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Materials. Dichloromethane (Fisher) was washed with fuming sulfuric acid, water, and aqueous $NaHCO_3$ and then distilled twice from CaH_2 under nitrogen. Benzene (Fisher) was refluxed over and distilled from CaH_2 under nitrogen and stored over sodium/potassium alloy. Triflic acid (3M, Chemistry Division) was distilled under vacuum. Methylmagnesium bromide, 3.0 M in Et_2O (Aldrich) was used as received. Octaphenylcyclotetrasilane was prepared according to a literature procedure.[22]

Synthesis of 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. In a typical experiment 1,2,3,4-tetraphenyl-1,2,3,4-tetrakis(trifluoromethylsulfonoxy)cyclotetrasilane was first prepared by adding triflic acid (43.7 μL, 0.494 mmol) dropwise with a microsyringe to a stirred suspension of $(Ph_2Si)_4$ (~90 mg, 0.123 mmol) in CH_2Cl_2 (2 mL). The reaction mixture became homogeneous. After ^{19}F NMR demonstrated that the reaction was complete (~6 h), CH_2Cl_2 was removed by trap-to-trap distillation. The crude intermediate was dissolved in benzene (2 mL), and a 3.0 M solution of MeMgBr in Et_2O (0.165 mL, 0.494 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and was then filtered through a 0.2-μm filter. The solvent was removed by trap-to-trap distillation to yield 0.053 g (90%) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane.

Acknowledgment. This work has been supported by the Office of Naval Research. K.M. acknowledges support by the National Science Foundation via a Presidential Young Investigator Award, as well as from Eastman Kodak, Hoechst Celanese, PPG Industries, and Xerox Corp. We also gratefully thank Dr. Coleen Pugh for helpful discussions regarding this paper.

OM920024H

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[22] Jarvie, A. W. P.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* 1961, *83*, 1921.

Reactions of 2-Furyl, 2-Thienyl, and *N*-Methyl-2-pyrrolyl Mercurials with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ Complexes. Synthesis of $Fe_2(CO)_6$ Complexes with Bridging $\eta^1{:}\eta^2$-Furyl and Thienyl Ligands

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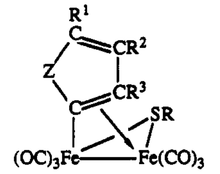
Received May 22, 1992

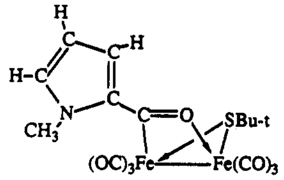
Reactions of furyl- and methyl-substituted furyl-, thienyl-, and methyl-substituted thienyl mercurials with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ gave products of type A



A

Z = O or S

in which the organic ligands are σ-bonded to iron via an α-carbon atom and π-bonded to the other iron atom via a C=C bond. On the other hand, 1-methyl-2-pyrrolyl mercurials reacted with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ to give B.



B

The compound $(\mu\text{-}\sigma,\pi\text{-}\overline{C{=}CHCH{=}CHO})(\mu\text{-}PhS)Fe_2(CO)_6$ (**10c**) crystallizes in the monoclinic space $P2_1/c$ with $a = 7.805$ (1) Å, $b = 17.091$ (2) Å, $c = 13.344$ (2) Å, $\beta = 96.90$ (1)°, $V = 1767.1$ Å^3, and $Z = 4$. Refinement by full-matrix, least-squares techniques has resulted in residuals of $R = 0.027$ and $R_w = 0.036$, based on 248 parameters refined and 2403 unique observations. The furyl group in the compound bridges the two iron centers, being σ-bound to one metal while π-bonded to the other via the adjacent olefin linkage. The oxygen atom and the other olefin linkage in this group point away from the metals and remain uncomplexed.

Introduction

We have reported recently concerning reactions of vinylic mercuric halides with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes.[1] Two types of products were obtained in such reactions, $(\mu\text{-}\eta^1{:}\eta^2\text{-vinyl})(\mu$-alkanethiolato)hexacarbonyldiiron(Fe–Fe) (1) and (μ-α,β-unsaturated acyl)(μ-alkanethiolato)hexacarbonyldiiron(Fe–Fe) (2) complexes. Scheme I shows their probable method of formation. Which type of product was formed depended on the nature of the substituents on the vinylic carbon atoms. With $CH_2{=}CHHgBr$, $ClCH{=}CHHgCl$, and $PhCH{=}$

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

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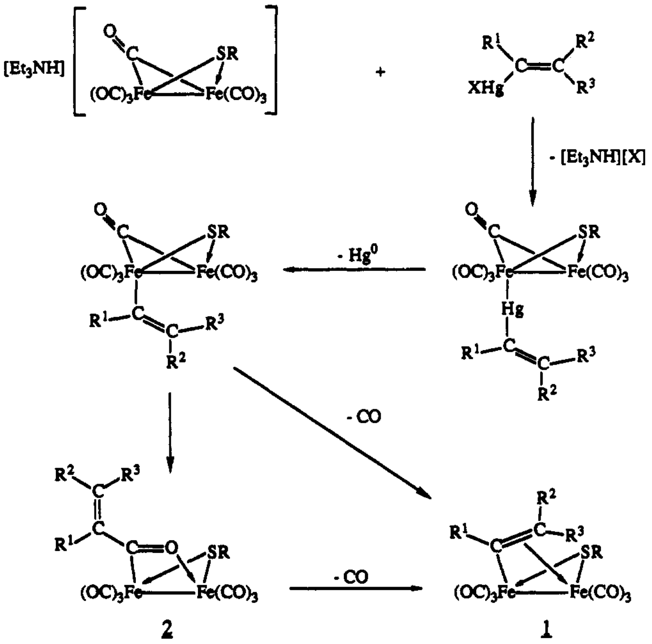
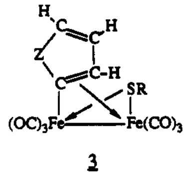
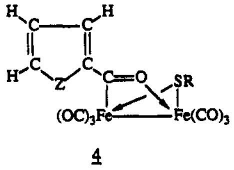
Scheme I. Proposed Mechanism for the Formation of the Acyl- and Vinyl-Bridged Diiron Hexacarbonyl Complexes

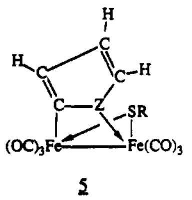


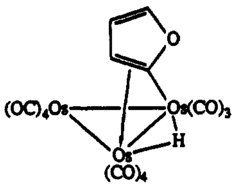
CHHgCl type 1 complexes were obtained; with $(CH_3)_2C{=}CHHgBr$ the type 2 complex was obtained. A mixture of both types was obtained with $CH_2{=}C(CH_3)HgBr$, $CH_3CH{=}CHHgBr$, and $CH_3CH{=}C(CH_3)HgBr$.

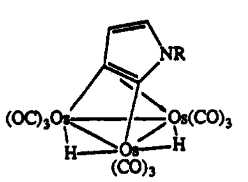
Extension of this chemistry to reactions of α-furyl, α-thienyl, and α-pyrollyl mercurials was of interest. Three types of products might be expected to form: 3 (analogous to 1), in which the organic ligand is a μ-η^1:η^2 three-electron donor, 4 (analogous to 2), in which the initially formed μ-acyl complex has not decarbonylated, and 5, in which the organic ligand also is bridging, but the oxygen, sulfur, or nitrogen lone electron pairs are donated to the iron atom rather than the π electrons of the C=C bond. An osmium carbonyl cluster complex, 6, that contains a μ-η^1:η^2-bonded furyl ligand has been reported,[2] and the pyrollyl complex 7 has a similar structure.[3] Thiophene can be bonded to an iron atom via sulfur, 8,[4] and via carbon, 9,[5] but no complexes of type 5 are known of α-furyl or α-thienyl ligands. In order to ascertain which of these possible types of complexes is formed, we have investigated reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes with α-furyl, α-thienyl, and N-methyl-α-pyrrolyl mercurials.


3
(Z = O, S, NR')


4
(Z = O,S, NR')


5
(Z = O,S, NR')


6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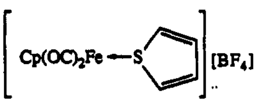
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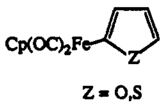
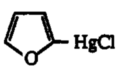
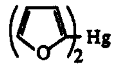
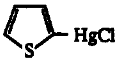
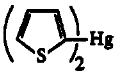


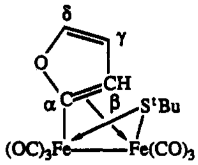
9

Table I. Products of the Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ with Furyl and Thienyl Mercurials

R in $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$	mercurial	% yield $(\mu\text{-}RS)_2Fe_2(CO)_6$ [a]	% yield μ-η^1,η^2 product [b]
t-Bu		54	42
Et		44	51
Ph		69	22
t-Bu		9	75
Et		29	67
Ph		50	38
2,4,6-$Me_3C_6H_2$		18	39
Et		76	24
Ph		82	2
Et		47	36
Ph		73	0

[a] Based on S. [b] Based on Fe.

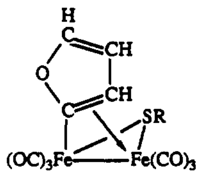
Table II. ^1H NMR Spectral Data for 10a

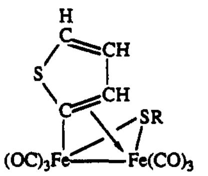


δ (ppm)	assignment
1.38	s, 9 H, $C(CH_3)_3$
5.29	d, J = 3.07 Hz, 1 H, C=*C*HCH=CHO
6.25	t, J = 2.60 Hz, 1 H, C=CHC*H*=CHO
7.86	d, J = 2.00 Hz, 1 H, C=CHCHC*H*O

Results and Discussion

The reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes[6] in THF solution with 2-(chloromercurio)furan and -thiophene and with bis(2-furyl)- and bis(2-thienyl)mercury proceeded readily at room temperature, as indicated by gas evolution and formation of a sand gray precipitate, by the red to red-brown color change and by monitoring by thin-layer chromatography. In some reactions small globules of mercury formed in the gray precipitate on standing. Two products usually were formed: the $(\mu\text{-}RS)_2Fe_2(CO)_6$ (mixture of a,e and e,e isomers) complexes, which are the oft-encountered byproducts of reactions of the $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ complexes, and products of types 10 and 11. The yields of the latter were


10 a, R = t-Bu
b, R = Et
c, R = Ph
d, R = 2,4,6-$Me_3C_6H_2$


11 a, R = Et
b, R = Ph

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(2) Himmelreich, D.; Müller, G. *J. Organomet. Chem.* **1985**, *297*, 341.

(3) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2563.

(4) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55.

(5) Nesmeyanov, A. N.; Kolobova, N. E.; Goncharenko, L. V.; Anisimov, K. N. *Bull. Acad. Sci. USSR* **1976**, *25*, 142.

