d**.

Other examples of the reactivity of doubly bridging carbyne complexes with acetylenes have been reported and are instructive with respect to reactivity comparisons as well as mechanistic considerations. Ros and co-workers have studied diiron hexacarbonyl complexes differing from **1** only in that they contained a μ-σ,π-vinyl ligand instead of a bridging thiolate ligand, (μ₂-CH₃CH₂OC)(μ-σ,π-R¹C=CHR²)Fe₂(CO)₆, and investigated their reactivity with activated acetylenes.[9] When the substitutents of the μ-σ,π-vinyl ligand are phenyl groups, reaction with dimethyl acetylenedicarboxylate and hexafluoro-2-butyne gave products containing an unsymmetrically bonded allyl unit composed of the original carbyne carbon atom and the two acetylenic carbon atoms (eq 6). A terminal carbonyl ligand had been lost and the μ-σ,π-vinyl ligand remained unperturbed. These reactions are particularly noteworthy since their similarity to the insertion reactions presented here with the vinylcarbyne complex **2a** and, especially, **1a**, is obvious, yet the resulting products are quite different in that our products contained an inserted carbonyl ligand which triply bridged the original carbyne carbon atom and the Fe₂(CO)₅ framework. Since the ethoxycarbyne complexes **1** and **9** differ only in the second bridging ligand,
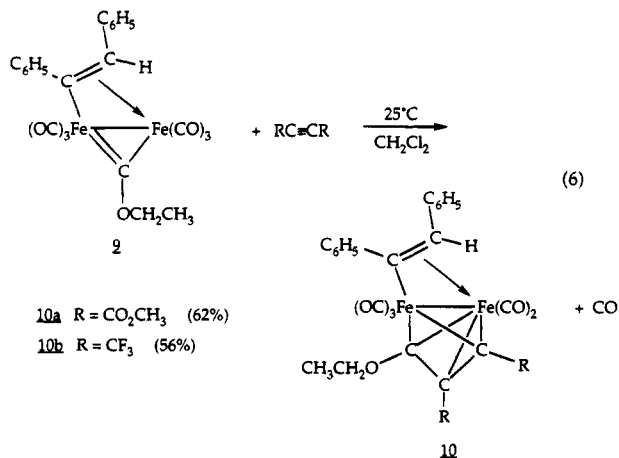
μ-thiolate versus μ-σ,π-vinyl, it can be deduced that this supposedly spectator ligand plays an important role in determining the course of insertion reactions with activated acetylenes.

This is borne out by the observation that when the substituents on the μ-σ,π-vinyl ligand are all protons, (μ₂-CH₃CH₂OC)(μ-σ,π-CH=CH₂)Fe₂(CO)₆, **11**, reaction with hexafluoro-2-butyne gave a product, **12**, in which the μ-σ,π-vinyl ligand, the ethoxycarbyne ligand, and the acetylene had combined to form a complex bridging organic ligand (eq 7).[9a] In this case, loss of carbon
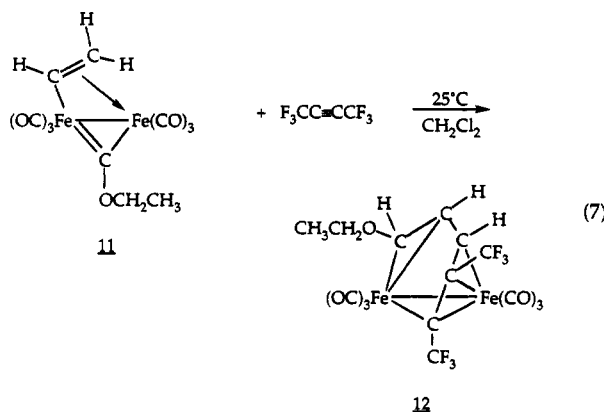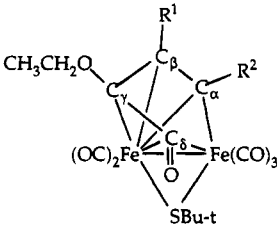

monoxide was not observed, the μ-σ,π-vinyl ligand had not remained unperturbed, and a 1,2-hydrogen shift from the μ-σ,π-vinyl ligand to the carbyne carbon atom had occurred. This example clearly demonstrates the importance of the other bridging ligand in ethoxycarbyne complexes in determining the outcome of the acetylene insertion reaction.

