Reactions of Triethylammonium Salts of the 
[(µ-CO)(µ-RS)Fe₂(CO)₆]⁻ Anions with Alkynylmercury Compounds. Unexpected Products via Hydrogen Migration Processes†

Dietmar Seyferth,* David P. Ruschke, and William M. Davis

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Martin Cowie and Allen D. Hunter

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received January 26, 1994

The reaction of [Et₃NH][(µ-CO)(µ-RS)Fe₂(CO)₆] with bis(alkynyl)mercury compounds gave different products depending on the nature of the organomercurial. Bis(phenylethynyl)mercury and bis(1-hexynyl)mercury gave µ-η¹:η²-acetylide complexes, (µ-η¹:η²-C=CR)(µ-RS)Fe₂(CO)₆, while bis(3-methoxy-1-propynyl)mercury and bis(3-(dimethylamino)-1-propynyl)mercury formed doubly bridging vinylcarbyne products, (µ-XCH=CHC)(µ-RS)Fe₂(CO)₆, where X = OCH₃, N(CH₃). The vinylcarbyne products resulted from a net 1,2-hydrogen shift from the propargylic carbon atom to the β-carbon atom of the original acetylenic unit. In addition, the reaction with bis(3-methoxy-1-propynyl)mercury gave a tetrairon cluster, [(µ-CH₃OCH₂-CHC)(µ-RS)Fe₂(CO)₆]₂Hg, composed of two butterfly diiron hexacarbonyl moieties (each of which possessed doubly bridging vinylidene and thiolate ligands) bridged by a mercury atom on the butterfly hinges. X-ray crystal structure determinations were carried out on the vinylcarbyne complex (µ-CH₃OCH=CHC)(µ-RS)Fe₂(CO)₆ as well as the dimeric mercury product [(µ-CH₃OCH=CHC)(µ-t-BuS)Fe₂(CO)₆]₂Hg. The reactions of propargylic substituted 1-bromoalkynes also were dependent on the nature of the acetylene. 3-Methoxy-1-bromopropyne formed the µ-η¹:η²-acetylide complex (µ-η¹:η²-C=CHRCH₂OCH₃)(µ-t-BuS)Fe₂(CO)₆, as well as the doubly bridging vinylcarbyne product, while 3-dimethylamino-1-bromopropyne gave only the vinylcarbyne complex. The vinylcarbyne complex (µ-CH₃OCH=CHC)(µ-t-BuS)Fe₂(CO)₆ was converted to the formyl-substituted µ-η¹:η²-vinyl complex (µ-η¹:η²-CH=CHC=O)(µ-t-BuS)Fe₂(CO)₆ upon treatment with aqueous hydrochloric acid or trifluoroacetic acid.

Introduction

In an earlier paper,¹ we reported reactions of the triethylammonium salts of the [(µ-CO)(µ-RS)Fe₂(CO)₆]⁻ anions with alkyl-, aryl-, and vinylmercuric halides. With alkyl- and arylmercuric halides, products of the type (µ-RC=O)(µ-RS)Fe₂(CO)₆ (R = alkyl, aryl) were formed, most likely via the process shown in Scheme 1. However, with vinylmercuric halides, two types of products, 1 and 2, were formed, their yields depending on the substituents on the vinyl carbon atoms. Type 2 complexes were produced by decarbonylation of 1, as was shown in separate experiments.

R₁C=CHR₂

Scheme 1

In view of these findings, it was of interest to see how [Et₃NH][(µ-CO)(µ-RS)Fe₂(CO)₆] complexes react with alkynylmercury compounds. In prior work² we had found that bromoalkynes react with [Et₃NH][(µ-CO)(µ-RS)Fe₂(CO)₆] complexes to give products of type (µ-η¹:η²-R'CH=CHR=O)(µ-RS)Fe₂(CO)₆ (3; eq 1); therefore, such


0276-7333/94/2313-3834$04.50/0 © 1994 American Chemical Society
complexes might be expected to be formed in the reactions of \([\text{Et}_3\text{NHI}(\mu-\text{CO})(\mu-\text{RS})\text{Fe}_2(\text{CO})_6]\) with alkynylmercury compounds.