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

Table III. Relevant ^{13}C NMR Spectral Data for $(\mu\text{-}\sigma,\pi\text{-}\overline{\text{C=CHCH=CHO}})(\mu\text{-}t\text{-BuS})Fe_2(CO)_6$ (10a)

δ (ppm)	assignment
93.21	d, J = 178.1 Hz, C=C_βHCH=CHO
111.70	d, J = 177.5 Hz, C=CHC_γH=CHO
154.98	d, J = 200.7 Hz, C=CHCH=C_δHO
180.43	s, C_α=CHCH=CHO
210.33	s, terminal *C*O's

higher when the difuryl and dithienyl mercurials were used, as the yield data in Table I show. The two products could be separated without difficulty by medium-pressure column chromatography.

^1H and ^{13}C NMR spectroscopy was useful in the initial identification of the complexes of type 10. Table II summarizes the ^1H NMR spectral data for **10a**. The protons of the furyl ligand were assigned on the basis of the chemical shifts and splitting patterns of the resonances. The triplet at 6.25 ppm was readily assigned to the proton on C_γ, which would be coupled to the protons on the adjacent carbon atoms, C_β and C_δ. In uncomplexed furan the protons on the carbon atoms adjacent to oxygen give rise to a resonance more downfield than those on the more distant carbon atoms.[7] Thus, the doublet at 7.86 ppm was attributed to the proton nearest to oxygen, on C_δ. The remaining doublet, at 5.29 ppm, then was assigned to the proton on the carbon atom which is involved in π-coordination to iron, C_β. This shift is somewhat more upfield than the corresponding peak for uncomplexed furan, but the π-coordination of the olefin bond to iron causes shielding of this proton and leads to an upfield shift. This shielding effect also was observed in the case of the μ-η^1:η^2-vinyl complexes.[1]

The relevant ^{13}C NMR spectral data for complex **10a** are summarized in Table III. Comparison of the chemical shifts to those for free furan again was useful in assigning the spectrum. For furan the equivalent carbon atoms farthest from oxygen, C_β, give rise to a resonance at 110.4 ppm, while the carbon atoms adjacent to oxygen, C_α, give rise to a resonance at 143.6 ppm.[8] It was determined from this information that the carbon atoms in **10a** that are adjacent to oxygen give rise to the downfield resonances at 154.98 and 180.43 ppm. Since C_α possesses no protons, it was assigned to the singlet at 180.43 ppm. The σ-coordination of this carbon atom to iron would account for the downfield shift of this peak. This left the doublet at 154.98 ppm, which was assigned to C_δ. The doublet at 93.21 ppm was assigned to C_β, as shielding would account for the upfield shift of this resonance, as also was observed in the ^1H NMR spectrum. Finally, C_γ was assigned to the doublet at 111.70 ppm. This is in close agreement with the corresponding resonance for furan at 110.4 ppm.

The J_{CH} coupling constants also provided some clues which were useful in assigning the peaks. For furan J_{CH} for C_α is 201.8 Hz,[9] while C_δ of **10a** has a coupling constant of 200.7 Hz. The J_{CH} coupling constant for C_β of furan is 174.7 Hz. The corresponding carbon atoms of **10a**, C_β and C_γ, have coupling constants of 178.1 and 177.5 Hz, again within close agreement with the value for furan.

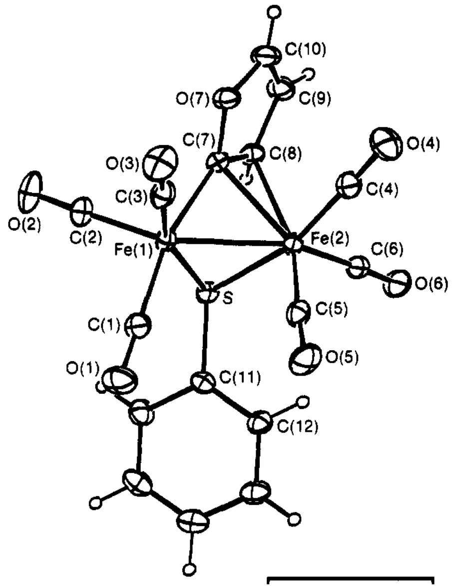

Figure 1. ORTEP plot of $(\mu\text{-}\sigma,\pi\text{-}\overline{\text{C=CHCH=CHO}})(\mu\text{-PhS})Fe_2(CO)_6$ (**10c**).

Table IV. Intramolecular Bond Distances (Å) for $(\mu\text{-}\sigma,\pi\text{-}\overline{\text{C=CHCH=CHO}})(\mu\text{-PhS})Fe_2(CO)_6$ (10c)

Fe(1)–Fe(2)	2.5197 (5)	O(5)–C(5)	1.141 (3)
Fe(1)–S	2.2762 (7)	O(6)–C(6)	1.137 (3)
Fe(1)–C(1)	1.815 (3)	O(7)–C(7)	1.396 (3)
Fe(1)–C(2)	1.797 (3)	O(7)–C(10)	1.373 (3)
Fe(1)–C(3)	1.785 (3)	C(7)–C(8)	1.395 (4)
Fe(1)–C(7)	1.954 (2)	C(8)–C(9)	1.437 (4)
Fe(2)–S	2.2746 (7)	C(8)–H(8)	0.91 (2)
Fe(2)–C(4)	1.784 (3)	C(9)–C(10)	1.315 (4)
Fe(2)–C(5)	1.786 (3)	C(9)–H(9)	0.94 (3)
Fe(2)–C(6)	1.799 (3)	C(10)–H(10)	0.92 (3)
Fe(2)–C(7)	2.147 (2)	C(10)–C(12)	1.385 (3)
Fe(2)–C(8)	2.334 (3)	C(11)–C(16)	1.387 (4)
S–C(11)	1.788 (2)	C(12)–C(13)	1.380 (3)
O(1)–C(1)	1.128 (3)	C(13)–C(14)	1.373 (4)
O(2)–C(2)	1.128 (3)	C(14)–C(15)	1.370 (4)
O(3)–C(3)	1.136 (3)	C(15)–C(16)	1.392 (4)
O(4)–C(4)	1.139 (3)		

Another interesting feature of the ^{13}C NMR spectrum for **10a** is the very intense singlet at 210.33 ppm, which corresponds to the carbon atoms of the terminal carbonyl groups on iron. A singlet had been observed in the ^{13}C NMR spectra of the μ-η^1:η^2-vinyl complexes which resolved into two resonances at −60 °C. It was concluded that the bridging vinyl ligand was fluxional between the two metals centers and that at low temperature this process could be slowed down. If the carbonyl groups on a given iron center are equivalent, then at low temperature the two peaks account for the slowing down of this fluxional process. Conversely, the singlet observed at room temperature indicates that all of the carbonyl groups are equivalent. It was possible that the same sort of fluxional process may be occurring in the case of **10a**. A low-temperature NMR experiment was carried out with this complex, but even lowering the temperatures to −80 °C failed to produce any change in the ^{13}C NMR spectrum. We conclude that the furyl ligand of **10a** may be fluxional, but, if so, the process is so facile that even at low temperature it is not slowed down with respect to the NMR time scale.

While the ^1H and ^{13}C NMR spectral data were consistent with the presence of products of type **3** rather than **5**, confirmation was given by an X-ray diffraction study of **10c**, an ORTEP plot of which is shown in Figure 1. Relevant bond lengths and angles are given in Tables IV and V, respectively. As is shown in Figure 1, the furyl ligand is σ-bonded to Fe(1) through C(1) (or Cα) and is π-bound to Fe(2) through the olefin bond between C(7) and C(8). Atoms C(9) and C(10) are the two uncoordinated olefin atoms of the furyl ring. The asymmetrical bonding

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[7] *Spectrometric Identification of Organic Compounds*; Silverstein, R. M., Bassler, G. C., Merrill, R. C., Eds.; Wiley: New York, 1981; p 232.

[8] *Carbon-13 NMR Spectroscopy*; Kalinowski, H.-O., Berger, S., Braun, S.; Wiley: New York, 1988; p 384.

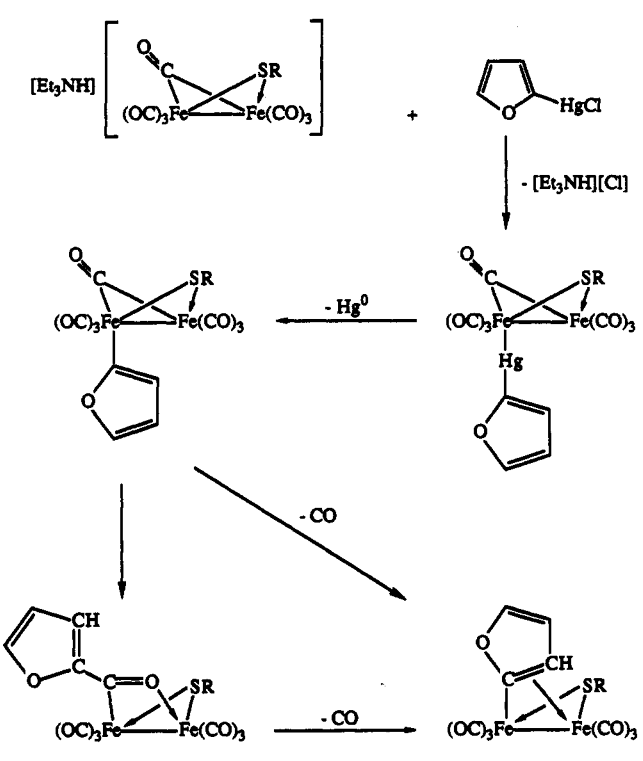
[9] References 8, p 506.