It also was instructive to compare the reactivity of our neutral vinylcarbyne complexes with that of the cationic methylidyne complexes reported by Casey and co-workers.[10] Reaction of the cationic diiron complex containing a bridging carbonyl and a bridging methylidyne ligand, [(C₅H₅)(CO)Fe]₂(μ-CO)(μ-CH)]⁺, **13**, with acetylenes (not necessarily activated acetylenes) gave cationic products **14**, in which a terminal carbonyl ligand had been inserted to form an η₁,η₄-vinylketene ligand composed of the carbyne carbon atom, the two acetylenic carbon atoms, and the carbon atom of the

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(8) The phenomenon of diastereotopic methylene protons giving rise to complex multiplets in the ¹H NMR spectra is often encountered in the ethanethiolate ligand (SCH₂CH₃) when it is attached to a chiral Fe₂(CO)₆ framework: ref 3.

(9) (a) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087. (b) Ros, J.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Organomet. Chem.* **1984**, *260*, C40.

(10) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447.

Table 5. Summary of the Relevant ^{13}C NMR Spectral Data for 8a–d

complex	R^1	R^2	δ_{C_α}	δ_{C_β}	δ_{C_γ}	δ_{C_δ}
8a	H	CO_2CH_3	106.51 (s)	103.92 (d), $J_{CH} = 169.8$ Hz	129.24 (s)	223.57 (s)
	CO_2CH_3	H	109.82 (d), $J_{CH} = 174.5$ Hz	100.32 (s)	128.42 (s)	246.44 (s)
8b	CO_2CH_3	CO_2CH_3	104.79 (s)	101.17 (s)	121.60 (s)	229.54 (s)
8c	H	$C(O)CH_3$	108.39 (s)	106.11 (d), $J_{CH} = 169.7$ Hz	127.85 (s)	226.01 (s)
	$C(O)CH_3$	H	112.85 (d), $J_{CH} = 165.8$ Hz	102.85 (s)	126.08 (s)	244.87 (s)
8d	CH_3	CO_2CH_3	110.83 (s)	104.22 (s)	123.92 (s)	231.58 (s)

Scheme 2
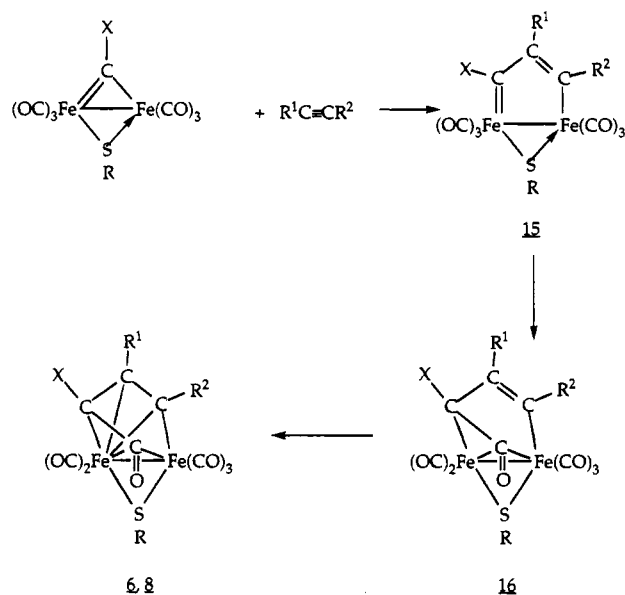
inserted carbonyl ligand (eq 8). Here, the other bridging

$$R^1 = R^2 = H$$
$$R^1 = R^2 = C_6H_5$$
$$R^1 = H, R^2 = C_6H_5$$
$$R^1 = H, R^2 = CH_3$$
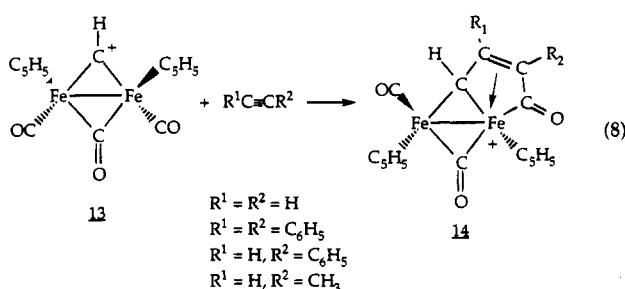
ligand, a carbonyl ligand, had again remained unperturbed. This example further demonstrated the insertion product variability and emphasized the dependence on the nature of the substituent on the carbyne carbon atom, of the other bridging ligand, and of the overall charge of the original carbyne complex.