\[
\begin{align*}
\text{[Et}_3\text{NH]} & \quad \begin{array}{c}
\text{O} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} + \begin{array}{c}
\text{R'C=CR'} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} \quad \begin{array}{c}
\text{S} \\
\text{SR}
\end{array} \quad 25^\circ \text{C} \\
\text{THF}
\end{align*}
\]

(1)

This was found to be the case when simple alkynylmercurials, \((\text{RC}=\text{C})_2\text{Hg}\), were used, but with \(\gamma\)-substituted propynylmercury compounds (\((\text{ZCH}_2\text{Ce})_2\text{Hg}\) \((\text{Z} = \text{CH}_3\text{O}, \text{CH}_3\text{N})\) more complicated chemistry was encountered.

**Results and Discussion**

**Reactions with Dialkynylmercury Compounds** \((\text{R'C}=\text{C})_2\text{Hg} \quad (\text{R'} = \text{C}_6\text{H}_5, \text{n-C}_4\text{H}_9)\). Since \(\text{RC}=\text{C}\) is a good anionic leaving group, these experiments were carried out with mercurials of type \((\text{R'C}=\text{C})_2\text{Hg}\), which are more stable than \(\text{RC}=\text{C}\text{H}_2\text{X}\). Reaction of \((\text{PhCN}=\text{C})_2\text{Hg}\) with \([\text{Et}_3\text{NHI}(\mu-\text{CO})(\mu-\text{EtS})\text{Fe}_2(\text{CO})_6]\) and of \((\text{n-C}_4\text{H}_9\text{Ce}=\text{C})_2\text{Hg}\) with \([\text{Et}_3\text{NHI}(\mu-\text{CO})(\mu-\text{t-BuS})\text{Fe}_2(\text{CO})_6]\) gave the respective \(\mu-\eta^1:\eta^2\)-alkynyl complexes \((\mu-\eta^1:\eta^2\)-alkynyl complexes showed fluxional behavior, very likely due to a flipping motion of the alkynyl ligand across the face of the \(\text{Fe}_2(\text{CO})_6\) core (eq 3).

\[
\begin{align*}
\text{[Et}_3\text{NH]} & \quad \begin{array}{c}
\text{O} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} + \begin{array}{c}
\text{R'C=CR'} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} \quad \begin{array}{c}
\text{S} \\
\text{SR}
\end{array} \quad 25^\circ \text{C} \\
\text{THF}
\end{align*}
\]

(2)

The respective \((\mu-\text{RS})\text{Fe}_2(\text{CO})_6\) complexes, which usually are byproducts in \([\text{Et}_3\text{NHI}(\mu-\text{CO})(\mu-\text{RS})\text{Fe}_2(\text{CO})_6]\) organomercurial reactions,\(^1\) was indicative of the formation of elemental mercury.\(^1\) A black, powdery precipitate of the bridging thiolate ligand. Similar to the \(\mu-\eta^1:\eta^2\)-vinyl complexes, the \(\mu-\eta^1:\eta^2\)-alkynyl complexes showed fluxional behavior, very likely due to a flipping motion of the alkynyl ligand across the face of the \(\text{Fe}_2(\text{CO})_6\) core (eq 3).

\[
\begin{align*}
\text{[Et}_3\text{NH]} & \quad \begin{array}{c}
\text{O} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} + \begin{array}{c}
\text{R'C=CR'} \\
\text{OC}_3\text{Fe} \\
\text{Fe}(\text{CO})_3
\end{array} \quad \begin{array}{c}
\text{S} \\
\text{SR}
\end{array} \quad 25^\circ \text{C} \\
\text{THF}
\end{align*}
\]

(3)

\(\eta^2\)-alkynyl complexes both were deep red oils and were isolated as mixtures of two inseparable isomers due to an axial or equatorial orientation of the \(R\) substituent.
Seyferth et al.

RS’ ‘C
H CYOCH,

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

2a, i.e., the product of the addition of the \([\mu\text{-CO})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\] anion to the C=C bond of \((\text{CH}_3\text{OCH}_2\text{C}=\text{C})\text{Hg}\). The extra (vinylidene) proton would be derived by protonation of the anionic intermediates by \([\text{Et}_3\text{NH}]+\), as was the case in reactions of simple acetylenes with \([\text{Et}_3\text{N}][\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]\).