Table V. Intramolecular Bond Angles (deg) for (μ-σ,π-$\overline{\text{C=CHCH=CHO}}$)(μ-PhS)$Fe_2(CO)_6$ (10c) Involving the Non-Hydrogen Atoms[a]

Fe(2)–Fe(1)–S	56.35 (2)	Fe(1)–S–Fe(2)	67.24 (2)
Fe(2)–Fe(1)–C(1)	110.22 (9)	Fe(1)–S–C(11)	111.71 (8)
Fe(2)–Fe(1)–C(2)	144.30 (9)	Fe(2)–S–C(11)	114.43 (9)
Fe(2)–Fe(1)–C(3)	103.96 (8)	C(7)–O(7)–C(10)	107.7 (2)
Fe(2)–Fe(1)–C(7)	55.64 (7)	Fe(1)–C(1)–O(1)	178.7 (2)
S–Fe(1)–C(1)	92.67 (8)	Fe(1)–C(2)–O(2)	177.8 (3)
S–Fe(1)–C(2)	102.53 (9)	Fe(1)–C(3)–O(3)	178.7 (3)
S–Fe(1)–C(3)	159.88 (8)	Fe(2)–C(4)–O(4)	177.9 (3)
S–Fe(1)–C(7)	82.28 (7)	Fe(2)–C(5)–O(5)	177.0 (2)
C(1)–Fe(1)–C(2)	98.2 (1)	Fe(2)–C(6)–O(6)	177.1 (2)
C(1)–Fe(1)–C(3)	90.8 (1)	Fe(1)–C(7)–Fe(2)	75.66 (8)
C(1)–Fe(1)–C(7)	165.3 (1)	Fe(1)–C(7)–O(7)	119.6 (2)
C(2)–Fe(1)–C(3)	96.6 (1)	Fe(1)–C(7)–C(8)	133.9 (2)
C(2)–Fe(1)–C(7)	96.3 (1)	Fe(2)–C(7)–O(7)	120.3 (2)
C(3)–Fe(1)–C(7)	89.5 (1)	Fe(2)–C(7)–C(8)	79.3 (1)
Fe(1)–Fe(2)–S	56.41 (2)	O(7)–C(7)–C(8)	106.5 (2)
Fe(1)–Fe(2)–C(4)	112.25 (9)	Fe(2)–C(8)–C(7)	64.7 (1)
Fe(1)–Fe(2)–C(5)	82.26 (8)	Fe(2)–C(8)–C(9)	123.3 (2)
Fe(1)–Fe(2)–C(6)	152.69 (9)	Fe(2)–C(8)–H(8)	98 (2)
Fe(1)–Fe(2)–C(7)	48.69 (7)	C(7)–C(8)–C(9)	107.5 (2)
Fe(1)–Fe(2)–C(8)	78.94 (7)	C(7)–C(8)–H(8)	128 (2)
S–Fe(2)–C(4)	165.67 (9)	C(9)–C(8)–H(8)	122 (2)
S–Fe(2)–C(5)	95.03 (8)	C(8)–C(9)–C(10)	106.7 (3)
S–Fe(2)–C(6)	96.29 (9)	C(8)–C(9)–H(9)	124 (2)
S–Fe(2)–C(7)	78.31 (7)	C(10)–C(9)–H(9)	129 (2)
S–Fe(2)–C(8)	78.01 (7)	O(7)–C(10)–C(9)	111.6 (2)
C(4)–Fe(2)–C(5)	91.7 (1)	O(7)–C(10)–H(10)	112 (2)
C(4)–Fe(2)–C(6)	94.6 (1)	C(9)–C(10)–H(10)	137 (2)
C(4)–Fe(2)–C(7)	87.5 (1)	S–C(11)–C(12)	122.2 (2)
C(4)–Fe(2)–C(8)	91.6 (1)	S–C(11)–C(16)	118.0 (2)
C(5)–Fe(2)C(6)	102.7 (1)	C(12)–C(11)–C(16)	119.6 (2)
C(5)–Fe(2)–C(7)	125.3 (1)	C(11)–C(12)–C(13)	120.5 (3)
C(5)–Fe(2)–C(8)	160.7 (1)	C(12)–C(13)–C(14)	120.0 (3)
C(6)–Fe(2)–C(7)	131.9 (1)	C(13)–C(14)–C(15)	120.0 (3)
C(6)–Fe(2)–C(8)	96.0 (1)	C(14)–C(15)–C(16)	120.8 (3)
C(7)–Fe(2)–C(8)	35.98 (9)	C(11)–C(16)–C(15)	119.0 (3)

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

Scheme II. Proposed Mechanism for the Formation of (μ-σ,π-$\overline{\text{C=CHCH=CHO}}$)(μ-RS)$Fe_2(CO)_6$ (10a)



mode described results in a shorter Fe(1)–C(7) distance (1.954 (2) Å) compared to Fe(2)–C(7) (2.147 (2) Å). Whereas the former separation is typical of an Fe–alkyl bond,[10] the latter is consistent with a π interaction, although it is at the long end of the range that appears typical of such interactions (2.02–2.13 Å).[11] The olefin moiety itself is asymmetrically bonded to Fe(2) such that the Fe(2)–C(8) separation of 2.334 (3) Å is extremely long, and is much longer than the Fe(2)–C(7) distance. It appears that this asymmetry results, in part, from the short nonbonded contact between H(8) and S (2.59 (2) Å). This interaction prevents a closer approach of this end of the olefin moiety to Fe(2) and gives rise to a slight bending back of this unit away from the sulfur atom, as shown by a comparison of the Fe(1)–C(7)–C(8) and Fe(1)–C(7)–O(7) angles of 133.9 (2) and 119.6 (2)°, respectively.

Within the furyl ligand the geometry displays the consequences of the π interaction with Fe(2). This is most clearly seen in the substantial lengthening of the coordinated C(7)–C(8) bond, to 1.395 (4) Å, compared to the uncomplexed C(9)–C(10) bond (1.315 (4) Å), which remains typical of a C=C double bond.[12] Other parameters within the ring are as expected; therefore the C(8)–C(9) separation is consistent with a single bond between sp^2-hybridized carbons and the C(7)–O(7) and C(10)–O(7) distances are also normal.[12] The slightly longer C–O distance involving C(7) (1.396 (3) vs 1.373 (3) Å) is consistent with the slight increase in covalent radius of C(7), resulting from its rehybridization toward sp^3 upon complexation to Fe(2).

As noted earlier, compound **10a** is apparently fluxional, since even at −80 °C only one carbonyl resonance is observed. The structure of the related compound **10c** shows that equilibration of the two $Fe(CO)_3$ moieties could readily occur via a slight twisting of the furyl group with respect to the Fe–Fe bond. Such a twisting would interconvert structures in which C(7) is α-bound to either Fe(1) or Fe(2) and would require movement of C(8) by only a few tenths of an angstrom, as can be seen by a comparison of the nonbonded Fe(1)–C(8) contact of 3.089 (3) Å compared to the bonded Fe(2)–C(8) distance of 2.334 (3) Å. The movement required for C(7) would be even less.

In spite of the asymmetric binding of the furyl group, the bridging thiolato group is symmetrically bound (Fe(1)–S = 2.2762 (7) Å, Fe(2)–S = 2.2746 (7) Å), and all parameters involving this group are normal. Although two isomers of **10c** are possible, having the phenyl substituent on S either axial or equatorial, only the one having an equatorial arrangement is observed owing presumably to unfavorable nonbonded interactions involving this group in the alternate structure. The carbonyls are also normal, although the two $Fe(CO)_3$ units are slightly staggered to each other by ca. 18°. The Fe(1)–Fe(2) separation of 2.5197 (5) Å is consistent with a single bond connecting the metals.

Examination of the NMR spectra of the thienyl-bridged complex, **10d**, provided sufficient evidence to conclude that the thienyl ligand bridges the two iron centers in the same manner as does the furyl ligand. The same trends in upfield shifts for the proton on C_β in the ^1H NMR spectrum and for C_β in the ^{13}C NMR spectrum were observed as for the furyl-bridged complexes. Also the J_{CH} coupling con-

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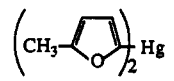
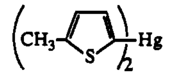
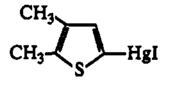
(10) Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4, Section 31.2.

(11) Deeming, A. J. In *Comprehensive Organometallics Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4, Section 31.3.

(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, 1987, 51–519.

Table VI. Products of the Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with Methyl-Substituted Furyl and Thienyl Mercurials

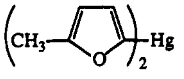
mercurial	% yield	
	$(\mu\text{-}RS)_2Fe_2(CO)_6$[a]	$\mu\text{-}\eta^1,\eta^2$ product[b]
	38	33
	22	37
	32	7

[a] Based on S. [b] Based on Fe.

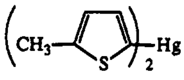
stants agreed well with those for free thiophene.

A proposed mechanism for the formation of **10** is shown in Scheme II and is of the same type as that outlined in Scheme I. The first step involves attack of the $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ anion as an iron nucleophile at the mercury atom of 2-(chloromercurio)furan. This would lead to a neutral intermediate which has an Fe–Hg bond. Then extrusion of Hg^0 would give an intermediate in which the furyl ligand is σ-bonded directly to iron. At this point the reaction may proceed in two ways. In the first, migration of the furyl ligand to one of the CO ligands on iron gives the acyl-bridged complex **12**. Then decarbonylation leads to the final product, **10**. An alternative pathway involves loss of carbon monoxide and coordination of the olefin bond between C_α and C_β to the other iron atom to lead directly to **10**. A similar mechanism probably is involved for the reaction with bis(2-furanyl)mercury or bis(2-thienyl)mercury.

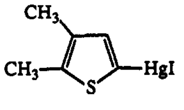
As noted in the Introduction, methyl substitution on the vinylic carbon atoms of the vinylmercuric halide serves to stabilize the α,β-unsaturated μ-acyl complex initially formed in the reaction with $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$. Accordingly, we examined the effect of methyl substitution in furyl- and thienyl mercurials. In the three examples investigated, the reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}PhS)Fe_2(CO)_6]$ with mercurials **13–15**, only $(\mu\text{-}PhS)_2Fe_2(CO)_6$ and the respective complexes of types **16** and **17** were isolated (Table VI).



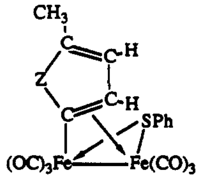
13



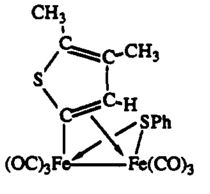
14



15

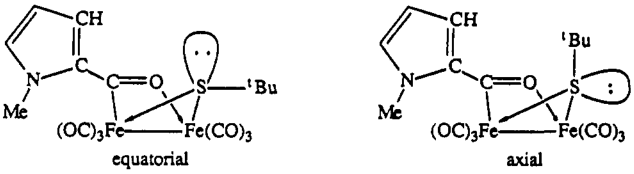


16: a, X = O
b, X = S



17

The reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 2-(chloromercurio)-1-methylpyrrole and bis(1-methyl-2-pyrrolyl)mercury gave the μ-acyl complex **18** in yields of 16% and 35%, respectively. In both reactions, $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$ was the major product.

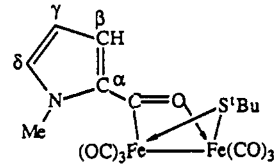


equatorial

axial

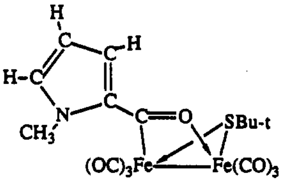
Figure 2. Isomers of $(\mu\text{-}C(O)\overline{C{=}CHCH{=}CHN}Me)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**18**).