Although not a great deal of information is available concerning the mechanism of the above insertion reactions, a proposed mechanism for the formation of the insertion products 6 and 8 from the reaction of activated acetylenes with the vinylcarbyne complex 2a and the ethoxycarbyne complex 1a, respectively, is given in Scheme 2. The first step in the mechanism involves the insertion of the acetylene into an iron–carbyne bond to form a five-membered dimetallacycle, 15. Such inser-

tions are well documented in the literature.[11] As discussed above, the presence of only one isomer of addition for the unsymmetrical acetylenes (methyl propiolate, 3-butyn-2-one, and methyl 2-butynoate) in 6a, 6c, 6d, and 8d probably results from steric constraints, placing the least bulky acetylenic substituent nearest the substituent of the carbyne carbon atom. Even when both positional isomers were observed, in 8a and 8c, the major isomer again was that which minimized nonbonded steric interactions with the substituent of the carbyne carbon atom. At this point, a terminal carbonyl ligand on the iron atom still bonded to the original carbyne carbon atom could bridge these two centers as well as the other iron atom as in 16. The original acetylene, now essentially a vinyl ligand, could then bind to the electron deficient iron atom, the one with only two terminal carbonyl ligands, in a π-fashion forming the observed insertion products 6 and 8. Although this mechanism does not include the thiolate ligand directly, the comparison with the work of Ros et al.[9] discussed above clearly indicates that the thiolate ligand plays an important role in determining the outcome of these types of insertion reactions. Intermediate 15 contains a three-carbon ligand which is the same, except for the substituents on the carbon atoms, as one encountered in complexes prepared in earlier work by the reaction of ethoxyacetylene with Li[(μ-CO)-(μ-RS)Fe$_2$(CO)$_6$].[12] The anionic product formed in this reaction gave 17 on treatment with acetyl chloride.
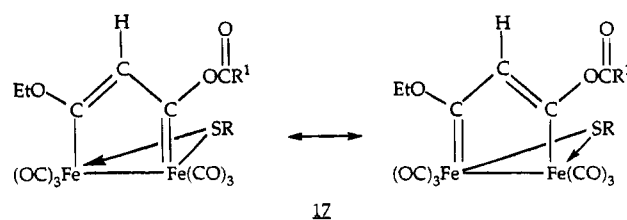
Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium/

(11) (a) Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 867. (b) Chisholm, M. H.; Heppert, J. A.; Huffman, J.C. *J. Am. Chem. Soc.* **1984**, *106*, 1151. (c) Beanan, L. R.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062.

(12) (a) Hoke, J. B.; Dewan, J. C.; Seyferth, D. *Organometallics* **1987**, *6*, 1816. (b)Seyferth, D.; Hoke, J. B.; Dewan, J. C.; Hofmann, P.; Schnellbach, M. *Organometallics*, submitted.

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[13] and triethyloxonium tetrafluoroborate[14] were prepared by literature procedures. Methyl propiolate, 3-butyn-2-one, methyl 2-butynoate, and phenylpropargyl aldehyde were purchased from Farchan Laboratories, purified by vacuum distillation at room temperature, and purged with nitrogen prior to use. Dimethyl acetylenedicarboxylate, phenylacetylene, (trimethylsilyl)acetylene, and trifluoroacetic acid were purchased from Aldrich, purified by distillation when necessary, and purged with nitrogen prior to use.

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 F₂₅₄, 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. Masses were correlated using the following isotopes: [1]H, ^{12}C, ^{14}N, ^{16}O, ^{19}F, [32]S, and [56]Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory in Herlev, Denmark. Photolyses were performed in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) operating at 254 nm.

Since the important IR and ^{1}H and ^{13}C NMR data for **6a–d** and **8a–d** are given in Tables 2–5, their complete IR, ^{1}H and ^{13}C NMR data, as well as 70 eV EI–MS data, are given in the supplementary material.

X-ray Crystallography. Structure of (μ-C(O)C(CH=CHOCH₃)C(H)C(CO₂CH₃))(μ-t-BuS)Fe₂(CO)₆, 6a. A suitable quality, brown prism crystal (which had been grown in pentane) 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 25.16° < 2θ < 32.80° corresponded to a monoclinic cell with dimensions given in Table 6. For Z = 4 and FW = 522.09, the calculated density is 1.544 g/cm³. Based on the systematic absences of h0l: h ≠ 2n and 0k0: k ≠ 2n and the successful solution and refinement of the structure, the space group was determined to be P2₁/a (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

(13) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.
(14) *Organic Syntheses*; Baumgarten, H. E., Ed.; John Wiley and Sons: New York, 1973; p 1080.

