Analysis of the reaction mixture by GC after 1 h at ambient temperature showed a low-RT product (30%) and a high-RT product (70%). The product ratio was confirmed by ^{1}H NMR integration, 70% β trans and 30% α. HRGCMS: calcd for $C_{14}H_{22}O_3Si$ (M$^+$), m/e 266.1338; found for low-RT product, m/e 266.1344, high-RT product, m/e 266.1292. HREIMS (direct probe): found m/e 266.1292.

11-trans: ^{1}H NMR 1.27 (t, J = 7 Hz, 9 H, d), 3.88 (q, J = 7 Hz, 6 H, c), 6.18 (d, J = 19.5 Hz, 1 H, a), 7.23 (d, J = 19.5 Hz, 1 H, b); ^{13}C NMR 18.32 (d), 58.74 (c), 117.72 (b), 126.81 (o), 128.30 (p), 128.57 (m), 131.58 (i), 149.19 (a).

11-α: ^{1}H NMR 1.20 (t, J = 7 Hz, 9 H, d), 3.83 (q, J = 7 Hz, 6 H, c), 5.97 (d, J = 3 Hz, 1 H, a), 6.14 (d, J = 3 Hz, 1 H, a'); ^{13}C NMR 18.16 (d), 58.16 (c), 126.88 (o), 126.94 (p), 128.76 (m), 137.66 (a), 143.42 (b).

These results agree with those reported.[21]

Supplementary Material Available: Tables of isotropic and anisotropic displacement coefficients and H atom coordinates for 1-trans and 1-α and ^{1}H and ^{13}C NMR spectra (33 pages); listings of structure factor amplitudes for 1-trans and 1-α (27 pages). Ordering information is given on any current masthead page.


Reactions of Triiron Dodecacarbonyl with Alkynyl- and Allenyllithium Reagents: Formation of Dinuclear Products

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Reactions of alkynyllithium reagents with $Fe_3(CO)_{12}$ result in formation of $Li[(\mu\text{-}CO)(\mu\text{-}RC\equiv C)Fe_2(CO)_6]$, whose reaction with a sulfenyl chloride, R'SCl, gives $(\mu\text{-}RC\equiv C)(\mu\text{-}R'S)Fe_2(CO)_6$ in moderate yield. The reaction of $CH_2=C=C(OMe)Li$ with $Fe_3(CO)_{12}$, followed by addition of an acid chloride yields a ferrole complex.
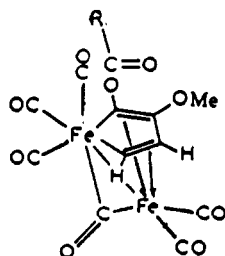
2 **a,** R = Ph
    b, R = t-Bu

The structure of the PhC(O)Cl-derived product (**2a**, R = Ph) was determined by X-ray diffraction. This compound crystallizes in the space group $P2_1/a$ with a = 12.444 (2) Å, b = 8.837 (2) Å, c = 18.429 (3) Å, β = 105.77 (1)°, and Z = 4. Final R_1 = 0.050 and R_2 = 0.058.

Introduction

Our earlier studies have shown that lithium and sodium thiolates react with $Fe_3(CO)_{12}$ to form a dinuclear anion, $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$. This species shows broad reactivity toward electrophilic substrates that are potential 3-electron donors.[1–10] In an attempt to determine how general the concept shown in eq 1 is, we have investigated the reactions of $Fe_3(CO)_{12}$ with two types of unsaturated organolithium reagents whose organic groups are potential 3-electron donors.

$$Fe_3(CO)_{12} \xrightarrow{\text{Nu}^-} [(\mu\text{-}CO)(\mu\text{-}Nu)Fe_2(CO)_6]^- \xrightarrow{\text{E}^+}$$
$$[(\mu\text{-}E)(\mu\text{-}Nu)Fe_2(CO)_6] \quad (1)$$
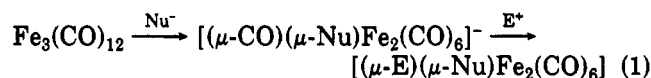
Results and Discussion

Alkynyllithium Reagents. When a solution of (*tert*-butylethynyl)lithium ((3,3-dimethylbut-1-ynyl)lithium) in THF was added at room temperature to a THF solution of an equimolar quantity of $Fe_3(CO)_{12}$, a color change from green to dark red was observed. To the solution thus formed was added, at −78 °C, an equimolar quantity of *t*-BuSCl. From the reaction mixture one product could be isolated, $(\mu\text{-}\sigma,\pi\text{-}t\text{-}BuC\equiv C)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$, a red solid, in 40% yield. This compound had been prepared earlier by the reaction of *t*-BuC≡CBr with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$.[7] A similar reaction in which EtSCl was the reactive electrophile gave $(\mu\text{-}\sigma,\pi\text{-}t\text{-}BuC\equiv C)(\mu\text{-}EtS)Fe_2(CO)_6$ in 40% yield. Also prepared in 36% yield from PhC≡CLi was $(\mu\text{-}\sigma,\pi\text{-}PhC\equiv C)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$. These products most likely were formed by the reaction sequence shown in Scheme I, so the general process of eq