Table VII. Relevant ^{13}C NMR Spectral Data for 18



δ (ppm)	assignment
109.73	d, J = 173.9 Hz, $C(O)C{=}CHC_\gamma HCHNMe$
127.08	d, J = 171.9 Hz, $C(O)C{=}C_\beta HCH{=}CHNMe$
131.61	d, J = 179.4 Hz, $C(O)C{=}CHCH{=}C_\delta HNMe$
139.04	s, $C(O)C_\alpha{=}CHCH{=}CHNMe$
261.61	s, $C(O)C{=}CHCH{=}CHNMe$

The NMR spectral data were in agreement with the indicated structure of **18**. In its ^1H NMR spectrum none of the resonances were shifted upfield, as in the case of **3**. This was a good indication that the pyrrolyl ligand did not bridge the two iron centers in a σ,π manner. The spectrum also indicated that **18** exists as an inseparable mixture of two isomers. This is in contrast to the complexes of types **10** and **11** in which only one isomer was obtained in all cases. These isomers are due to an axial or equatorial orientation of the thiolate ligand with respect to a plane defined by Fe_2S, as shown in Figure 2. Earlier studies have determined that protons on thiolate ligands with an axial orientation resonate at higher field in the ^1H NMR spectrum than do those with an equatorial orientation.[13] Thus, the upfield resonances in the ^1H spectrum of **18** can be attributed to the axial isomer which is the major isomer.



18

The ^{13}C NMR spectrum of **18** provided evidence which proved that the pyrrolyl group was attached to a bridging acyl group. The relevant spectral data for the major (axial) isomer are summarized in Table VII. As with **10** and **11**, comparison of the resonances for the pyrrolyl ligand of **18** with those for free 1-methylpyrrole was useful in making assignments. For 1-methylpyrrole the carbon atoms farthest from nitrogen give rise to a resonance at 107.8 ppm.[8] Thus, the doublet at 109.73 in the spectrum for **18** was assigned to C_γ, which would be expected to be least affected by coordination to the acyl group. The doublet at 127.08 ppm was assigned to C_β, the other carbon atom which is two bonds away from nitrogen. Further support for these assignments was provided by the J_{CH} coupling constants. For 1-methylpyrrole, the J_{CH} coupling constant for the analogous carbon atoms is 168.8 Hz,[9] which compares well with the coupling constants for both C_β and C_γ of **18**. The uncoordinated carbon atom adjacent to ni-

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[13] King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

trogen, C_δ, gives rise to the remaining doublet at 131.61 ppm. This is somewhat downfield from the analogous resonance for 1-methylpyrrole at 183.3 ppm; however, the coupling constants, again, prove that this assignment is correct. For 1-methylpyrrole the J_{CH} coupling constant for the carbon atoms adjacent to nitrogen is 183.3 Hz, while for 18 the doublet at 131.61 ppm has a J_{CH} value of 179.4 Hz. The singlet at 139.04 ppm which corresponds to C_α, is much farther upfield than the resonance for the carbon atom of the heterocycle which is σ-bonded to iron in the case of 10 and 11. This suggested that the pyrrolyl ligand of complex 18 was not coordinated to iron in a μ-σ,π manner. The singlet at 261.61 ppm showed that complex 18 contains an additional carbon atom. By examination of the ^{13}C NMR spectral data for the bridging α,β-unsaturated acyl complexes, it was determined that this peak was in the range for a bridging acyl carbon atom. Another feature of the spectrum for 18 which is noteworthy is the presence of eight peaks in the region corresponding to the carbon atoms of the terminal carbonyl groups on iron. Since the product was isolated as a mixture of isomers, it is not surprising that more than six peaks are observed in this region. Several resonances also were observed in this region in the ^{13}C NMR spectra of the α,β-unsaturated acyl complexes. In contrast, the μ-σ,π-vinyl complexes give rise to only one or two resonances in this region.

Since the μ-vinylacyl complexes could be decarbonylated in THF to give the corresponding μ-$\eta^1{:}\eta^2$-vinyl complexes, it was of interest to investigate whether 18 could be decarbonylated in a similar manner. Complex 18 was stirred in refluxing THF for 5.5 h. However, this reaction only produced $(\mu\text{-}t\text{-BuS})_2Fe_2(CO)_6$ in 49% yield (based on S) as an isolable new product and 18 was recovered in 30% yield. In addition, some insoluble material was obtained, which resulted from the decomposition of 18. Thus, the decarbonylation attempt was not successful.

Two questions immediately arise from the results of this study. First, it is of interest to establish why in all cases the olefin moiety coordinates to the second metal in preference to the oxygen or sulfur atoms of the furyl or thienyl groups, respectively, and second, why compound 18 is the only case in this study in which an acyl product is observed. We propose that binding via the olefin bond occurs because π back-donation to the furyl or thienyl group is an important component of the bonding. The accompanying bridging thiolato group is a good electron donor, so coordination of the other purely donor oxygen or sulfur ring atoms is not favored. Instead, the olefin moiety, which can function as *both* a donor *and* an acceptor, binds to the second metal. In answer to the second question it appears that the formation of an acyl group for compound 18 is driven by steric interactions involving the methyl substituent on the nitrogen atom, the carbonyl ligands and the *tert*-butyl group. If the methylpyrrolyl product under question were to assume the electronically favored structure, much as shown for 10c in Figure 1, the methyl substituent on nitrogen would come into close contact with the carbonyls on Fe(1), which would apparently not be able to avoid these unfavorable contacts owing to interactions with the bulky *tert*-butyl group.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydro (THF) and diethyl ether were 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 phenylmercaptans were purged with nitrogen and used without further purification. Mercuric chloride (Alfa) and *n*-butyllithium (Morton Thiokol) were used as received. Furan, thiophene, 2-methylfuran, 2-methylthiophene, 2,3-dibromothiophene, and 1-methylpyrrole were purchased from Aldrich and used as received. Literature procedures were followed for the preparations of 2-(chloromercurio)furan,[14] 2-(chloromercurio)thiophene,[15] bis(2-furyl)mercury,[14] bis(2-thienyl)mercury,[15] 2-(chloromercurio)-5-methylfuran,[14] bis(5-methyl-2-thienyl)mercury,[15] and [2-(chloromercurio)-4,5-dimethylthienyl)]mercury.[14] The 2-lithio derivative of 1-methylpyrrole was prepared according to a literature procedure,[16] as was triiron dodecacarbonyl[17]

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 silica acid (ca. 200 mL) in a 350-mL glass fritted funnel was used. Further purification was achieved by column chromatography with a 450- × 25-mm medium-pressure column using Sigma S-0507 230–400-mesh or Aldrich, 60-Å, 230–400-mesh silica gel. In addition, preparative thin-layer chromatography plates (EM Science 60 F_{254}, silica gel, 20 × 20 × 0.25 cm) were used as needed. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized at −20 °C. All yields are based on Fe unless otherwise indicated.

Solution (NaCl windows) or KBr pellet infrared spectra were obtained using a Perkin-Elmer 1600 Series FTIR instrument. Proton NMR spectra were recorded on a Bruker WM-250 or a Varian XL-300 spectrometer operating at 250 and 300 MHz, respectively. Carbon-13 NMR spectra were recorded on a Varian XL-300 spectrometer operating at 75.4 MHz. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^1H, ^{12}C, ^{14}N, ^{16}O, ^{32}S, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray Crystallography. X-ray Data Collection. Structure of $(\mu\text{-}\eta^1{:}\eta^2\text{-}\overline{C{=}CHCH{=}CHO})(\mu\text{-PhS})Fe_2(CO)_6$ (10c). Deep red crystals of $(\mu\text{-}\eta^1{:}\eta^2\text{-}\overline{C{=}CHCH{=}CHO})(\mu\text{-PhS})Fe_2(CO)_6$ were grown from pentane at −20 °C. A suitable single crystal was mounted in air on a glass fiber. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 22 °C using graphite-monochromated Mo Kα radiation. A summary of data collection details and crystal data appears in Table VIII.

Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $16.0° \leq 2\theta \leq 27.6°$. The diffraction symmetry and systematic absences uniquely defined the space group as $P2_1/c$. Background counts were obtained by extending the peak scans 25% on either side of the scan range. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals. There was no significant variation in the intensities of these standards, so no correction was applied. Of the 3215 unique reflections measured, 2403 were observed and used in subsequent calculations. Absorption corrections were applied to the data by using the method of Walker and Stuart.[18]

Solution and Refinement of Structure. The structure was solved by use of MULTAN,[19] which succeeded in locating the iron and sulfur atoms. Subsequent least-squares refinements[20] and

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(14) Gilman, H.; Wright, G. F. *J. Am. Chem. Soc.* **1933**, *55*, 3302.

(15) Cherbuliez, E.; Giddey, C. *Helv. Chim. Acta* **1952**, *32*, 160.

(16) Shirley, D. A.; Gross, B. H.; Roussel, P. A. *J. Org. Chem.* **1955**, *20*, 225.

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

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 1581.

(19) Main, P.; Lessinger, L.; Woofson, M. M.; Germain, G.; Declercq, J. P. MULTAN 11/82, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; University of York, England, and University of Louvain, Louvain, Belgium, 1982.

(20) Programs used were those on the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

Table VIII. Crystal Data and Intensity Collection Details for $(\mu\text{-}\sigma,\pi\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-PhS})\mathrm{Fe_2(CO)_6}$ (10c)

empirical formula	$C_{16}H_8Fe_2O_7S$
fw	456.00
cryst color	red
cryst dimens (mm)	0.1 × 0.1 × 0.1
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
lattice params	
a (Å)	7.805 (1)
b (Å)	17.091 (2)
c (Å)	13.344 (2)
β (deg)	96.90 (1)
V (Å^3)	1767.1
Z	4
D_{calc} (g/cm^3)	1.714
μ(Mo K*α*) (cm^{-1})	17.89
corrections applied	empirical abs
range of transm factors	0.867–1.502
radiation (λ (Å))	Mo K*α* (0.71069)
monochromator	incident beam, graphite crystal
takeoff angle (deg)	3.00
detector aperture (mm)	3.00 + tan *θ*, horizontal 4.00, vertical
cryst to detector dist (mm)	208
scan type	*θ*–2*θ*
scan rate (deg/min)	6.7–1.4
scan width (deg)	0.60 + 0.347 tan *θ*
$2\theta_{max}$ (deg)	50.0
data collcn index range	*h*,*k*,±*l*
total no. of reflns measd	3215, averaged
no. observns ($I > 3\sigma(I)$)	2403
no. of variables	248
agreement factors *R*, R_{w}, GOF	0.027, 0.036, 1.30

Table IX. Final Positional Parameters for $(\mu\text{-}\sigma,\pi\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-PhS})\mathrm{Fe_2(CO)_6}$ (10c)