Table 6. Crystal Data for 6a

empirical formula	$C_{18}H_{18}Fe_2O_9S$
formula weight	522.09
crystal color, habit	brown, prism
crystal dimensions (mm)	0.150 × 0.080 × 0.260
crystal system	monoclinic
no. reflections used for unit cell determination (2θ range)	25 (25.2–32.8°)
ω scan peak width at half-height	0.29
lattice parameters:	a = 17.442(6) Å
	b = 10.218(2) Å
	c = 13.700(3) Å
	B = 113.10(2)°
	V = 2246(1) Å³
space group	P2₁/a (no. 14)
Z value	4
D_{calcd}	1.544 g/cm³
F_{000}	1064
$\mu_{(Mo\ K\alpha)}$	14.60 cm⁻¹

Table 7. Positional Parameters and B_{eq} for 6a

atom	x	y	z	B_{eq}
Fe(1)	0.19806(5)	0.22127(8)	0.25534(6)	3.57(3)
Fe(2)	0.35291(5)	0.20059(8)	0.34402(6)	3.24(3)
S(1)	0.2870(1)	0.1864(1)	0.1716(1)	4.05(6)
O(1)	0.2109(3)	−0.1006(4)	0.2107(3)	5.4(2)
O(2)	0.3152(3)	−0.1447(4)	0.3661(3)	5.2(2)
O(3)	0.4493(3)	0.4092(5)	0.7280(4)	6.2(2)
O(11)	0.0706(3)	0.0771(5)	0.0790(4)	6.8(2)
O(12)	0.1007(3)	0.2163(5)	0.3872(4)	6.5(3)
O(13)	0.1315(4)	0.4828(6)	0.1721(5)	8.6(3)
O(21)	0.4908(3)	0.0244(6)	0.3709(5)	8.2(3)
O(22)	0.4571(3)	0.4358(5)	0.3957(4)	6.3(2)
O(9)	0.2691(3)	0.4350(4)	0.4145(3)	4.2(2)
C(1)	0.2632(3)	0.0706(5)	0.3379(4)	3.3(2)
C(2)	0.2590(4)	−0.0658(6)	0.2965(5)	4.0(2)
C(3)	0.3158(6)	−0.2788(7)	0.3337(7)	7.4(4)
C(4)	0.3119(3)	0.0929(5)	0.4457(4)	3.4(2)
C(5)	0.3235(3)	0.2229(5)	0.4826(4)	3.3(2)
C(6)	0.3788(4)	0.2545(6)	0.5911(5)	4.3(2)
C(7)	0.3997(4)	0.3721(7)	0.6287(5)	4.9(3)
C(8)	0.4804(5)	0.308(1)	0.8034(6)	7.4(4)
C(11)	0.1207(4)	0.1286(7)	0.1481(5)	5.0(3)
C(12)	0.1387(4)	0.2188(6)	0.3351(5)	4.4(3)
C(13)	0.1581(5)	0.3837(7)	0.2015(6)	5.5(3)
C(21)	0.4375(4)	0.0947(7)	0.3624(6)	4.9(3)
C(22)	0.4172(4)	0.3449(6)	0.3710(5)	3.9(2)
C(31)	0.3011(5)	0.3135(7)	0.0833(6)	5.7(3)
C(32)	0.3694(7)	0.260(1)	0.0514(9)	9.9(6)
C(33)	0.3258(6)	0.4480(8)	0.1344(7)	8.7(5)
C(34)	0.2199(6)	0.3228(8)	−0.0127(6)	7.2(4)
C(9)	0.2782(3)	0.3189(5)	0.4011(5)	3.6(2)
H(1)	0.2637	−0.3182	0.3218	9.0
H(2)	0.3257	−0.2811	0.2703	9.0
H(3)	0.3590	−0.3250	0.3881	9.0
H(4)	0.3365	0.0220	0.4926	4.1
H(5)	0.4017	0.1834	0.6385	5.2
H(6)	0.3768	0.4413	0.5794	5.9
H(7)	0.4352	0.2628	0.8097	8.9
H(8)	0.5126	0.2498	0.7811	8.9
H(9)	0.5145	0.3453	0.8700	8.9
H(10)	0.3523	0.1769	0.0181	11.9
H(11)	0.3778	0.3184	0.0027	11.9
H(12)	0.4190	0.2504	0.1123	11.9
H(13)	0.3776	0.4414	0.1930	10.4
H(14)	0.3306	0.5072	0.0836	10.4
H(15)	0.2843	0.4781	0.1575	10.4
H(16)	0.1774	0.3517	0.0084	8.6
H(17)	0.2264	0.3830	−0.0618	8.6
H(18)	0.2063	0.2389	−0.0449	8.6

scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0°. Scans of (0.89 + 0.35 tan θ)° were made at a speed of 8.0°/min (in ω). The weak reflections (I < 10.0σ-(I)) were rescanned (maximum of 2 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 40 cm.

Of the 5621 reflections which were collected, 5449 were unique (R_{int} = 0.063); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 197 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα is 14.6 cm^{-1}. An empirical absorption correction, using the program DIFABS,[15] was applied which resulted in transmission factors ranging from 0.90 to 1.36. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[16] 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[17] was based on 2733 observed reflections ($I > 3.00\sigma(I)$) and 271 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.052 and R_w = 0.064.

The standard deviation of an observation of unit weight[18] was 1.48. 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 θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and −0.33 e/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in F_{calcd},[20] and the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[21] All calculations were performed using the TEXSAN[22] crystallographic software package of Molecular Structure Corp.

Thermal Rearrangement of (μ_2-CH$_3$CH$_2$OC)(μ-t-BuS)-Fe$_2$(CO)$_6$. A three-necked 100 mL round-bottomed flask equipped with a stir-bar, a glass stopper, a rubber septum, a reflux condenser, and a gas inlet adapter was charged with (μ_2-CH$_3$CH$_2$OC)(μ-t-BuS)Fe$_2$(CO)$_6$[3] (0.29 g, 0.68 mmol) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 20 mL of toluene. The orange solution was heated at reflux for 4 h during which time the solution turned progressively deeper red in color although no change was indicated by TLC analysis of the reaction mixture. The solvent was removed on a rotary evaporator to give an oily orange-red residue which was purified by filtration chromatography. Pentane/CH$_2$Cl$_2$ (1/1 v/v) gave 0.28 g (0.67 mmol, 98%) of the μ-acyl complex (μ-CH$_3$CH$_2$C=O)(μ-t-BuS)-

Fe$_2$(CO)$_6$, **4a**, (a mixture of two inseparable isomers) as a slightly air-sensitive, red oil. IR (CCl$_4$, cm^{-1}): 2980 (m), 2955 (m), 2935 (m), 2905 (w), 2880 (vw), 1512 (m, br, $\nu_{C=O}$ acyl), 1472 (w), 1458 (m), 1400 (w), 1379 (w), 1368 (m), 1323 (w), 1296 (vw), 1159 (s), 1088 (m), 1018 (m, br), 923 (s), 710 (w), 624 (m), 610 (s), 583 (s, br). Terminal carbonyl region (CCl$_4$, cm^{-1}): 2085 (s), 2040 (vs), 2015 (vs), 1998 (vs), 1969 (s), 1940 (sh). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.72 (t, J = 7.86 Hz, 1.6H, CH_3CH$_2$C=O, major isomer), 0.75 (t, J = 7.36 Hz, 1.4H, CH_3-CH$_2$C=O, minor isomer), 1.27 (s, 4.3H, SC(CH_3)$_3$, minor isomer), 1.48 (s, 4.7H, SC(CH_3)$_3$, major isomer), 2.43−2.96 (complex m, 2H, CH$_3$CH_2C=O, both isomers). Isomer ratio (major/minor) = 1.1/1.0. ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ$_C$ 8.29 (q, J_{CH} = 129.3 Hz, CH$_3$CH$_2$C=O, minor isomer), 8.46 (q, J_{CH} = 127.9 Hz, CH$_3$CH$_2$C=O, major isomer), 34.24 (q, J_{CH} = 128.1 Hz, SC(CH$_3$)$_3$, major isomer), 34.68 (q, J_{CH} = 125.8 Hz, SC-(CH$_3$)$_3$, minor isomer), 47.69 (s, SC(CH$_3$)$_3$, minor isomer), 49.68 (s, SC(CH$_3$)$_3$, major isomer), 54.19 (t, J_{CH} = 130.0 Hz, CH$_3$CH$_2$C=O, major isomer), 54.31 (t, J_{CH} = 131.6 Hz, CH$_3$CH$_2$C=O, minor isomer), 206.56, 208.39, 210.16, 210.35, 211.48, and 212.06 (all s, terminal CO's, both isomers), 299.29 (s, CH$_3$CH$_2$C=O, major isomer), 300.31 (s, CH$_3$CH$_2$C=O, minor isomer). Mass spectrum (EI): *m/z* (relative intensity): 426 (M$^+$, 12), 398 (M$^+$ − CO, 9), 370 (M$^+$ − 2CO, 26), 342 (M$^+$ − 3CO, 34), 314 (M$^+$ − 4CO, 31), 286 (M$^+$ − 5CO, 67), 258 (M$^+$ − 6CO, 100), 230 (^{t}BuSFe$_2$CH$_3$CH$_2$$^+$, 13), 202 (HSFe$_2CH_3$-CH$_2$C=O$^+$, 48), 201 (SFe$_2CH_3CH_2$-C=O$^+$, 19), 200 (SFe$_2CH_2$-CH$_2$C=O$^+$, 46), 174 (HSFe$_2CH_3CH_2$$^+$, 5), 173 (SFe$_2CH_3CH_2$$^+$, 4), 172 (SFe$_2CH_2CH_2$$^+$, 7), 145 (HSFe$_2$$^+$, 12), 144 (SFe$_2$$^+$, 25), 90 (^{t}BuSH$^+$, 5), 57 (^{t}Bu$^+$ or CH$_3$CH$_2$C=O$^+$, 58), 41 (C$_3$H$_5$$^+$, 48), 40 (C$_3H_4$$^+$, 3), 39 (C$_3H_3$$^+$, 11). Anal. Calcd for C$_{13}H_{14}Fe_2O_7$S: C, 36.65; H, 3.31. Found: C, 37.13; H, 3.13.