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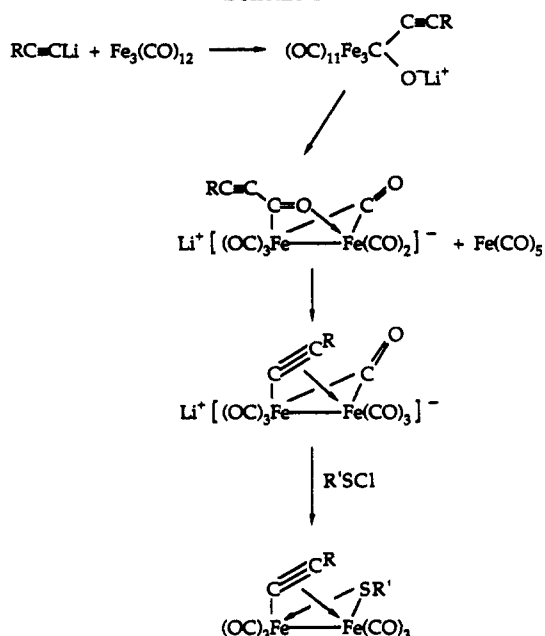(6) Seyferth, D.; Hoke, J. B. *Organometallics* **1988**, *7*, 524.

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Scheme I

1 is applicable to RC≡CLi reagents. The less than moderate yields suggest that another mode of attack of RC≡CLi on $Fe_3(CO)_{12}$ takes place, but this does not lead to a stable, isolable product.

Since reactive organometallic reagents (RLi, RMgX) react with metal carbonyls with initial attack at the carbon atom of a C≡O ligand,[11] the reaction course shown in Scheme I is suggested for the formation of (μ-σ,π-RC≡C)(μ-R'S)Fe₂(CO)₆ in the RC≡CLi/Fe₃(CO)₁₂/R'SCl reaction.

The method of choice for preparation of complexes of type (μ-σ,π-RC≡C)(μ-R'S)Fe₂(CO)₆, however, remains the reaction of bromoacetylenes with [Et₃NH][(μ-CO)(μ-R'S)Fe₂(CO)₆], which gives high product yields.[7]

(1-Methoxyallenyl)lithium. The reactions of [Et₃NH][(μ-CO)(μ-RS)Fe₂(CO)₆] with propargyl halides, HC≡CCR₂'X, gave μ-σ,π-allenyl complexes of type 1.[1] Thus, it was of interest to see if the reaction of an allenyllithium reagent with Fe₃(CO)₁₂, followed by addition of an appropriate electrophile, also would give a μ-σ,π-allenyl complex.
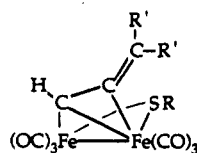
1

The reagent chosen was (1-methoxyallenyl)lithium, CH₂=C=C(OMe)Li.[12] It was prepared at -78 °C by the action of *n*-butyllithium on methoxyallene in THF. The resulting CH₂=C=C(OMe)Li solution then was added to an Fe₃(CO)₁₂ solution in THF that had been cooled to -78 °C. When the reaction mixture was allowed to warm, a color change from green, due to Fe₃(CO)₁₂, to dark red occurred. On the assumption that an anionic iron carbonyl complex had been formed, benzoyl chloride was added. Appropriate workup gave a yellow crystalline solid in 29%

Figure 1. ORTEP representation of the molecular structure of 2a. Probability ellipsoids are drawn at the 30% level.

yield. A similar CH₂=C=C(OMe)Li/Fe₃(CO)₁₂ reaction mixture was treated with pivaloyl chloride. Similar workup gave yellow crystals whose ¹H and ¹³C NMR spectra were very similar to that of the benzoyl chloride derived product when the difference between the added acyl groups was taken into consideration. The structure of the benzoyl chloride derived product was shown by means of a single-crystal X-ray diffraction study to be that of a substituted ferrole, 2a (Figure 1). This is a well-known class of organoiron carbonyl compounds that commonly are formed in reactions of acetylenes with diverse iron carbonyl derivatives.[13]

Structurally, two types of ferroles are known:[13] (1) those with an eclipsed conformation of the CO ligands on the two iron atoms, 3, and (2) those in which two CO ligands

3

4

are staggered and one CO ligand of the iron atoms that is not in the ferracyclopentadiene ring is semibridging between the two iron atoms, as in 4. Few examples of the former type are known,[14] and the factors determining the conformation of a particular ferrole are open to question.[13b,15] It is believed that the function of the semibridging CO ligand in the molecules is to behave as a π-acceptor of charge density from the iron atom of the ferrole ring.[13] Ferrole 2 adopts the more common con-

(11) Fischer, H. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; pp 4-8.