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Fe(1)	0.15115 (4)	0.13369 (2)	0.26111 (3)	3.023 (8)
Fe(2)	0.01599 (5)	−0.00037 (2)	0.25547 (3)	2.996 (8)
S	0.04312 (8)	0.07250 (4)	0.11561 (5)	3.18 (1)
O(1)	−0.1168 (3)	0.2557 (1)	0.2393 (2)	6.19 (7)
O(2)	0.4373 (3)	0.2257 (1)	0.2003 (2)	7.32 (7)
O(3)	0.2224 (3)	0.1693 (1)	0.4762 (1)	5.76 (6)
O(4)	0.0718 (3)	−0.0799 (2)	0.4505 (2)	7.25 (7)
O(5)	−0.2806 (2)	0.0848 (1)	0.3155 (2)	5.80 (6)
O(6)	−0.1556 (3)	−0.1343 (1)	0.1484 (2)	6.21 (6)
O(7)	0.3769 (2)	0.0219 (1)	0.3761 (1)	4.07 (5)
C(1)	−0.0151 (4)	0.2085 (2)	0.2467 (2)	4.03 (7)
C(2)	0.3249 (4)	0.1907 (2)	0.2221 (2)	4.29 (7)
C(3)	0.1951 (3)	0.1546 (2)	0.3928 (2)	3.86 (7)
C(4)	0.0474 (4)	−0.0483 (2)	0.3750 (2)	4.54 (8)
C(5)	−0.1640 (3)	0.0533 (2)	0.2905 (2)	3.90 (7)
C(6)	−0.0851 (3)	−0.0833 (2)	0.1897 (2)	4.05 (7)
C(7)	0.2807 (3)	0.0361 (2)	0.2827 (2)	3.22 (6)
C(8)	0.2963 (3)	−0.0305 (2)	0.2241 (2)	3.70 (7)
C(9)	0.4056 (4)	−0.0848 (2)	0.2842 (2)	4.87 (8)
C(10)	0.4494 (4)	−0.0511 (2)	0.3722 (2)	4.97 (8)
C(11)	−0.1530 (3)	0.1169 (2)	0.0600 (2)	3.51 (6)
C(12)	−0.3117 (3)	0.0806 (2)	0.0592 (2)	4.12 (7)
C(13)	−0.4591 (4)	0.1150 (2)	0.0110 (2)	4.92 (8)
C(14)	−0.4489 (4)	0.1859 (2)	−0.0363 (2)	5.25 (9)
C(15)	−0.2924 (5)	0.2223 (2)	−0.0361 (2)	5.71 (9)
C(16)	−0.1421 (4)	0.1881 (2)	0.0111 (2)	4.87 (8)

difference Fourier syntheses led to the location of all remaining atoms. Atomic scattering factors[21] and anomalous dispersion terms[22] were taken from the usual tabulations. All hydrogen atoms were located, but only the three on the furyl group were refined; the others were input as fixed contributions in their idealized positions, with thermal parameters fixed at 20% greater than their attached carbon atom. At the outset the position of the furyl oxygen atom was not obvious; however, interchanging this oxygen atom with the *β* carbon of this ring resulted in anomalous thermal parameters for both atoms. In addition, the hydrogen (H(8)) attached to C(8) was clearly located and refined well, whereas the oxygen atom (O(7)) had no residual electron density in the vicinity that could be attributed to a hydrogen. The final positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table IX.

Preparation of Bis(5-methyl-2-furyl)mercury. A 2-L conical flask was charged with 25.18 g (81.4 mmol) of 2-(chloromercurio)-5-methylfuran and 400 mL of acetone. The mixture was stirred until the mercurial had dissolved. A solution of 24.4 g (162.5 mmol) of sodium iodide in 6 mL of water and 25 mL of acetone was added. A white precipitate resulted. The reaction mixture was stirred at room temperature overnight. Subsequently, 800 mL of water was added to dissolve the inorganic salts. The water-insoluble mercurial was recrystallized from acetone/water at 20 °C to give 8.6 g (29%) of a white powder, **13**, mp 96–98 °C. Anal. Calcd for $C_{10}H_{10}O_2Hg$: C, 33.10; H, 2.78. Found: C, 32.17; H, 2.89. ^{1}H NMR ($CD_3C(O)CD_3$, 300 MHz): *δ* 1.37 (s, 6 H, C*H*$_3$) 5.16 (d, *J* = 2.73 Hz, 2 H, HgC=CHC*H*=CMeO), 5.42 (d, *J* = 3.11 Hz, 2 H, HgC=C*H*CH=CMeO). ^{13}C NMR ($CD_3C(O)CD_3$, 75.4 MHz): *δ* 13.86 (q, *J* = 127.9 Hz, *C*H$_3$), 105.73 (d, *J* = 170.6 Hz, HgC=CH*C*H=CMeO), 122.77 (d, *J* = 184.9 Hz, HgC=*C*HCH=CMeO), 156.11 (s, HgC=CHCH=*C*MeO), 188.69 (s, Hg*C*=CH=CH=CMeO).

Preparation of 2-(Iodomercurio)-4,5-dimethylthiophene. As in the above experiment, a suspension of 3.15 g (9.06 mmol) of 2-(chloromercurio)-4,5-dimethylthiophene was treated with 2.72 g (18.12 mmol) of NaI in 0.7 mL of water and 3 mL of acetone in order to prepare the symmetrical diorgano mercurial. Precipitation with 300 mL of water and extraction of the solid with hot acetone gave 2.27 g of a white powder, mp 173–178 °C (dec), which was 2-(iodomercurio)-4,5-dimethylthiophene. Anal. Calcd for C_6H_7SIHg: C, 16.43; H, 1.61. Found: C, 16.91; H, 1.88. ^{1}H NMR ($CD_3C(O)CD_3$, 300 MHz): *δ* 2.10 (s, 3 H, C*H*$_3$), 2.32 (s, 3 H, C*H*$_3$), 6.83 (br, 1 H, HgC=C*H*CMe=CMeS). ^{13}C NMR ($CD_3S(O)CD_3$ + Cr(acac)$_3$, 75.4 MHz): *δ* 12.89 (q, *J* = 128.1 Hz, *C*H$_3$), 13.39 (q, *J* = 126.4 Hz, *C*H$_3$), 132.62 (s, HgC=CH*C*Me=CMeS), 135.49 (s, HgC=CHCMe=*C*MeS), 138.14 (d, *J* = 175.0 Hz, HgC=*C*HCMe=CMeS), 160.12 (br, Hg*C*=CHCMe=CMeS).

Preparation of Bis(1-methyl-2-pyrrolyl)mercury. A 250-mL three-necked, round-bottomed flask equipped with a stir-bar, a condenser with a gas inlet adapter, and two rubber septa was degassed by three evacuation/nitrogen-back-fill cycles. The system then was charged with 150 mL of diethyl ether, 7.1 mL (80 mmol) of 1-methylpyrrole, and 39 mL (80 mmol, 2.06 M in hexane) of *n*-BuLi. The mixture was heated at reflux for 4.5 h, during which time a white precipitate formed. The reaction mixture was cooled to room temperature and 11 g (40 mmol) of mercuric chloride was added as a solid against a strong flow of nitrogen. The mixture was stirred at room temperature for 17 h, during which time the white precipitate was replaced by a tan precipitate. The solid was removed by filtration with suction and washed with water to remove LiCl. The solid was dissolved in a mixture of boiling acetone/ethanol (1:1 v/v) and filtered with suction to remove insoluble material. The volume of solvent was reduced, and the solution was placed in a freezer at −20 °C to crystallize. The yellow powder which formed yielded 5.8 g (16 mmol, 40%) of bis(1-methyl-2-pyrrolyl)mercury, melting range 108–112 °C (dec). Anal. Calcd for $C_{10}H_{12}HgN_2$: C, 33.28; H, 3.36; N, 7.76. Found: C, 32.91; H, 3.39; N, 7.60. ^{1}H NMR ($CD_3C(O)CD_3$, 300 MHz): *δ* 3.78 (s, 6 H, HgC=CHCH=CNC*H*$_3$), 6.09 (s, 4 H, HgC=C*H*CH=CHNMe), 6.84 (s, 2 H, HgC=CHCH=C*H*NMe). ^{13}C NMR ($CD_3C(O)CD_3$, 75.4 MHz): *δ* 38.48 (q, *J* = 137.1 Hz, N*C*H$_3$), 108.09 (d, *J* = 170.1 Hz, HgC=CH*C*H=CHNMe), 119.11 (d, *J* = 170.8 Hz, HgC=*C*HCH=CHNMe), 125.21 (d, *J* = 181.0 Hz, HgC=CHCH=*C*HNMe), 166.19 (s, Hg*C*=CHCH=CHNMe).

Standard in Situ Preparation of [Et$_3$NH][(*μ*-CO)(*μ*-RS)Fe$_2$(CO)$_6$]. A 100-mL Schlenk flask equipped with a rubber septum and a stir-bar was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and degassed by three evacuation/nitrogen-back-fill cycles. The flask then was charged successively with 30 mL of THF, 3.00 mmol of the appropriate thiol, and 0.42 mL (0.30 g, 3.00 mmol) of triethylamine. The mixture was stirred for 15 min

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[21] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

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

at room temperature during which time slow gas evolution and a gradual color change from dark green to brown-red were observed. The resulting $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ reagent solution then was used in situ without further purification.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with 2-(Chloromercurio)furan. To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) was added against a strong flow of nitrogen 0.91 g (3.00 mmol) of 2-(chloromercurio)furan as a solid. An immediate reaction ensued with rapid gas evolution and a color change to red-brown. After the reaction mixture had been stirred for 2.5 h at room temperature, the color of the solution had changed to bright red and a gray precipitate had formed. TLC indicated the formation of three orange products. The solvent was removed in vacuo to yield a red solid which was dissolved in pentane and filtered through a thin pad of silicic acid to remove decomposition materials, using a pentane eluant. Further purification of the products was achieved by medium-pressure column chromatography. Pentane eluted an orange band which gave 0.37 g (0.80 mmol, 54% based on S, *a/e*:*e/e* = 1.5) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[23] Continued elution with pentane removed a second orange band which yielded 0.54 g (1.24 mmol, 42%) of $(\mu\text{-}\sigma,\pi\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6$ (**10a**) as an air-stable, red, crystalline solid after recrystallization from pentane, mp 81.0–82.0 °C. Anal. Calcd for $C_{14}H_{12}Fe_2O_7S$: C, 38.56; H, 2.78. Found: C, 38.61; H, 2.87. IR (CCl_4, cm^{-1}): 3119 (w), 3008 (w), 2970 (w), 2942 (w), 2925 (w), 2899 (w), 2864 (w), 1546 (w), 1472 (m), 1459 (m), 1394 (w), 1364 (s), 1154 (s), 1132 (s), 1069 (w), 1035 (s), 996 (s), 878 (w), 866 (w). IR, terminal carbonyl region (CCl_4, cm^{-1}): 2072 (vs), 2035 (vs), 1994 (vs), 1965 (s). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 9 H, $C(CH_3)_3$), 5.29 (d, *J* = 3.07 Hz, 1 H, FeC=C*H*CH=CHO), 6.25 (t, *J* = 2.60 Hz, 1 H, FeC=CHC*H*=CHO), 7.86 (d, *J* = 2.00 Hz, 1 H, FeC=CHCH=C*H*O). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 33.48 (q, *J* = 127.4 Hz, $SC(CH_3)_3$), 47.47 (s, $SC(CH_3)_3$), 93.21 (d, *J* = 178.1 Hz, FeC=*C*HCH=CHO), 111.70 (d, *J* = 177.5 Hz, FeC/dbdCH*C*H=CHO), 154.98 (d, *J* = 200.7 Hz, FeC=CHCH=CHO), 180.73 (s, Fe*C*=CHCH=CHO), 210.33 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 436 (M^+, 24), 408 ($M^+ - CO$, 22), 380 ($M^+ - 2CO$, 37), 352 ($M^+ - 3CO$, 39), 324 ($M^+ - 4CO$, 48), 296 ($M^+ - 5CO$, 67), 268 ($M^+ - 6CO$, 85), 212 ($Fe_2SH(C{=}CHCH{=}CHO)^+$, 100), 144 (Fe_2S^+, 31), 100 ($C{=}CHCH{=}CHO^+ + SH$, 10), 68 ($C{=}CHCH{=}CHO^+ + 1H$, 7), 56 (Fe^+, 20). Further elution with pentane eluted a minor orange band which was discarded.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ with Bis(2-furyl)mercury. To the standard $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ reagent solution (2.98 mmol) against a strong flow of nitrogen was added as a solid 1.01 g (3.00 mmol) of bis(2-furyl)mercury. An immediate reaction ensued with slow gas evolution and a color change to red-brown. After the reaction mixture had been stirred for 1.5 h at room temperature, the color of the solution had changed to bright red and a gray-white precipitate had formed. TLC indicated the formation of three orange products. The solvent was removed in vacuo to yield a red solid which was dissolved in pentane and filtered through a thin pad of silicic acid to remove decomposition materials, using a pentane eluant. Further purification of the products was achieved by medium-pressure column chromatography. Pentane eluted an orange band which gave 0.06 g (0.14 mmol, 9% based on S, *a/e*:*e/e* = 1.6) of $(\mu\text{-}t\text{-}BuS)_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[23] Continued elution with pentane removed a second orange band which yielded 0.97 g (2.23 mmol, 75%) of **10a**, identified by comparison of its ^1H NMR spectrum with that of an authentic sample (experiment above). Further elution with pentane eluted a minor orange band which was discarded.