However, the NMR spectra of 6 were not in agreement with this structure. In the \(^1\text{H} \) NMR spectrum two signals, a complex two-proton multiplet at 4.0 ppm and a one-proton triplet at 6.2 ppm \((J = 6.3 \text{ Hz})\), were observed in addition to the t-BuS and \(\text{CH}_3\text{O} \) resonances. The \(^{13}\text{C} \) NMR spectrum showed a triplet at 74 ppm, a doublet at 140 ppm, and a singlet at 221 ppm, in addition to signals due to the \(\text{CH}_3\text{OCS} \) ligand and five singlets in the terminal CO region (207–211 ppm).

In order to unambiguously determine the structure of the Hg-containing product of the \([\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\] reaction, an X-ray diffraction study was carried out. The complex crystallized in the space group \(P2_1/c\) (No. 14) with some disorder in the outer regions of the molecule. An ORTEP plot showing 40% probability ellipsoids is given in Figure 3. The structure is not an expected one. The complex 6 contains two \(\text{Fe}_2(\text{CO})_6\) units, each of which is bridged by a t-BuS ligand and a \(\text{CH}_3\text{OCH}=\text{C}\) vinylidene ligand, and the two \(\text{Fe}_2(\text{CO})_6\) units also are bridged by the mercury atom. The line drawing shown in Figure 2b makes this clear. The two \([\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\] units are virtually identical (see Table 1 for bond distances and angles). The molecule contains two Fe–Fe single bonds (average \(d(\text{Fe–Fe}) = 2.646 \) Å), symmetrical t-BuS bridges (average \(d(\text{Fe–S}) = 2.260 \) Å), and symmetrical vinylidene bridges (average \(d(\text{Fe–C}) = 1.97 \) Å). The C=C distance of the vinylidene ligands (average \(d(\text{C=C}) = 1.32 \) Å) is in the range normally associated with C=C bonds in olefins, 1.34 Å. Each of the \([\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\] units can be regarded as essentially monoanionic, with each Fe atom having a formal charge of 2+, making the overall complex neutral. The geometry of the mercury atom in 6 is between square planar and tetrahedral, with a dihedral angle of 35.5° between the two planes formed by Fe(1)–Fe(3)–Hg and Fe(2)–Fe(4)–Hg. Thus, in the solid state, this complex is not completely symmetrical about a plane that bisects the two Fe–Fe bonds and contains the Hg atom. It could be that these distortions in the solid state result from packing (intermolecular forces). The \(^1\text{H} \) and \(^{13}\text{C} \) NMR solution spectra of 6 in any case

![Figure 3. ORTEP plot of \([\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\] showing 40% probability ellipsoids.](image)

Table 1. Relevant Bond Distances (Å) and Angles (deg) for \([\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6\]Hg (6)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)–Hg</td>
<td>2.774(2)</td>
</tr>
<tr>
<td>Fe(2)–Hg</td>
<td>2.776(2)</td>
</tr>
<tr>
<td>Fe(3)–Hg</td>
<td>2.772(2)</td>
</tr>
<tr>
<td>Fe(4)–Hg</td>
<td>2.778(2)</td>
</tr>
<tr>
<td>Fe(1)–Fe(3)</td>
<td>2.647(3)</td>
</tr>
<tr>
<td>Fe(2)–Fe(4)</td>
<td>2.645(2)</td>
</tr>
<tr>
<td>Fe(1)–S(1)</td>
<td>2.260(4)</td>
</tr>
<tr>
<td>Fe(2)–S(2)</td>
<td>2.266(4)</td>
</tr>
<tr>
<td>Fe(3)–S(1)</td>
<td>2.260(3)</td>
</tr>
<tr>
<td>Fe(4)–S(2)</td>
<td>2.264(4)</td>
</tr>
<tr>
<td>Fe(1)–C(1)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Fe(2)–C(2)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Fe(3)–C(1)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>Fe(4)–C(2)</td>
<td>1.97(1)</td>
</tr>
<tr>
<td>C(1)–C(3)</td>
<td>1.32(2)</td>
</tr>
<tr>
<td>C(2)–C(4)</td>
<td>1.31(1)</td>
</tr>
</tbody>
</table>