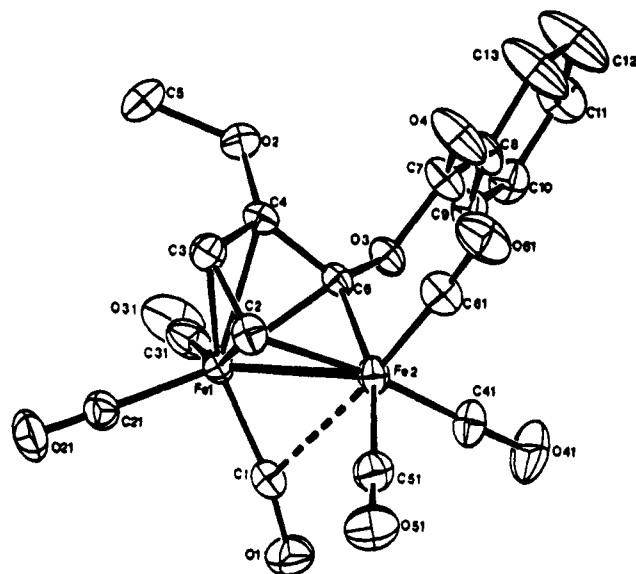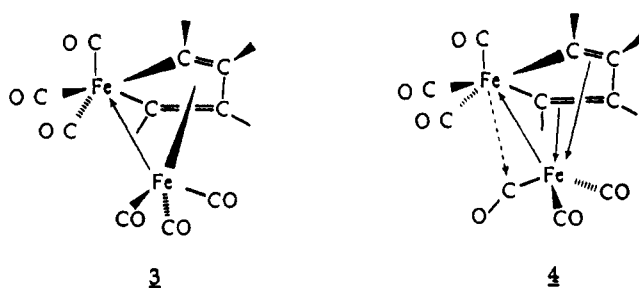(12) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* 1968, *87*, 916.

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Table I. Bond Lengths and Bond Angles in Ferrole 2a (Estimated Standard Deviations in the Last Digit in Parentheses)

Bond Lengths (Å)

Fe(1)–Fe(2)	2.522 (1)		

Ferrole Ring

Fe(2)–C(2)	1.955 (5)	Fe(2)–C(6)	1.920 (4)
C(2)–C(3)	1.410 (6)	C(3)–C(4)	1.428 (6)
C(4)–C(6)	1.410 (6)		

Bonds between the Ferrole Ring and Fe(1)

Fe(1)–C(2)	2.077 (5)	Fe(1)–C(3)	2.128 (5)
Fe(1)–C(4)	2.177 (4)	Fe(1)–C(6)	2.066 (4)

CO Ligands

Fe(1)–C(1)	1.776 (5)	Fe(2)–C(1)	2.596 (5)
Fe(1)–C(21)	1.801 (5)	Fe(1)–C(31)	1.778 (5)
Fe(2)–C(41)	1.814 (6)	Fe(2)–C(51)	1.830 (5)
Fe(2)–C(61)	1.758 (5)	C(1)–O(1)	1.143 (6)
C(21)–O(21)	1.122 (5)	C(31)–O(31)	1.146 (6)
C(41)–O(41)	1.124 (6)	C(51)–O(51)	1.122 (6)
C(61)–O(61)	1.147 (6)		

Methoxy and Benzoyl Groups

C(4)–O(2)	1.343 (5)	C(5)–O(2)	1.476 (6)
C(6)–O(3)	1.420 (5)	C(7)–O(3)	1.354 (5)
C(7)–O(4)	1.186 (6)	C(7)–C(8)	1.501 (6)
C(8)–C(9)	1.389 (7)	C(9)–C(10)	1.397 (6)
C(10)–C(11)	1.395 (9)	C(11)–C(12)	1.385 (9)
C(12)–C(13)	1.407 (9)	C(8)–C(13)	1.382 (7)

Bond Angles (deg)
Involving the Ferrole Ligand Only

Fe(1)–Fe(2)–C(2)	53.5 (1)	Fe(1)–Fe(2)–C(6)	53.4 (1)
Fe(2)–Fe(1)–C(2)	49.1 (1)	Fe(2)–Fe(1)–C(3)	76.1 (1)
Fe(2)–Fe(1)–C(4)	74.7 (1)	Fe(2)–Fe(1)–C(6)	48.2 (1)
Fe(1)–C(2)–Fe(2)	77.4 (2)	Fe(1)–C(2)–C(3)	72.4 (3)
Fe(1)–C(3)–C(2)	68.5 (3)	Fe(1)–C(3)–C(4)	72.5 (3)
Fe(1)–C(4)–C(3)	68.8 (3)	Fe(1)–C(4)–C(6)	66.4 (2)
Fe(1)–C(6)–C(4)	74.9 (3)	Fe(1)–C(6)–Fe(2)	78.4 (1)
Fe(2)–C(2)–C(3)	116.9 (3)	C(2)–C(3)–C(4)	112.0 (4)
C(3)–C(4)–C(6)	111.5 (4)	Fe(2)–C(6)–C(4)	117.9 (3)
C(2)–Fe(1)–C(4)	67.1 (2)	C(3)–Fe(1)–C(4)	38.7 (2)
C(2)–Fe(1)–C(6)	73.4 (2)	C(3)–Fe(1)–C(6)	68.0 (2)
C(4)–Fe(1)–C(6)	38.7 (2)	C(2)–Fe(2)–C(6)	79.5 (2)