Reaction of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}2,4,6\text{-}Me_3C_6H_2S)Fe_2(CO)_6]$ with Bis(2-furyl)mercury. The $[Et_3NH][(\mu\text{-}CO)\text{-}(\mu\text{-}2,4,6\text{-}Me_3C_6H_2S)Fe_2(CO)_6]$ reagent (2.98 mmol) was generated using the general procedure described above. Against a strong flow of argon, 1.01 g (3.01 mmol) of bis(2-furyl)mercury was added as a solid. An immediate reaction ensued with rapid gas evolution and a color change to red. After the reaction mixture had been stirred for 1 h at room temperature, the color of the solution was bright red, and a gray precipitate had formed. The solvent was removed in vacuo to yield a brown solid which was dissolved in pentane and filtered through a thin pad of silica gel using pentane as eluant. Concentration of the solution in vacuo and cooling to −20 °C yielded 0.16 g (0.27 mmol, 18% based on S) of $(\mu\text{-}2,4,6\text{-}Me_3C_6H_2S)_2Fe_2(CO)_6$ as an air-stable, orange-red crystalline solid after recrystallization from pentane, mp 210–213°C. Anal. Calcd for $C_{24}H_{22}Fe_2O_6S_2$: C, 49.51; H, 3.81. Found: C, 49.47; H, 3.84. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 6 H, $p\text{-}(CH_3)C_6H_2S$), 2.58 (s, 12 H, $o\text{-}(CH_3)_3C_6H_2S$), 6.86 (s, 4 H, $(CH_3)_3C_6H_2S$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 20.63 (q, *J* = 125.7 Hz, $p\text{-}(CH_3)_3C_6H_2S$), 25.29 (q, *J* = 128.2 Hz, $o\text{-}(CH_3)_3C_6H_2S$), 130.05 (d, 159.9 Hz, $m\text{-}(CH_3)_3C_6H_2S$), 131.30, 137.09, 139.07 (all s, $(CH_3)_3C_6H_2S$), 207.52 (br, terminal *C*O's), 210.47 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 582 (M^+, 3), 526 ($M^+ - 2CO$, 14), 442 ($M^+ - 5CO$, 13), 414 ($M^+ - 6CO$, 100), 295 ($Fe(C_6H_2(CH_3)_3)_2H^+$, 18), 294 ($Fe(C_6H_2(CH_3)_3)^+$, 23), 270 ($S(C_6H_2(CH_3)_3)_2{}^+$, 44), 152 ($C_6H_2(CH_3)_3SH^+$, 22), 151, ($C_6H_2(CH_3)_3S^+$, 10), 150 ($C_6H_2(CH_3)_3S^+ - H$, 33), 149 ($C_6H_2(CH_3)_3S^+ - 2H$, 25), 119 ($C_6H_2(CH_3)_3{}^+$, 54), 91 ($C_6H_4CH_3{}^+$, 46), 83 ($C_6H_{11}{}^+$, 20), 57 (FeH^+, 15).

Concentration of the mother liquor solution and cooling to −20 °C yielded 0.58 g (1.16 mmol, 39%) of $(\mu\text{-}\eta^1\text{:}\eta^2\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-}2,4,6\text{-}Me_3C_6S)Fe_2(CO)_6$ (**10d**) as an air-stable, red crystalline solid after recrystallization from pentane, mp 136–138 °C. Anal. Calcd for $C_{19}H_{14}Fe_2O_7S$: C, 45.82; H, 2.83. Found: C, 46.05; H, 2.86. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.22 (s, 3 H, $p\text{-}(CH_3)_3C_6H_2S$), 2.51 (s, 6 H, $o\text{-}(CH_3)_3C_6H_2S$), 5.31 (d, *J* = 3.11 Hz, 1 H, FeC=C*H*CH=CHO), 6.44 (t, *J* = 2.60 Hz, 1 H, FeC=CHC*H*=CHO), 6.85 (s, 2 H, $(CH_3)_3C_6H_2S$), 7.95 (d, *J* = 1.69 Hz, 1 H, FeC=CHCH=C*H*O). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 20.65 (q, *J* = 125.9 Hz, $p\text{-}(CH_3)_3C_6H_2S$), 25.01 (q, *J* = 127.3 Hz, $o\text{-}(CH_3)_3C_6H_2S$), 93.80 (d, *J* = 174.2 Hz, FeC=*C*HCH=CHO), 111.91 (d, *J* = 178, 9 Hz, FeC=CH*C*H=CHO), 130.00 (d, *J* = 158.1 Hz, $m\text{-}(CH_3)_3C_6H_2S$), 132.30, 136.94, 138.55 (all s, $(CH_3)_3C_6H_2S$), 155.36 (d, *J* = 202.5 Hz, FeC=CHCH=*C*HO), 182.08 (s, Fe*C*=CHCH=CHO), 209.54 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 498 (M^+, 5), 470 ($M^+ - CO$, 3), 442 ($M^+ - 2CO$, 18), 414 ($M^+ - 3CO$, 5), 386 ($M^+ - 4CO$, 17), 358 ($M^+ - 5CO$, 32), 330 ($M^+ - 6CO$, 100), 300 ($Fe_2(SC_6H_2(CH_3)_3(C{=}CHC)^+$, 53), 287 ($Fe_2(SC_6H_2(CH_3)_3)\,(C{\equiv}C)^+$, 13), 165 ($FeSPh^+$, 21), 149 ($SC_6H_2(CH_3)_3{}^+ - 2H$, 39), 144 ($Fe_2S^+$, 46), 119 ($C_6H_2(CH_3)_3{}^+$, 13), 57 ($FeH^+$, 30).

Other Reactions of $[Et_3NH][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ Complexes with Furyl and Thienyl Mercurials. Procedures using those described above were used in the preparation of the following complexes.

$(\mu\text{-}\eta^1\text{:}\eta^2\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-}EtS)Fe_2(CO)_6$ (10b): 51% yield, a red solid, mp 45.0–47.0 °C (pentane). Anal. Calcd for $C_{12}H_8Fe_2O_7S$: C, 35.33; H, 1.98. Found: C, 35.40; H, 2.04. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, *J* = 7.26 Hz, 3 H, SCH_2CH_3), 2.40 (q, *J* = 7.42 Hz, 2 H, SCH_2CH_3), 5.02 (d, *J* = 2.57 Hz, 1 H, FeC=C*H*CH=CHO), 6.29 (t, *J* = 2.38 Hz, 1 H, FeC=CHC*H*=CHO), 7.84 (d, *J* = 2.26 Hz, 1 H, FeC=CHCH=C*H*O). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 17.99 (q, *J* = 128.3 Hz, SCH_2CH_3), 32.69 (t, *J* = 238.4 Hz, SCH_2CH_3), 90.59 (d, *J* = 175.9 Hz, FeC=*C*HCH=CHO), 112.03 (d, *J* = 179.0 Hz, FeC=CH*C*H=CHO), 154.72 (d, *J* = 199.2 Hz, FeC=CHCH=*C*HO), 182.34 (s, Fe*C*=CHCH=CHO), 209.70 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 408 (M^+, 19), 380 ($M^+ - CO$, 23), 352 ($M^+ - 2CO$, 8), 324 ($M^+ - 3CO$, 23), 296 ($M^+ - 4CO$, 15), 268 ($M^+ - 5CO$, 16), 240 ($M^+ - 6CO$, 86), 222 ($Fe_2SC(C{=}CHCH{=}CO)^+$, 10), 212 ($Fe_2SH(C{=}CHCH{=}CHO)^+$, 38), 211 ($FeS(C{=}CHCH{=}CHO)^+$, 24), 210 ($Fe_2S(C{=}CHCH{=}CO)^+$, 11), 183 ($Fe_2SC{=}CHCH^+ + 1H$, 53), 169 (Fe_2SCCH^+, 14), 144 (Fe_2S^+, 100), 142 ($FeSCHCHCO^+$, 19), 134 (unknown, 8), 101 ($CH{=}CHCH{=}CHO^+ + SH$, 6), 81 ($FeCCH^+$, 7), 56 (Fe^+, 13).