*Estimated standard deviations in the least significant figure are given in parentheses.
show equivalent proton and carbon signals. On the basis of the determined structure, the yield of \( \text{6} \) produced in the \([\text{Et}_3\text{NH}][\mu-\text{CO}]_{\mu-t-\text{BuS}}\text{Fe}_2(\text{CO})_6] / (\text{CH}_3\text{OCH}_2\text{C} = \text{C} \text{H}_2)\text{Hg} \) reaction was 36%. An analogous mercury product was obtained in 40% yield in the reaction of \([\text{Et}_3\text{NH}][\mu-\text{CO}]_{\mu-\text{EtS}}\text{Fe}_2(\text{CO})_6] / (\text{CH}_3\text{OCH}_2\text{C} = \text{C} \text{H}_2)\)Hg.

Transition-metal clusters in which four metal atoms are spiro-bridged by a mercury atom are known.\(^5\) Most of these cluster complexes contain more than four metal atoms, e.g., \([\mu-\text{C}_2\text{t- BuS}]\text{Fe}_2(\text{CO})_6\text{Hg} \). In these the mercury occupies a metal–metal edge-bridging position; hence, only two metal atoms of each polymetal unit of the cluster are involved. One complex containing a \( \mu_2\text{HgM}_2 \) system has been isolated, \([\text{Ni}_2(\mu-\text{CNCH}_3)_{\text{-}}(\text{CNCH}_3)(\text{Ph}_3\text{PCH}_2\text{PPPh}_2)\text{Hg}]\text{[NiCl}_4] \). in which the \([\text{HgNi}_4(\text{Ph}_3\text{PCH}_2\text{PPPh}_2)\] core has the structure \( \text{7} \). The similarity to \( \text{6} \) is striking in that the dihedral angle between the two \( \text{Ni}_2\text{Hg} \) planes is 34.6(1).\(^6\) This suggests that the asymmetry above is not merely a solid-state effect. Complex \( \text{8} \) has been suggested as the product of the disproportionation of complexes of type \( \mu_2\text{HgP}(\mu-\text{HgP})_2\text{CO}_2\text{Hg} / \text{CpW(CO)}_3\text{Hg} \); \( \text{OC}_5\)FmHg, \( \text{OC}_5\text{Fe(OCO)}_5\text{Hg} \), but it was not isolated and only a \( ^{31}\text{P} \) NMR signal at +10 ppm (vs \text{Hg}.)

The orange-red product from the \([\text{Et}_3\text{NH}][\mu-\text{CO}]_{\mu-t-\text{BuS}}\text{Fe}_2(\text{CO})_6] / (\text{CH}_3\text{OCH}_2\text{C} = \text{C} \text{H}_2)\)Hg reaction which was eluted by pentane does not contain mercury. It contains a bridging \( \text{t-BuS} \) ligand, and according to the \( ^1\text{H} \) NMR spectrum, only one isomer is present. As noted above, the organic ligand is not the \( \mu_2\text{HgP}(\mu-\text{HgP})_2\text{CO}_2\text{Hg} / \mu_2\text{Hg-P} / \text{CpW(CO)}_3\text{Hg} \); \( \text{OC}_5\)FmHg, \( \text{OC}_5\text{Fe(OCO)}_5\text{Hg} \), but it was not isolated and only a \( ^{31}\text{P} \) NMR signal at +10 ppm (vs \text{Hg}.) in THF was cited as evidence for its presence.\(^8\)

**Table 2. Relevant Bond Distances (\( \text{Å} \)) and Angles (deg) for (\( \mu\text{-CH}_3\text{OCH} = \text{CHC} \))Fe\(_2\)
(\( \text{CO}_2\text{Hg} \)) (9)**