Involving the Carbonyl Ligands Only

Fe(1)–C(1)–O(1)	169.6 (5)	Fe(1)–C(21)–O(21)	177.8 (5)
Fe(1)–C(31)–O(31)	177.1 (5)	Fe(2)–C(1)–O(1)	123.0 (4)
Fe(2)–C(41)–O(41)	187.7 (5)	Fe(2)–C(51)–O(51)	175.9 (5)
Fe(2)–C(61)–O(61)	177.8 (5)	Fe(1)–C(1)–Fe(2)	67.5 (2)
C(1)–Fe(1)–Fe(2)	72.0 (2)	C(1)–Fe(2)–Fe(1)	40.6 (1)
C(1)–Fe(1)–C(21)	95.7 (2)	C(1)–Fe(1)–C(31)	97.3 (2)
C(1)–Fe(2)–C(41)	82.4 (2)	C(1)–Fe(2)–C(51)	88.7 (2)
C(1)–Fe(2)–C(61)	173.9 (2)	C(21)–Fe(1)–Fe(2)	128.9 (2)
C(21)–Fe(1)–C(31)	97.0 (2)	C(31)–Fe(1)–Fe(2)	133.1 (2)
C(41)–Fe(2)–C(51)	95.6 (2)	C(41)–Fe(2)–C(61)	98.2 (2)
C(51)–Fe(2)–C(61)	97.2 (2)	C(61)–Fe(2)–Fe(1)	134.7 (2)
C(51)–Fe(2)–Fe(1)	111.8 (2)	C(41)–Fe(2)–Fe(1)	112.1 (2)

Involving Both the Ferrole and the Carbonyl Ligands

C(1)–Fe(1)–C(2)	105.1 (2)	C(1)–Fe(1)–C(3)	143.8 (2)
C(1)–Fe(1)–C(4)	139.8 (2)	C(1)–Fe(1)–C(6)	101.2 (2)
C(21)–Fe(1)–C(2)	90.7 (2)	C(21)–Fe(1)–C(3)	91.3 (2)
C(21)–Fe(1)–C(4)	122.9 (2)	C(21)–Fe(1)–C(6)	159.3 (2)
C(31)–Fe(1)–C(2)	155.4 (2)	C(31)–Fe(1)–C(3)	117.0 (2)
C(31)–Fe(1)–C(4)	89.2 (2)	C(31)–Fe(1)–C(6)	92.7 (2)
C(1)–Fe(2)–C(2)	83.4 (2)	C(1)–Fe(2)–C(6)	80.9 (2)
C(41)–Fe(2)–C(2)	165.2 (2)	C(41)–Fe(2)–C(6)	94.2 (2)
C(51)–Fe(2)–C(2)	88.3 (2)	C(51)–Fe(2)–C(6)	164.7 (2)
C(61)–Fe(2)–C(2)	95.4 (2)	C(61)–Fe(2)–C(6)	93.0 (2)

Involving the Methoxy Group

C(4)–O(2)–C(5)	117.4 (4)	C(3)–C(4)–O(2)	126.9 (4)
C(6)–C(4)–O(2)	121.4 (4)	Fe(1)–C(4)–O(2)	129.1 (3)

Involving the Benzoyl Group

Fe(1)–C(6)–O(3)	123.2 (3)	Fe(2)–C(6)–O(3)	126.9 (3)
C(4)–C(6)–O(3)	114.7 (4)	C(6)–O(3)–C(7)	115.9 (3)
O(3)–C(7)–O(4)	123.1 (5)	O(3)–C(7)–C(8)	111.6 (4)
O(4)–C(7)–C(8)	125.3 (4)	C(7)–C(8)–C(9)	122.2 (4)
C(7)–C(8)–C(13)	116.4 (5)	C(9)–C(8)–C(13)	121.4 (5)
C(8)–C(9)–C(10)	119.3 (5)	C(8)–C(13)–C(12)	118.6 (6)
C(9)–C(10)–C(11)	120.4 (5)	C(10)–C(11)–C(12)	119.3 (5)
C(11)–C(12)–C(13)	121.1 (6)		

formation and has a semibridging CO ligand.

The Fe(1)–Fe(2) distance in 2 is 2.522 (1) Å, which is within the range of Fe–Fe bond lengths (2.49–2.53 Å) that have been reported for ferroles.[13b] The C–C bond lengths in the ferrole ring are nearly equivalent (C–C(av) = 1.41 Å), indicating a degree of π-electron delocalization in the ferrole ring as has been observed previously.[16,17] For comparison, the length of the C–C bonds in purely carbocyclic aromatic systems is 1.395 ± 0.003 Å.[18] A complete listing of bond lengths and angles is given in Table I.