$(\mu\text{-}\eta^1\text{:}\eta^2\text{-}\overline{\mathrm{C{=}CHCH{=}CHO}})(\mu\text{-}PhS)Fe_2(CO)_6$ (10c): a red solid, mp 93.0–93.5 °C (from 8:1 pentane/CH_2Cl_2). Anal. Calcd for $C_{16}H_8Fe_2O_7S$: C, 42.14; H, 1.77. Found: C, 42.62; H, 2.07. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.17 (d, *J* = 3.11 Hz, 1 H, FeC=C*H*CH=CHO), 6.25 (dd, ^1J = 2.84 Hz, ^2J = 1.86 Hz, 1 H, FeC=CHC*H*=CHO), 7.23 (m, 3 H, Ph), 7.32 (m, 2 H, Ph), 7.90 (d, *J* = 2.13 Hz, 1 H, FeC=CHCH=C*H*O). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 90.20 (d, *J* = 170.4 Hz, FeC=*C*HCH=CHO), 112.10

(d, *J* = 179.6 Hz, FeC=CH*C*H=CHO), 127.83 (d, *J* = 160.1 Hz, Ph), 128.66 (d, *J* = 161.1 Hz, Ph), 132.02 (d, *J* = 160.0 Hz, Ph), 137.74 (s, ipso Ph), 155.01 (d, *J* = 205.9 Hz, FeC=CHCH=*C*HO), 181.84 (s, Fe*C*=CHCH=CHO), 209.31 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 456 (M$^+$, 5), 428 (M$^+$ – CO, 3), 400 (M$^+$ – 2CO, 8), 372 (M$^+$ – 3CO, 2), 344 (M$^+$ – 4CO, 6), 316 (M$^+$ – 5CO, 16), 288 (M$^+$ – 6CO, 79), 259 (Fe$_2$SPh(C=CHCH)$^+$, 40), 245 (Fe$_2$SPh(C=C)$^+$, 16), 183 (Fe$_2$S(C=CHCH)$^+$ + 1H, 11), 169 (Fe$_2$S(C=CH)$^+$, 26), 165 (FeSPh$^+$, 19), 144 (Fe$_2$S$^+$, 100), 127 (FeS(C=CHCH)$^+$ + 1H, 16), 111 (FeOC=CHCH$^+$ + 1H, 14), 97 (FeOC=CH$^+$ + 1H, 22), 85 (FeOCH$^+$, 20), 71 (FeCH$^+$, 2H, 30), 56 (Fe$^+$, 29).

(μ-η^1:η^2-$\overline{\mathrm{C{=}CHCH{=}C(CH_3)O}}$)($\mu$-PhS)Fe$_2(CO)_6$ (16a): 33% yield, a red solid, mp 130–132 °C (from pentane). Anal. Calcd for $C_{17}H_{10}Fe_2O_7S$: C, 43.44; H, 2.14. Found: C, 43.48; 2.18. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.19 (s, CH$_3$, minor isomer), 2.24 (s, CH_3, major isomer), 4.23 (d, *J* = 3.5 Hz, FeC=C*H*CH=CMeO minor isomer), 5.20 (d, *J* = 3.04 Hz, FeC=C*H*CH=CMeO major isomer), 5.64 (d, *J* = 3.0 Hz, FeC=CHC*H*=CMeO minor isomer), 5.92 (d, *J* = 2.17 Hz, FeC=CHC*H*=CMeO major isomer), 7.21 (m, 3 H, Ph), 7.31 (m, 2 H, Ph). Ratio major/minor isomer, 8/1. ^{13}C NMR (CDCl$_3$, 75.4 MHz), major isomer: δ 14.06 (q, *J* = 129.4 Hz, *C*H$_3$), 94.47 (d, *J* = 176.2 Hz, FeC=*C*HCH=CMeO), 107.57 (d, *J* = 174.0 Hz, FeC=CH*C*H=CMeO), 127.73 (d, *J* = 162.8 Hz, *p*-Ph), 128.58 (d, *J* = 159.5 Hz, Ph), 132.05 (d, *J* = 163.5 Hz, Ph), 138.03 (s, ipso-Ph), 166.86 (m, FeC=CHCH=*C*MeO), 179.49 (dd, ^2J and ^3J = 14 and 6 Hz, Fe*C*=CHCH=CMeO), 209.71 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 470 (M$^+$, 40), 442 (M$^+$ – CO, 6), 414 (M$^+$ – 2CO, 22), 358 (M$^+$ – 4CO, 9), 330 (M$^+$ – 5CO, 19), 302 (M$^+$ – 6CO, 86), 300 (Fe$_2$(SPh)(C$_4$CH$_3$O)$^+$, 13), 259 (Fe$_2$SPh)(C$_3$H$_2$)$^+$, 27), 182 (Fe$_2$S(C$_3$H$_2$)$^+$, 13), 169 (Fe$_2$S(C$_2$H)$^+$, 30), 165 (Fe(CCHCHCH$_3$)$^+$, 20), 160 (Fe$_2$C$_4$$^+$, 15), 151 (Fe$_2$(C$_2CH_3$)$^+$, 19) 144, (Fe$_2S^+$, 100), 57 (FeH$^+$, 22), 56 (Fe$^+$, 22).

(μ-η^1:η^2-$\overline{\mathrm{C{=}CHCH{=}CHS}}$)($\mu$-EtS)Fe$_2(CO)_6$ (11a): 24% yield, a red solid, mp 48.0–50.0 °C (from pentane). Anal. Calcd for $C_{12}H_8Fe_2O_6S_2$: C, 33.99; H, 1.90. Found: C 33.98; H, 1.96. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.36 (t, *J* = 7.30 Hz, 3 H, SCH$_2$CH_3), 2.44 (q, *J* = 7.12 Hz, 2 H, SCH_2CH$_3$), 5.37 (d, *J* = 2.36 Hz, 1 H, FeC=C*H*CH=CHS), 7.08 (t, *J* = 3.80 Hz, 1 H, FeC=CHC*H*=CHS), 7.78 (d, *J* = 5.17 Hz, FeC=CHCH=C*H*S). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 17.97 (q, *J* = 128.3 Hz, SCH$_2$*C*H$_3$), 32.96 (t, *J* = 140.9 Hz, S*C*H$_2$CH$_3$), 99.27 (d, *J* = 168.6 Hz, FeC=*C*HCH=CHS), 130.12 (d, *J* = 171.1 Hz, FeC=CH*C*H=CHS), 139.91 (d, *J* = 186.0 Hz, FeC=CHCH=*C*HS), 155.38 (s, Fe*C*=CHCH=CHS), 209.48 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 396 (M$^+$ – CO, 7), 368 (M$^+$ – 2CO, 20), 340 (M$^+$ – 3CO, 10), 312 (M$^+$ – 4CO, 14), 284 (M$^+$ – 5CO, 11), 256 (M$^+$ – 6CO, 100), 228 (Fe$_2$SH(C=CHCH=CHS)$^+$, 64), 201 (Fe$_2$S(SC=CH)$^+$, 17), 169 (Fe$_2$SC=CH$^+$, 17), 178 (unknown, 14), 156 (Fe$_2$SC$^+$, 5), 144 (Fe$_2$S$^+$, 86), 142 (FeSEt(C=CH)$^+$, 22), 121 (unknown, 4), 113 (FeSC=CH$^+$, 5), 89 (FeSH$^+$, 6), 69 (FeCH$^+$, 5), 56 (Fe$^+$, 8).

(μ-η^1:η^2-$\overline{\mathrm{C{=}CHCH{=}CHS}}$)($\mu$-PhS)Fe$_2(CO)_6$ (11b): 2% yield, a red solid, which was characterized only by means of its ^{1}H NMR spectrum because of its low yield. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.50 (d, *J* = 3.00 Hz, 1 H, FeC=C*H*CH=CHS), 7.25 (m, 5 H, Ph), 7.48 (s, 1 H, FeC=CHC*H*=CHS), 7.83 (d, *J* = 5.28 Hz, FeC=CHCH=C*H*S).

(μ-η^1:η^2-$\overline{\mathrm{C{=}CHCH{=}C(CH_3)S}}$)($\mu$-PhS)Fe$_2(CO)_6$ (16b): 37% yield, a red solid, mp 96–98 °C (from pentane). Anal. Calcd for $C_{17}H_{10}Fe_2O_6S$: C, 42.01; H, 2.07. Found: C, 42.12; H, 2.12. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.40 (s, 3 H, CH_3), 5.45 (d, *J* = 3.35 Hz, 1 H, FeC=C*H*CHCMeS), 6.75 (m, 1 H, FeC=CHC*H*CMeS), 7.25 (m, 3 H, Ph), 7.33 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ_C 15.76 (q, *J* = 130.3 Hz, *C*H$_3$), 101.59 (d, *J* = 169.1 Hz, FeC=*C*HCHCMeS), 127.51 (d, *J* = 168.3 Hz, *p*-Ph), 127.90 (d, *J* = 162.5 Hz, Ph), 128.72 (d, *J* = 203.3 Hz, FeC=CH*C*H=CMeS), 131.90 (d, *J* = 165.6 Hz, Ph), 137.78 (s, ipso-Ph), 153.26 (t, ^2J and ^3J ca. 9 Hz, Fe*C*=CHCH=CMeS), 155.73 (m, FeC=CHCH=*C*MeS), 209.44 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 486 (M$^+$, 4), 458, (M$^+$ – CO, 3), 430 (M$^+$ – 2CO, 15), 402 (M$^+$ – 3CO, 4), 374 (M$^+$ – 4CO, 11), 346 (M$^+$ – 5CO, 17), 318 (M$^+$ – 6CO, 100), 316 (Fe$_2$(SPh)(C$_4$CH$_3$S)$^+$, 21), 285 (Fe$_2$(SPh)(C$_4$HCH$_3$)$^+$, 19), 176 (Fe$_2$S$_2$$^+$, 62), 173 (Fe$_2$S(CH$_2CH_3$)$^+$, 23), 159 (Fe$_2SCH_3$$^+$, 15), 144 (Fe$_2S^+$, 26), 141 (Ph$_2S_2$$^+$, 12), 110 (PhSH$^+$, 12), 97 (C=CCH=CCH$_3S^+$, 16), 57 (FeH$^+$, 17), 56 (Fe$^+$, 13).

(μ-η^1:η^2-$\overline{\mathrm{C{=}CHC(CH_3){=}C(CH_3)S}}$)($\mu$-PhS)Fe$_2(CO)_6$ (17): 7% yield, a red solid, mp 98–101 °C (from pentane). This product was prepared from 2-(iodomercurio)-4,5-dimethylthiophene. Anal. Calcd for $C_{18}H_{12}Fe_2O_6S_2$: C, 43.23; H, 2.42. Found: C, 43.02; H, 2.48. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.21 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 5.15 (s, 1 H, FeC=C*H*CMe=CMeS), 7.25 (m, 3 H, Ph), 7.34 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 13.47 (q, *J* = 127.8 Hz, all *C*H$_3$), 102.79 (d, *J* = 165.7 Hz, FeC=*C*HCMe=CMeS), 127.88 (d, *J* = 162.7 Hz, *p*-Ph), 128.65 (d, *J* = 159.9 Hz, Ph), 131.94 (d, *J* = 161.1 Hz, Ph), 135.33 (br, FeC=CH*C*Me=CMeS), 137.89 (s, ipso-Ph), 147.15 (br, FeC=CHCMe=*C*MeS), 153.13 (d, ^2J = 10 Hz, Fe*C*=CHCMe=CMeS), 209.38 (s, terminal *C*O's). Mass spectrum (EI), *m/z* (relative intensity): 500 (M$^+$, 4), 472 (M$^+$ – CO, 4), 444 (M$^+$ – 2CO, 15), 416 (M$^+$ – 3CO, 5), 388 (M$^+$ – 4CO, 11), 360 (M$^+$ – 5CO, 16), 332 (M$^+$ – 6CO, 100), 330 (Fe$_2$(SPh)C$_4$(CH$_3$)$_2$S$^+$ – H, 55), 253 (Fe$_2$(SPh)S$^+$, 16), 176 (Fe$_2$S$_2$$^+$, 70), 166 (Fe(SPh)H$^+$, 17), 149 (FeS$_2CH_2CH_3$$^+$, 22), 144 (Fe$_2S^+$, 27), 110 (FeCHCHCHCH$_3$$^+$, 14), 57 (FeH$^+$, 30).