<table>
<thead>
<tr>
<th>Bond/Dihedral</th>
<th>molecule 1</th>
<th>molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)–Fe(2)</td>
<td>2.5214(6)</td>
<td>2.5035(7)</td>
</tr>
<tr>
<td>Fe(1)–S(1)</td>
<td>2.265(1)</td>
<td>2.257(1)</td>
</tr>
<tr>
<td>Fe(2)–S(1)</td>
<td>2.263(1)</td>
<td>2.261(1)</td>
</tr>
<tr>
<td>Fe(1)–C(7)</td>
<td>1.860(3)</td>
<td>1.843(3)</td>
</tr>
<tr>
<td>Fe(2)–C(7)</td>
<td>1.881(3)</td>
<td>1.879(4)</td>
</tr>
<tr>
<td>Fe(2)–S(1)</td>
<td>2.211(7)</td>
<td>2.202(7)</td>
</tr>
<tr>
<td>C(7)–C(8)</td>
<td>1.146(5)</td>
<td>1.146(6)</td>
</tr>
<tr>
<td>C(8)–C(9)</td>
<td>1.317(5)</td>
<td>1.214(7)</td>
</tr>
<tr>
<td>C(9)–O(7)</td>
<td>1.353(5)</td>
<td>1.406(6)</td>
</tr>
<tr>
<td>O(7)–C(10)</td>
<td>1.411(5)</td>
<td>1.394(7)</td>
</tr>
<tr>
<td>Fe(1)–Fe(2)–C(7)</td>
<td>47.28(9)</td>
<td>47.1(1)</td>
</tr>
<tr>
<td>Fe(2)–Fe(1)–C(7)</td>
<td>48.0(1)</td>
<td>48.4(1)</td>
</tr>
<tr>
<td>Fe(1)–C(7)–Fe(2)</td>
<td>84.7(1)</td>
<td>85.4(2)</td>
</tr>
<tr>
<td>Fe(1)–C(7)–S(1)</td>
<td>134.5(2)</td>
<td>130.0(3)</td>
</tr>
<tr>
<td>Fe(2)–C(7)–S(1)</td>
<td>139.5(2)</td>
<td>143.9(3)</td>
</tr>
<tr>
<td>C(7)–C(8)–C(9)</td>
<td>122.7(3)</td>
<td>117.3(5)</td>
</tr>
<tr>
<td>C(8)–C(9)–O(7)</td>
<td>129.3(3)</td>
<td>124.4(6)</td>
</tr>
<tr>
<td>C(9)–O(7)–C(10)</td>
<td>117.1(3)</td>
<td>122.1(4)</td>
</tr>
<tr>
<td>Fe(1)–S(1)–Fe(2)</td>
<td>67.67(3)</td>
<td>67.29(3)</td>
</tr>
<tr>
<td>Fe(1)–S(1)–O(11)</td>
<td>116.7(1)</td>
<td>118.8(1)</td>
</tr>
<tr>
<td>Fe(2)–S(1)–C(11)</td>
<td>115.3(1)</td>
<td>116.6(1)</td>
</tr>
</tbody>
</table>

\( ^a \) Estimated standard deviations in the least significant figure are given in parentheses.

Complex 9 contains an \( \text{Fe–Fe} \) single bond (average \( d(\text{Fe(1)}–\text{Fe(2)}) = 2.513(7) \) \( \text{Å} \)) and a symmetrically bridging 2-methyl-2-propanethiolate ligand (average \( d(\text{Fe(1)}–\text{S(1)}) = 2.261(1) \) \( \text{Å} \) and \( d(\text{Fe(2)}–\text{S(1)}) = 2.282(1) \) \( \text{Å} \)). The bridging \( \text{t-BuS} \) ligand has the \( \text{t-Bu} \) group in an axial orientation. The carbonye carbon atom bridges the \( \text{Fe(1)}–\text{CO}_2 \) core slightly asymmetrically (average \( d(\text{Fe(1)}–\text{C(7)}) = 1.852(1) \) \( \text{Å} \); \( d(\text{Fe(2)}–\text{C(7)}) = 1.880(4) \) \( \text{Å} \)). These bond distances are both shorter than those in related iron complexes containing bridging carbene or carbene-like systems.\(^9\) The observed asymmetry would appear to result from nonbonded interactions between \( \text{Fe(2)} / \text{Fe(22)} \) and the vinyl moiety, which is bent toward this metal atom. It is noteworthy that the two independent
molecules of 9 display significantly different parameters for the bridging vinylcarbyne ligand. These differences appear to be real, since parameters involving the rest of the two molecules are in excellent agreement.