The most interesting structural feature of 2 is the bonding of the semibridging CO in the molecule. The Fe(2)–C(1) distance of 2.596 (5) Å is comparatively long.[13b] This bond length in 5 is 2.484 Å,[5c] and in the parent ferracyclopentadiene, 6, the distance between the iron atom of the ring and the C of the semibridging CO is 2.508 (4) Å.[16] In addition, the Fe(1)–C(1)–O(1) angle of 169.6 (5)° is larger than any previously reported in a ferrole. These differences in bond lengths and angles may indicate that the structure of 2 is intermediate between the two forms, 3 and 4. Theoretical studies have suggested that oxygen substituents on the ferrole ring should stabilize the "sawhorse" configuration.[15]

The first step in the reaction of (1-methoxyallenyl)-lithium with Fe₃(CO)₁₂, as in the case of the alkynyl-lithiums, most likely involves attack by this nucleophile at a CO ligand on iron. As noted earlier, such a process has ample precedent in the literature.[11] The subsequent steps that possibly may lead to the formation of the ferrole 2 are outlined in Scheme II. The suggested steps are reasonable ones, the conversion of allenes to dinuclear π-allyliron complexes in which the allyl ligand is σ-bonded to one iron atom and π-bonded to the other is well-known.[19]

C-functional ferroles of type 2 might show interesting chemistry, and the anionic intermediate, 5, should react with electrophiles other than acid chlorides to give C-functional ferroles. Such extensions, however, are beyond the scope of our present interests.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Methylene chloride (CH₂Cl₂) was distilled from P₂O₅. Triiron dodecacarbonyl (Fe₃(CO)₁₂)[20] and 1-methoxyallene[12] were prepared according to literature procedures. All disulfides were obtained commercially and used as obtained except that they were degassed prior to their use by purging with a stream of nitrogen for 15 min. All other reagents were on hand and purified prior to their use. All yields are given with respect to Fe₃(CO)₁₂.

Infrared spectra were obtained on a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. ¹H NMR spectra were recorded on either a JEOL FX-90Q or a Bruker WH-250 NMR spectrometer operating at 90 or 270 MHz, respectively. ¹³C NMR were obtained with use of a Bruker WH-270 NMR spectrometer operating at 67.9 MHz. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Mass spectra were obtained with a Finnigan 3200 spec-

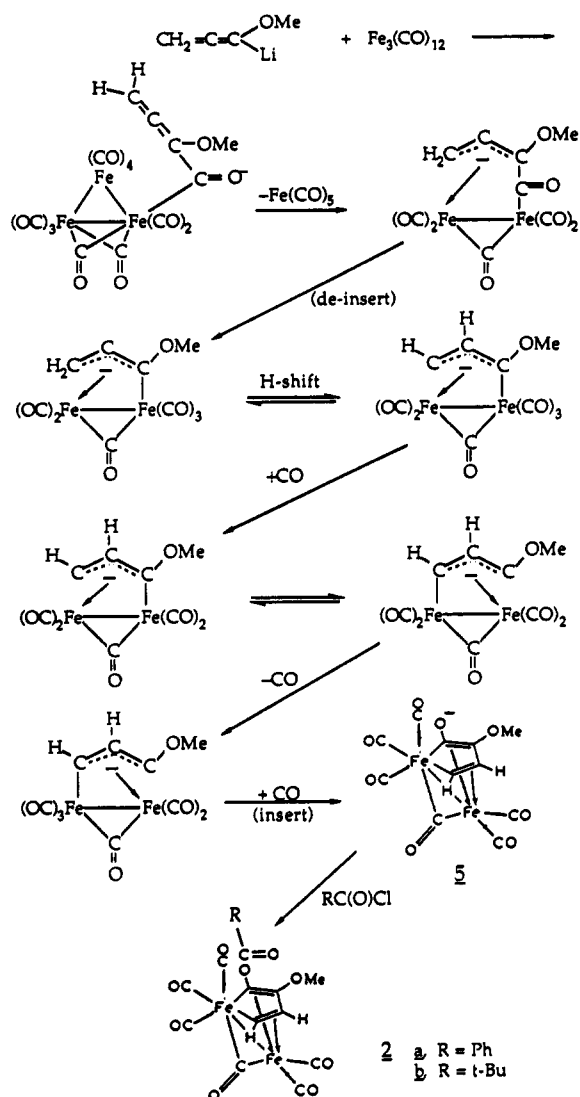(16) Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* 1976, *108*, 213.

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Scheme II

atom	x	y	z
Fe(1)	564.5 (5)	808.5 (7)	1665.0 (3)
Fe(2)	-1196.4 (5)	-727.3 (7)	1486.0 (4)
C(1)	616 (4)	-713 (6)	1046 (3)
O(1)	806 (4)	-1606 (5)	649 (2)
C(2)	-1100 (4)	1467 (5)	1386 (3)
C(3)	-533 (4)	2277 (5)	2037 (3)
C(4)	-26 (4)	1294 (5)	2650 (2)
O(2)	561 (3)	1702 (4)	3346.0 (18)
C(5)	959 (6)	3281 (7)	3456 (3)
C(6)	-140 (4)	-238 (5)	2428 (2)
O(3)	450 (3)	-1272 (3)	2984.0 (17)
C(7)	12 (4)	-1511 (6)	3571 (3)
O(4)	-847 (3)	-976 (5)	3606 (2)
C(8)	763 (4)	-2475 (6)	4168 (3)
C(9)	1734 (4)	-3122 (5)	4074 (3)
C(10)	2395 (5)	-4014 (6)	4651 (3)
C(11)	2099 (5)	-4219 (7)	5322 (3)
C(12)	1150 (7)	-3516 (12)	5414 (4)
C(13)	463 (6)	-2639 (10)	4833 (4)
C(21)	874 (4)	2266 (6)	1069 (3)
O(21)	1039 (4)	3201 (5)	702 (2)
C(31)	1941 (4)	608 (7)	2266 (3)
O(31)	2813 (3)	425 (7)	2666 (2)
C(41)	-913 (5)	-2743 (6)	1573 (3)
O(41)	-749 (4)	-3993 (5)	1637 (3)
C(51)	-2006 (4)′	-795 (6)	496 (3)
O(51)	-2533 (4)	-759 (5)	-104 (2)
C(61)	-2334 (4)	-685 (6)	1879 (3)
O(61)	-3065 (3)	-612 (6)	2146 (2)