Reaction of [Et$_3$NH][(μ-CO)(μ-*t*-BuS)Fe$_2$(CO)$_6$] with 2-(Chloromercurio)-1-methylpyrrole. The standard [Et$_3$NH][(μ-CO)(μ-*t*-BuS)Fe$_2$(CO)$_6$] reagent solution (2.98 mmol) was generated at room temperature. Against a strong flow of nitrogen, 0.91 g (3.01 mmol) of 2-(chloromercurio)-1-methylpyrrole was added as a solid. An immediate reaction ensued with slow gas evolution. After the reaction mixture had been stirred for 1.5 h at room temperature, the color of the solution had changed to red-brown and a white-gray precipitate had formed. TLC indicated the formation of two-orange products. The solvent was removed in vacuo to yield a red solid which was dissolved in pentane and filtered through a thin pad of silicic acid to remove decomposition materials. Pentane eluted a major orange band which gave 0.56 g (1.21 mmol, 81% based on S, *a/e*:*e/e* = 1.4) of (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[23] Pentane/CH$_2$Cl$_2$ (5:1 v/v) eluted a yellow band. Further purification of this product was achieved by medium-pressure column chromatography. Pentane eluted an orange band which yielded 0.22 g (0.46 mmol, 15%) of (μ-C(O)$\overline{\mathrm{C{=}CHCH{=}CHN}}$Me)($\mu$-*t*-BuS)Fe$_2(CO)_6$ (an inseparable mixture of isomers) (18) as an air-stable, red, crystalline solid after recrystallization from pentane/CH$_2$Cl$_2$ (4:1 v/v), mp 101–103 °C. Anal. Calcd for $C_{16}H_{15}Fe_2NO_7S$: C, 40.28; H, 3.18; N, 2.94. Found: C, 40.61; H, 3.28; N, 2.93. IR (CCl$_4$, cm^{-1}): 2963 (w), 2940 (w), 2922 (w), 2896 (vw), 1570 (vw), 1526 (s, ν(C=O) acyl) 1454 (s), 1420 (m), 1385 (w), 1366 (s), 1340 (m), 1239 (m), 1172 (vs), 1155 (m), 1077 (m), 688 (m). IR terminal carbonyl region (CCl$_4$, cm^{-1}): 2069 (vs), 2030 (vs), 1998 (vs), 1959 (vs), 1932 (sh). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.27 (s, 4.74 H, SC(CH_3)$_3$, major isomer), 1.52 (s, 4.26 H, SC(CH_3)$_3$, minor isomer), 3.62 (s, 1.30 H, NCH_3, minor isomer), 3.65 (s, 1.70 H, NCH_3, major isomer), 6.22 (m, 1 H, C(O)C=CHC*H*=CHNMe, both isomers), 6.42 (dd, ^1J = 2.25 Hz, ^2J = 1.00 Hz, 0.40 H, C(O)C=C*H*CH=CHNMe, minor isomer), 6.45 (dd, ^1J = 2.55 Hz, ^2J = 1.00 Hz, 0.60 H, C(O)C=C*H*CH=CHNMe, major isomer), 7.07 (m, 0.40 H, C(O)C=CHCH=C*H*NMe, minor isomer), 7.11 (m, 0.60 H, C(O)C=CHCH=C*H*NMe, major isomer). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 34.38 (q, *J* = 130.4 Hz, SC(*C*H$_3$)$_3$, major isomer), 34.78 (q, *J* = 129.2 Hz, SC(*C*H$_3$)$_3$, minor isomer), 37.72 (q, *J* = 140.2 Hz, N*C*H$_3$, major isomer), 37.91 (q *J* = 138.3 Hz, N*C*H$_3$, minor isomer), 48.21 (s, S*C*(CH$_3$)$_3$, minor isomer), 49.32 (s, S*C*(CH$_3$)$_3$, major isomer), 109.73 (d, *J* = 173.9 Hz, C(O)C=CH*C*H=CHNMe, both isomers), 126.62 (d, *J* = 172.7 Hz, C(O)C=*C*HCH=CHNMe, minor isomer), 127.08 (d, *J* = 171.9 Hz, C(O)C=*C*HCH=CHNMe, major isomer), 131.34 (d, *J* = 183.3 Hz, C(O)C=CHCH=*C*HNMe, minor isomer), 131.61 (d, *J* = 179.4 Hz, C(O)C=CHCH=*C*HNMe, major isomer), 138.74 (s, C(O)*C*=CHCH=CHNMe, minor isomer), 139.04 (s, C(O)*C*=CHCH=CHNMe, major isomer), 207.35, 210.00, 210.10, 210.77, 211.15, 212.05, 212.43, 213.33 (all s, terminal *C*O's, both isomers), 261.61 (s, *C*(O)C=CHCH=CHNMe, major isomer), 263.03 (s,*C*(O)C=CHCH=CHNMe, minor isomer). Mass

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spectrum (EI), m/z (relative intensity): 449 ($M^+ - CO$, 12), 421 ($M^+ - 2CO$, 20), 393 ($M^+ - 3CO$, 24), 365 ($M^+ - 4CO$, 15), 337 ($M^+ - 5CO$, 41), 309 ($M^+ - 6CO$, 66), 281 ($M^+ - 7CO$, 41), 253 (Fe_2S-*t*-Bu(CH=CHCH=CH)$^+$, 46), 225 (Fe_2S-*t*-Bu(C=C)$^+$, 100), 210 (Fe_2SH(C=CHCH=CHN)$^+$, 12), 199 (Fe_2SH(NHC=CHCH)$^+$ + 1H, 25), 160 ($Fe_2SH(NH)^+$, 19), 149 (Fe_2(C=CHCH)$^+$, 14), 144 (Fe_2S^+, 36), 125 (Fe_2CH^+, 12), 111 (FeNMeCH=CH$^+$, 18), 97 (FeNMeC$^+$, 24), 85 (FeNMe$^+$, 28), 81 (FeCCH$^+$, 33), 71 (FeNH$^+$, 35), 57 (FeH$^+$, 84), 41 (CNMe$^+$, 47).

Reaction of [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$] with Bis(1-methyl-2-pyrrolyl)mercury. The standard [Et_3NH][(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$] reagent solution (2.98 mmol) was generated at room temperature. Against a strong flow of nitrogen, 1.09 g (3.01 mmol) of bis(1-methyl-2-pyrrolyl)mercury was added as a solid. The reaction mixture was stirred for 2 h at room temperature during which time a color change to red-brown and the formation of a gray precipitate were observed. TLC indicated the formation of two orange products. The solvent was removed in vacuo to yield a red solid which was dissolved in pentane and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.33 g (0.71 mmol, 48% based on S, *a/e:e/e* = 1.5) of (μ-*t*-BuS)$_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[15] Pentane/CH_2Cl_2 (4:1 v/v) eluted a yellow band. Further purification of this product was achieved by thin-layer chromatography on preparative TLC plates of silica. Pentane eluted an orange band which yielded 0.50 g (1.04 mmol, 35%) of (μ-C(O)C=CHCH=CHNMe)(μ-*t*-BuS)$Fe_2(CO)_6$ (18) (an inseparable mixture of isomers), identified by comparison of its ^1H NMR with that of an authentic sample (experiment above).

Attempted Decarbonylation of (μ-C(O)C=CHCH=CHNMe)(μ-*t*-BuS)Fe(CO)$_6$. A 100-mL Schlenk flask equipped with a rubber septum and a stir-bar was charged with 0.22 g (0.46 mmol) of (μ-C(O)C=CHCH=CHNMe)(μ-*t*-BuS)$Fe_2(CO)_6$ (18) and degassed by three evacuation/nitrogen-back-fill cycles. The flask then was charged with 20 mL of THF and heated at reflux. After 5.5 h the color of the reaction mixture had changed from bright to dark red. TLC indicated the formation of a new product in addition to the presence of unreacted starting material and insoluble decomposition materials. The solvent was removed in vacuo to leave a brown-red oil which was purified by chromatography on preparative TLC plates of silica. Pentane eluted an orange band which gave 0.05 g (0.11 mmol, 49% based on S) of (μ-*t*-BuS)$_2Fe_2(CO)_6$, identified by comparison of its ^1H NMR spectrum with that of an authentic sample.[23] The second band to elute was yellow and gave 0.06 g (0.14 mmol, 30%) of unreacted (μ-C(O)C=CHCH=CHNMe)(μ-*t*-BuS)$Fe_2(CO)_6$ (18) identified by comparison of its ^1H NMR spectrum with that of an authentic sample. A brown band of decomposed iron-containing material remained at the origin.

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Supplementary Material Available: A listing of IR data for new compounds and tables of thermal parameters and hydrogen atom parameters for compound 10c (3 pages). Ordering information is given on any current masthead page.

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Pentamethylcyclopentadienyl Ligand Activation in a Cationic Zirconocene Complex: Formation of an Unusual Pendant Allyl Ligand with 1,3-Butadiene

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Activation of a C_5Me_5 ligand on reaction of $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}$ (1) with excess 1,3-butadiene affords an unusual linked cyclopentadienyl–allyl ligand in $[(C_5Me_5)Zr\{\eta^5{:}\eta^3\text{-}C_5Me_4(CH_2CH_2CHCHCH_2)\}]^+$ (2). Formation of 2 proceeds via elimination of 2-pentene from an observable η^3-allyl intermediate, followed by trapping of the putative tetramethylfulvene product by diene insertion. Stable Lewis-base-free η^3-allyl complexes, $[Cp'_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}]^+$ (Cp′ = C_5Me_5 (**3b**), $(Me_3C)C_5H_4$ (**3c**)), are obtained with 1,2-propadiene.

Introduction

The highly regio- and stereospecific oligo- and polymerization of 1,3-dienes using soluble Ziegler–Natta catalysts, particularly those based on lanthanide metals, is of great practical importance.[1] Although group 4 metallocene/methylaluminoxane systems catalyze the oligo- and polymerization of 1-alkenes[2] and the cyclopolymerization of nonconjugated dienes,[3] reactivity toward conjugated dienes has been observed only in copolymerization reactions with 1-alkenes.[4] Lewis-base-free d^0 metallocene cations

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