Photolytic Rearrangement of (μ_2-CH$_3$CH$_2$OC)(μ-t-BuS)-Fe$_2$(CO)$_6$. A 100 mL round-bottomed quartz flask equipped with a stir-bar and a rubber septum was charged with (μ_2-CH$_3$CH$_2$OC)(μ-t-BuS)Fe$_2$(CO)$_6$[3] (0.25 g, 0.59 mmol) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 20 mL of toluene. The orange solution was photolyzed for 3 d in a Rayonet photochemical reactor operating at 254 nm. No change was apparent by TLC analysis of the reaction mixture although the solution turned progressively deeper orange in color. The solvent was removed on a rotary evaporator to give an orange-red oil which was purified by filtration chromatography. Pentane eluted a deep red band which gave 0.25 g (0.58 mmol, 99%) of the μ-acyl complex (μ-CH$_3$CH$_2$C=O)(μ-t-BuS)Fe$_2$(CO)$_6$, **4a**, (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 (experiment above).

Thermal Rearrangement of (μ_2-CH$_3$CH$_2$OC)(μ-PhS)Fe$_2$-(CO)$_6$. The procedure described above was used in the thermally induced rearrangement of 0.064 g (0.14 mmol) of the title complex in 20 mL of toluene (4 h reflux). The solvent was removed *in vacuo* to give an oily orange-red residue which was purified by filtration chromatography. Pentane eluted a deep red band which gave 0.063 g (0.14 mmol, 98%) of the μ-acyl complex (μ-CH$_3$CH$_2$C=O)(μ-PhS)Fe$_2$(CO)$_6$, **4b**, (a mixture of two inseparable isomers) as a slightly air-sensitive red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[23]

Photolytic Rearrangement of (μ_2-CH$_3$CH$_2$OC)(μ-PhS)-Fe$_2$(CO)$_6$. The procedure described above was used in the photolysis of 0.41 g (0.92 mmol) of the title compound in the Rayonet reactor for 2 d. Workup as above gave 0.40 g (0.89 mmol, 97%) of the μ-acyl complex (μ-CH$_3$CH$_2$C=O)(μ-PhS)Fe$_2$-(CO)$_6$, **4b**, (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.[23]

Reactions of (μ_2-CH$_3$OCH=CHC)(μ-t-BuS)Fe$_2$(CO)$_6$, 2a, with Activated Acetylenes. (a) Methyl Propiolate. A 100 mL Schlenk flask equipped with a stir-bar and a rubber

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

(16) Structure solution methods: PHASE: Patterson Heavy Atom Solution Extractor. Calabrese, 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, Netherlands.