trometer using electron impact ionization at 70 eV. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Structure of Ferrole 2a. A yellow crystal of **2a** obtained as described in the Experimental Section was selected and found suitable for X-ray diffraction studies. It was fixed to the tip of a glass fiber and mounted on an Enraf-Nonius CAD4F-11 diffractometer. Diffraction data were collected with use of Mo Kα radiation at -70 °C. Data collection, reduction, and refinement procedures are detailed elsewhere.[21] A semiempirical absorption correction (μ = 15.0 cm⁻¹ for Mo Kα radiation) was applied. A total of 4448 reflections (±h,+k,+l) was collected in the range 3° ≤ 2θ ≤ 55°. The 2931 having $F_o > 4\sigma(F_o)$ were used in the solution and refinement of the structure. Full-matrix least-squares refinement, ignoring H atoms and refining all other atoms anisotropically (262 variables), led to final weighted and unweighted agreement factors of 5.0% and 5.8%, respectively. Computations were performed with the program system SHELX-76. A final difference Fourier map showed no significant features.

Crystal Data. Complex **2a** crystallizes in the monoclinic space group P2₁/a with a = 12.444 (2), b = 8.837 (2), c = 18.429 (3) Å; β = 105.77 (1)°; V = 1950.3 Å³; Z = 4; and ρ(calc) = 1.641 g/cm³. Atomic coordinates, bond lengths, and angles are given in Tables I and II. An ORTEP representation of the molecular structure of the ferrole is shown in Figure 1.

Reaction between (1-Methoxyallenyl)lithium and Fe₃(C-O)₁₂. Benzoyl Chloride Quench. (1-Methoxyallenyl)lithium

(21) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

was prepared by the addition of 0.88 mL of a 2.66 M solution of n-BuLi (2.34 mmol) to a stirred solution of 0.164 g of methoxyallene (2.34 mmol) in 5 mL of THF that had been cooled to -78 °C in an acetone/dry ice bath. After 15 min, this solution was added to a solution of 1.0 g of Fe₃(CO)₁₂ (1.98 mmol) in 40 mL of THF that had been cooled to -78 °C. The transfer was done via cannula wrapped in paper towels that had been soaked in acetone and cooled by periodic pouring of liquid nitrogen onto the towels. The resulting reaction mixture was stirred at -78 °C for 2 h. No color change was observed. The cold bath was removed, and the reaction mixture was allowed to warm to room temperature slowly. The reaction mixture changed in color from green to dark red. After 2 h at room temperature, 0.363 g of benzoyl chloride (2.58 mmol) was added to the reaction mixture by syringe. The reaction mixture was stirred at room temperature for 16 h. The solvents were removed in vacuo. The residue was taken up in 70:30 pentane/CH₂Cl₂ (v/v) and subjected to silicic acid filtration chromatography. Elution with pentane gave a minor yellow-orange band; this was discarded. The column then was eluted with pentane/CH₂Cl₂ mixtures of increasing polarity. A mixture of 50:50 pentane/CH₂Cl₂ (v/v) eluted a major yellow band. This gave 0.277 g of a yellow crystalline solid that was recrystallized from pentane/CH₂Cl₂ (mp 137-138 °C) and was identified as ferrole **2a** (0.277 g, 0.58 mmol, 29%). No other products were eluted by more polar solvent mixtures. Anal. Calcd for C₁₈H₁₀Fe₂O₉: C, 44.86; H, 2.09. Found: C, 44.77; H, 2.17. ¹H NMR (90 MHz, CD₂Cl₂): δ 3.82 (s, 3 H, OCH₃), 6.04 (d, J_{HH} = 6.0 Hz, 1 H, C(3)H), 6.57 (d, J_{HH} = 6.0 Hz, 1 H, FeC(2)H), 7.20-8.20 (m, 6 H, phenyl H). ¹³C NMR (67.9 MHz, CDCl₃): δ_C 58.9 (q, J_{CH} = 146.7 Hz, OCH₃), 91.6 (d, J_{CH} = 170.4 Hz, C(3)), 128.5, 129.9, 133.4 (phenyl ring C), 140.6 (d, J_{CH} = 162.6 Hz, C(2)), 152.1 (s, C(4)), 164.1 (s, C(6)), 205.1, 206.7, 209.1, 211.1 (all s, carbonyl C). IR (THF, NaCl): 2079 (s), 2040 (vs), 2004 (vs), 1960 (m, br), 1739 (m), 1720 (s), 1489 (w), 1425 (w), 1360 (w), 1317 (vw), 1298 (vw), 1262 (m), 1221 (m), 1145 (vw), 1106 (m), 802 (vw), 746 (vw), 710 (w), 688 (vw), 631 (vw), 609 (m), 590 (w, br), 522 (vw) cm⁻¹. Mass spectrum, m/z (relative intensity): 454 (M⁺ - CO, 21), 426 (M⁺ - 2 CO, 45), 398 (M⁺ - 3 CO, 36), 370 (M⁺ - 4 CO, 56), 342 (M⁺ - 5 CO, 82), 314 (M⁺ - 6 CO, 100), 288 (C₁₀H₈Fe₂O₃, 39), 273 (C₉H₅Fe₂O₃, 29), 258 (C₁₂H₁₀FeO₃, 21), 229 (C₈H₅Fe₂O, 17), 214 (C₁₁H₁₀FeO, 19), 201 (C₇H₅Fe₂, 25), 105 (C₇H₅O, 21), 77 (C₆H₅, 23), 56 (Fe, 14).