The solution 13C NMR spectrum of complex 9 was in agreement with the bridging carbyne structure. In particular, the carbyne carbon atom resonance at $\delta$C = 380.47 is far downfield, as expected.10 Note that a related Fe2(CO)$_6$ complex, 10, reported by Ros et al.11 were isolated in each case were the respective ($\mu$-RS)$_2$Fe(CO)$_5$ species and the bridging vinylcarbyne complex 11 (eq 4), which establishes at least a limited

$$[\text{Et}_3\text{NH}]\left[\text{Fe}_2(\text{CO})_6\right] + [\text{CH}_3\text{NCH}_2\text{COC}_2\text{H}_5] \rightarrow \text{Et}_3\text{NH} + [\text{CH}_3\text{NCH}_2\text{COC}_2\text{H}_5] \uparrow$$

(4)

generality, whose limits remain to be explored. The 13C NMR spectra of these products were indicative of the structure shown in eq 4. All showed typical bridging carbonyl carbon atom signals (major, minor isomers): 11a, $\delta$C = 375.32, 364.57; 11b, $\delta$C = 367.53 (both isomers); 11c, $\delta$C = 376.85, 362.97.

In an earlier paper we described the reaction of [Et$_3$NH]($\mu$-CO)(RS)$\text{Fe}_2$(CO)$_6$ complexes with bromoacetylenes (eq 5).2 In view of the results obtained with

$$[\text{Et}_3\text{NH}]\left[\text{Fe}_2(\text{CO})_6\right] + \text{RC} \equiv \text{Br} \rightarrow$$

(5)

(CH$_3$OCH$_2$C==C)Fe$_2$(CO)$_6$ and [(CH$_3$)$_2$NCCH$_2$C==C]Fe$_2$(CO)$_6$, it was of interest to study the reactions of [Et$_3$NH]($\mu$-CO)(RS)Fe$_2$(CO)$_6$ complexes with the corresponding bromoacetylenes. Three products were formed in the reaction of [Et$_3$NH]($\mu$-CO)(t-BuS)Fe$_2$(CO)$_6$ with CH$_3$OCH$_2$C==CBr: ($\mu$-t-BuS)Fe$_2$(CO)$_6$ (15%), the $\mu$-$\eta^1$-$\eta^2$-alkynyl complex 12 (43%), and the $\mu$-vinylcarbyne complex 9 (24%). Similar reaction of (CH$_3$)$_2$NCCH$_2$C==CBr with [Et$_3$NH]($\mu$-CO)(t-BuS)Fe$_2$(CO)$_6$ gave only the $\mu$-vinylcarbyne complexes 11a (49%), 11b (33%), and 11c (28%) in addition to the respective ($\mu$-RS)Fe$_2$(CO)$_6$.

In none of these reactions could a ($\mu$-CO)Fe$_2$(CO)$_6$-vinylcarbyne complex be isolated. TLC examination of the reaction mixture gave no hint of their formation.

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

$$\text{R} \equiv \text{Bu} \left(\text{Me}_3\text{Si}, \text{Ph}\right), \text{Et}$$

11, a R = t-Bu (29%)  
11, b Et (33%)  
11, c Ph (22%)
Reactions of \( [\mu-\text{CO}]_{2}[(\mu-\text{RS})\text{Fe}_{2}(\text{CO})_{6}]^{+} \) with Hg Compounds