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

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septum was charged with **2a** (0.54 g, 1.24 mmol) and degassed by three evacuation/nitrogen-backfill cycles. Thirty milliliters of THF was added and to the resulting deep red solution was added methyl propiolate (0.11 g, 1.29 mmol) by syringe. After the reaction mixture had been stirred at room temperature for 24 h, the color of the solution had turned from red to brown-black and TLC indicated complete consumption of the starting material. The solvent was removed *in vacuo* to yield a brown-black, oily solid which was taken up in pentane/CH_2Cl_2 (1/1 v/v) and passed through a thin pad of silicic acid. After removal of the solvent on a rotary evaporator, the brown-black residue was purified by medium pressure chromatography (pentane/CH_2Cl_2 1/1 v/v) eluted 0.058 g (20% based on S) of (t-BuS)₂Fe₂(CO)₆ (based on ¹H NMR)[24] and 0.019 g (4%) of **7**. Further elution with 1/2 v/v pentane/CH_2Cl_2 gave 0.28 g (43%) of **6a**, an air-stable, black solid, mp 93.5–95.5 °C (from pentane). Anal. Calcd for $C_{18}H_{18}Fe_2O_9S$: C, 41.41; H, 3.48. Found: C, 41.73; H, 3.60.

(b) Dimethyl Acetylenedicarboxylate. The same procedure was used in the reaction of **2a** (0.46 g, 1.05 mmol) with dimethyl acetylenedicarboxylate (0.16 g, 1.14 mmol). Medium pressure chromatography (pentane/CH_2Cl_2 (1/1 v/v)) eluted a faint orange band which after removal of the solvent gave 0.023 g (0.055 mmol, 5%) of **7** as an air-stable orange solid, identified by comparison of its ¹H NMR spectrum with that of an authentic sample.[2] Pentane/CH_2Cl_2 (3/7 v/v) then eluted a large black band which gave 0.46 g (0.80 mmol, 76%) of **6b** as an air-stable black solid, mp 99.5–101.5 °C (from pentane). Anal. Calcd for $C_{20}H_{20}Fe_2O_{11}S$: C, 41.41; H, 3.48. Found: C, 41.48; H, 3.56.

(c) 3-Butyn-2-one. The same procedure was used in the reaction of 0.81 g (1.85 mmol) of **2a** with 0.14 g (2.07 mmol) of HC≡CC(O)CH₃ (21 h reaction time). Medium pressure chromatography effected isolation of **2a** (0.099 g, 12%, 9/1 v/v pentane/CH_2Cl_2), **7**, (0.050 g, 7%, 1/1 v/v pentane/CH_2Cl_2), and **6c** (0.26 g, 32% based on unrecovered starting material, 1/2 v/v pentane/CH_2Cl_2), a slightly air-sensitive brown-black solid, mp 94.0–95.0 °C (from pentane). Anal. Calcd for $C_{18}H_{18}Fe_2O_8S$: C, 42.72; H, 3.58. Found: C, 42.41; H, 3.77.

(d) Methyl 2-Butynoate. The same procedure was used in the reaction of 0.52 g (1.18 mmol) of **2a** with 0.13 g (1.30 mmol) of CH₃C≡CCO₂CH₃ (44 h reaction time). The following were isolated by medium pressure chromatography (elution as in (c)): **2a** (0.18 g, 35%), **7** (0.12 g, 37%), and **6d** (0.15 g, 35% based on unrecovered starting material), a slightly air-sensitive, black solid, mp 110.0–111.0 °C (from pentane). Anal. Calcd for $C_{19}H_{20}Fe_2O_9S$: C, 42.57; H, 3.76. Found: C, 42.51; H, 3.90.

Attempted Reaction of (μ₂-(CH₃)₂NCH=CHC)(μ-t-BuS)-Fe₂(CO)₆, 3a, with Methyl Propiolate. A 100 mL Schlenk flask equipped with a stir-bar and a rubber septum was charged with (μ₂-(CH₃)₂NCH=CHC)(μ-t-BuS)Fe₂(CO)₆ (0.26 g, 0.58 mmol) and degassed by three evacuation/nitrogen-backfill cycles. Fifteen milliliters of THF and then methyl propiolate (0.060 mL, 0.057 g, 0.67 mmol) were added by syringe. After the reaction mixture had been stirred at room temperature for 51 h, TLC analysis of the reaction mixture indicated that no reaction had taken place and no decomposition was apparent. The reaction mixture was cannulated into a three-necked 100 mL round-bottomed flask equipped with a condenser, a stir-bar, a glass stopper, and a gas inlet adapter. The orange-yellow THF solution then was heated at reflux for 7 h during which time the color of the reaction mixture turned progressively more brown in color. TLC analysis indicated that the

starting material had virtually disappeared and only brown, immobile decomposition products remained. No further work-up was pursued.