Reaction between (1-Methoxyallenyl)lithium and Fe₃(C-O)₁₂. Pivaloyl Chloride Quench. (1-Methoxyallenyl)lithium was prepared as described above from 1.27 mL of a 2.37 M solution of *n*-BuLi (3.01 mmol) and 0.237 g of methoxyallene (3.38 mmol) in 10 mL of THF. This solution was added, by the above procedure, to a solution of 1.50 g of Fe₃(CO)₁₂ (2.98 mmol) in 50 mL of THF that had been cooled to −78 °C. The reaction mixture was stirred at −78 °C for 2 h and then was allowed to warm to room temperature slowly. During this time, it changed from green to dark red. After 36 h at room temperature, the solution was again cooled to −78 °C and 0.59 g of pivaloyl chloride (4.87 mmol) was added by syringe. The resulting mixture was stirred at −78 °C for 1 h and then at room temperature for 24 h. The solvents were removed in vacuo. The brown residue was taken up in 70:30 pentane/Et₂O (v/v) and subjected to silicic acid filtration chromatography. Elution with pentane gave a minor yellow-orange band, which was discarded. The column then was eluted with pentane/Et₂O mixtures of increasing polarity. A mixture of 80:20 pentane/Et₂O (v/v) eluted a major yellow band, which was concentrated and chromatographed on silica gel column (25 × 300 mm) with use of 95:5 pentane/Et₂O (v/v) as the eluent. This gave a yellow crystalline solid that was recrystallized from pentane (mp 97−98 °C) and identified as ferrole **2b** (0.277 g, 0.58 mmol, 29%). No other products were eluted by more polar solvent mixtures. Anal. Calcd for C₁₆H₁₄Fe₂O₉: C, 41.60; H, 3.06. Found: C, 41.67; H, 3.17. ¹H NMR (270 MHz, CDCl₃): δ 1.22 (s, 9 H, C(CH₃)₃), 3.77 (s, 3 H, OCH₃), 5.93 (d, J_{HH} = 5.9 Hz, 1 H, C(3)H), 6.41 (d, J_{HH} = 6.0 Hz, 1 H, FeC(2)H). ¹³C NMR (67.9 MHz, CDCl₃): δ_C 26.9 (q, J_{HH} = 127.1 Hz, SC(CH₃)₃), 39.1 (s, SC(CH₃)₃), 58.8 (q, J_{CH} = 146.4 Hz, OCH₃), 91.7 (d, J_{CH} = 170.6 Hz, C(3)), 139.8 (d, J_{CH} = 160.0 Hz, C(2)), 151.8 (s, COMe), 176.5 (s, COC-(O)C(CH₃)₃), 205.3, 206.6, 209.0, 211.2, 212.7 (all s, carbonyl C). IR (CCl₄, NaCl): 2960 (w), 2928 (m), 2858 (w), 2079 (s), 2041 (vs), 2006 (vs), 1998 (s), 1975 (m), 1960 (m), 1748 (m), 1484 (m), 1460 (w), 1420 (w), 1291 (w), 1263 (w), 1229 (w), 1100 (m), 1066 (w), 1028 (vw), 896 (vw), 677 (vw), 654 (vw), 630 (vw), 620 (w), 605 (w), 598 (w), 580 (w) cm⁻¹.

Reaction between (*tert*-Butylethynyl)lithium and Fe₃-(CO)₁₂. *tert*-Butanesulfenyl Chloride Quench. (*tert*-Butylethynyl)lithium was prepared by the dropwise addition of 1.12 mL of a 2.66 M solution of *n*-BuLi in hexane (2.98 mmol) to a solution of 0.25 g of *tert*-butylacetylene (3.00 mmol) in 5 mL of THF that had previously been cooled to −78 °C. The resulting solution was stirred at −78 °C for 15 min and then for an additional 1 h at room temperature. The resulting lithium *tert*-butylacetylide solution was added dropwise via cannula to a stirred solution of 1.50 g of Fe₃(CO)₁₂ (2.98 mmol) in 40 mL of THF at room temperature. The solution changed color from green (Fe₃(CO)₁₂) to dark red. At the same time, *tert*-butanesulfenyl chloride was prepared by the reaction of 0.71 g (3.98 mmol) of Me₃CSSCMe₃ and 0.54 g (3.98 mmol) of SO₂Cl₂ in 5 mL of CH₂Cl₂ at −78 °C.[22] The Me₃CSCl solution was added via cannula to the dark red reaction mixture that had been cooled to −78 °C. The resulting reaction mixture then was stirred at −78 °C for 15 min and at room temperature for 1 h. The solvent was removed in vacuo and the residue taken up in 50:50 pentane/CH₂Cl₂ (v/v) and subjected to filtration chromatography (silicic acid). Elution with pentane gave one major band that yielded a red-orange, oily solid, identified as the known compound (μ-σ,π-(CH₃)₃CC≡C)(μ-(CH₃)₃CS)Fe₂(CO)₆ (0.63 g, 1.39 mmol, 40%) by comparison of its ¹H NMR and IR spectra with those of an authentic sample of this compound.[7]

Reaction between (*tert*-Butylethynyl)lithium and Fe₃-(CO)₁₂. Ethanesulfenyl Chloride Quench. (*tert*-Butylethynyl)lithium was prepared by addition of 1.12 mL of a 2.66 M solution of *n*-BuLi in hexane (2.98 mmol) and 3.00 mmol of *tert*-butylacetylene in 5 mL of THF, as described above, and added dropwise to a stirred solution of 1.50 g (2.98 mmol) of Fe₃(CO)₁₂ in 40 mL of THF at room temperature. Ethanesulfenyl chloride, prepared by reaction of 0.24 g (1.95 mmol) of EtSSEt and 0.27 g (1.99 mmol) of SO₂Cl₂, was added to the dark red reaction mixture at −78 °C. The resulting reaction mixture then was stirred at −78 °C for 30 min and then at room temperature overnight. Workup as above yielded a red-orange residue. This was taken up in pentane and chromatographed on a silica gel column (300 × 25 mm). Pentane eluted a major red band that yielded a red oil identified as the known compound (μ-σ,π-(CH₃)₃CC≡C)(μ-EtS)Fe₂(CO)₆ (0.50 g, 1.20 mmol, 40%) by comparison of its ¹H NMR, IR, and mass spectral data with those of an authentic sample of this compound.[7]

Reaction between (Phenylethynyl)lithium and Fe₃(CO)₁₂. *tert*-Butanesulfenyl Chloride Quench. (Phenylethynyl)lithium was prepared by the dropwise addition of 1.13 mL of a 2.66 M solution of *n*-BuLi in hexanes (3.00 mmol) to a solution of 0.31 g (3.00 mmol) of phenylacetylene in 10 mL of THF cooled to −78 °C. The resulting solution was stirred at −78 °C for 15 min and then 1 h at room temperature. The C₆H₅C≡CLi solution was added dropwise to a stirred solution of 1.50 g (2.98 mmol) of Fe₃(CO)₁₂ in 50 mL of THF at room temperature, causing a color change from green to dark red. *tert*-Butanesulfenyl chloride, prepared by the reaction of 0.35 g (1.96 mmol) of Me₃CSSCMe₃ and 0.27 g (1.96 mmol) of SO₂Cl₂ in 5 mL of CH₂Cl₂ at −78 °C, was added to the dark red reaction mixture at −78 °C. The resulting reaction mixture then was stirred at −78 °C for 15 min and at room temperature for 1 h. The solvents were removed in vacuo, and the residue was taken up in 80:20 pentane/CH₂Cl₂ (v/v) and subjected to filtration chromatography (silicic acid). Elution with pentane gave one major band that yielded a red-orange oily solid. This was identified as the known compound (μ-σ,π-C₆H₅C≡C)(μ-(CH₃)₃CS)Fe₂(CO)₆ (0.50 g, 1.07 mmol, 36%) by comparison of its ¹H NMR, ¹³C NMR, and mass spectral data with those of an authentic sample of this compound.[7]

Registry No. 2a, 135665-33-7; 2b, 135665-32-6; Fe₃(CO)₁₂, 17685-52-8; (μ-σ,π-(CH₃)₃CC≡C)(μ-(CH₃)₃CS)Fe₂(CO)₆, 99164-53-1; (μ-σ,π-(CH₃)₃CC≡C)(μ-EtS)Fe₂(CO)₆, 119219-42-0; (μ-σ,π-C₆H₅C≡C)(μ-(CH₃)₃CS)Fe₂(CO)₆, 119323-21-6; (1-methoxyallenyl)lithium, 135646-43-4; benzoyl chloride, 98-88-4; pivaloyl chloride, 37892-71-0; (*tert*-butylethynyl)lithium, 37892-71-0; *tert*-butanesulfenyl chloride, 52322-55-1; ethanesulfenyl chloride, 1496-75-9; (phenylethynyl)lithium, 4440-01-1.

Supplementary Material Available: Tables of final positional and thermal parameters (Table S1) and torsion and conformation angles for **2a** (Table S2) and a Pluto diagram of **2a** down the Fe–Fe bond showing the CO ligand conformations (6 pages); listings of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

(22) Still, I. W.; Kutney, G. W.; McLean, D. *J. Org. Chem.* **1982**, *47*, 560.