Reaction of (μ₂-CH₃CH₂OC)(μ-t-BuS)Fe₂(CO)₆, 1a, with Activated Acetylenes. (a) Methyl Propiolate. A 100 mL Schlenk flask equipped with a stir-bar and a rubber septum was charged with (μ₂-CH₃CH₂OC)(μ-t-BuS)Fe₂(CO)₆ (0.8 g, 1.88 mmol) and degassed by three evacuation/nitrogen-backfill cycles. To the flask then was added 25 mL of THF. To the resulting orange-red solution, methyl propiolate (0.19 g, 2.25 mmol) was added by syringe. After the reaction mixture had been stirred at room temperature for 28 h, the color of the solution had turned from orange-red to brown-black and TLC indicated the presence of a small amount of remaining starting material as well as a large brown-black product. The solvent was removed *in vacuo* to yield a brown-black oily solid whose purification by filtration chromatography gave 0.17 g (22%) of **1a** (3/1 v/v pentane/CH_2Cl_2) and 0.54 g (72% based on unrecovered starting material) (1/1 v/v CH_2Cl_2/acetone) of **8a** (a mixture of two inseparable isomers) as an air-stable, brown-black solid, mp 126.0–128.0 °C (from pentane/CH_2Cl_2). Anal. Calcd for $C_{17}H_{18}Fe_2O_9S$: C, 40.03; H, 3.56. Found: C, 39.90; H, 4.05.

(b) Dimethyl Acetylenedicarboxylate. The same procedure was used in the reaction of 0.62 g (1.44 mmol) of **1a** with 0.21 g (1.46 mmol) of dimethyl acetylenedicarboxylate. Filtration chromatography was used to purify the brown-black solid residue. Pentane eluted a faint orange band which after removal of the solvent gave 0.12 g (19%) of **1a**. Pentane/CH_2Cl_2 (1/1 v/v) then eluted a large brown band which gave 0.55 g (0.98 mmol, 83% based on unrecovered starting material) of **8b** as an air-stable, brown-black solid, mp 102.0–104.0 °C (from pentane/CH_2Cl_2). Anal. Calcd for $C_{19}H_{20}Fe_2O_{11}S$: C, 40.17; H, 3.55. Found: C, 40.27; H, 3.64.

(c) 3-Butyn-2-one. The same procedure was employed in the reaction of 0.8 g (1.88 mmol) of **1a** with 0.15 g (2.17 mmol) of HC≡CC(O)CH₃ (21 h reaction time). Filtration chromatography (elution as in (a)) gave 0.20 g (25%) of **1a** and 0.46 g (66% based on unrecovered starting material) of **8c** (a mixture of inseparable isomers) as an air-stable, brown-black solid, mp 121.0–124.0 °C (from pentane/CH_2Cl_2). Anal. Calcd for $C_{17}H_{18}Fe_2O_8S$: C, 41.33; H, 3.67%. Found: C, 41.37; H, 3.86.

(d) Methyl 2-Butynoate. The same procedure was used in the reaction of 0.61 g (1.43 mmol) of **1a** with 0.16 g (1.16 mmol) of CH₃C≡CCO₂CH₃ (32 h reaction time). Filtration chromatography (elution as in (a)) gave 0.12 g (20%) of **1a** and 0.35 g (58%, based on unrecovered starting material) of **8d** as an air-stable, brown-black solid, mp 93.5–94.5 °C (from pentane/CH_2Cl_2). Anal. Calcd for $C_{18}H_{20}Fe_2O_9S$: C, 41.25; H, 3.85. Found: C, 41.79; H, 4.05.

Supplementary Material Available: Tables of IR, ¹H and ¹³C NMR, and EI mass spectra; X-ray structure information: data collection and reduction, structure solution and refinement, experimental details; tables of positional parameters, intramolecular bond distances and angles involving the non-hydrogen atoms, intramolecular distances and angles involving the hydrogen atoms, U values, least square planes (31 pages). Ordering information is given on any current masthead page.

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