Organometallics, Vol. 13, No. 10, 1994 3839

13, containing a displaceable C\( \equiv \)CCH\(_{2}\)OCH\(_{3}\) substituent, could react with another \( [\mu-\text{CO}]_{2}[(\mu-\text{RS})\text{Fe}_{2}(\text{CO})_{6}]^{+} \) anion to give 14. Reaction of the two molar equivalents of C\( \equiv \)CCH\(_{2}\)OCH\(_{3}\) anion generated in these steps with 14 could then introduce the \( \mu-\eta^{1}\eta^{2} \)-C\( \equiv \)CCH\(_{2}\)OCH\(_{3}\) with loss of CO, giving 15. The latter then could be protonated by Et\(_{3}\)NH\(^{+}\) to give the observed 6. In support of the last reaction, it is known that vinylidene-metal complexes can be prepared by protonation of \( \alpha \)-alkynyl-metal complexes.\(^{12}\) The different reaction course that results when Hg(C\( \equiv \)CPh\(_{2}\))\(_{2}\) and Hg(C\( \equiv \)C-\( \alpha \)-C\(_{4}\)H\(_{8}\))\(_{2}\) react with \([\text{Et}_{3}\text{NH}][\mu-\text{CO}]_{2}[(\mu-\text{RS})\text{Fe}_{2}(\text{CO})_{6}]^{+}\) may be due to a lesser stability of the initial intermediate (analogous to 13 in the case of Hg(C\( \equiv \)CCH\(_{2}\)OCH\(_{3}\))\(_{2}\)) relative to extrusion of Hg and migration of the alkynyl group to the carbon atom of a CO ligand. It should be emphasized that this postulated reaction course is speculative; it has no experimental support, but it seems a reasonable one to us.

The formation of the \( \mu \)-carbyne complex 9 possibly could occur via a deprotonation (by the Et\(_{3}\)N released in the reaction course above) or reprotonation sequence of \( \mu-\eta^{1}\eta^{2}-\text{C}=\text{CCH}_{2}\text{OCH}_{3}[(\mu-\text{RS})\text{Fe}_{2}(\text{CO})_{6}]^{2-} \) as shown in Scheme 2. This reaction course also is speculative.

Hydrolysis of the Vinylecarbyne Complex 9. The \( \mu \)-vinylcarbyne complexes obtained in these reactions are vinyl ethers, and as such they might be expected to undergo acid hydrolysis. This was found to be the case.

When a THF solution of 9 was treated with an equimolar amount of aqueous hydrochloric acid, or even with water alone, an immediate color change from deep red to light orange occurred. Removal of THF \( \text{in vacuo} \), extraction of the residue with diethyl ether, and subsequent evaporation of the extracts gave a nearly quantitative yield of an air-stable orange solid. The latter was identified as the \( \mu-\eta^{1}\eta^{2}-\alpha,\beta \)-unsaturated aldehyde complex 16.

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

Independent preparation of a \( \mu-\eta^{1}\eta^{2} \) unsaturated aldehyde complex was effected by the reaction of \([\text{Et}_{3}\text{NH}][\mu-\text{CO}]_{2}[(\mu-\text{EtS})\text{Fe}_{2}(\text{CO})_{6}]^{+}\) with phenylpropargylaldehyde (eq 7). The IR and \(^{1}H\) NMR spectra of the product confirmed its structure as written.

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

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

**Experimental Section**

**General Comments.** All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triethylamine was distilled under nitrogen from calcium hydride and purged with nitrogen prior to use. Ethyl, tert-butyl, and phenyl mercaptans were purged with nitrogen and used without further purification. Triiron dodecacarbonyl, 13 3-methoxy-1-bromopropylene, and 3-(dimethylamino)-1-bromopropyne were prepared by literature procedures. n-Butyllithium (Alfa), mercuric chloride (Alfa), potassium iodide (Mallinckrodt), and sodium hydroxide (Mallinckrodt) were used as received. Phenylacetylene, 1-hexyne, methyl propargyl ether, 3-(dimethylamino)-1-propyne, propargyl alcohol, and (trimethylsilyl)-acetylene were purchased from Aldrich, vacuum-distilled at room temperature when necessary, and purged with nitrogen prior to use.

The progress of all reactions was monitored by thin-layer chromatography (Baker Flex, Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of Mallinckrodt 100 mesh or Sigma SIL-R 100+ mesh silicic acid (ca. 200 mL) in a 350-mL glass fritted filter funnel was used in most cases. Further purification by column chromatography was accomplished with a 300 × 25 mm or a 450 × 25 mm medium-pressure column using Silica S-0507 230–400 mesh silica gel. In addition, preparative thin-layer chromatography plates (EM Science 60 F$_{254}$, silica gel, 20 × 20 × 0.025 cm) were used as needed. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at −20°C. All yields are based on Fe unless otherwise indicated.

Solution infrared spectra (NaCl solution cells) were obtained using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on a JEOL FX-90Q, a Bruker WM-250, a Varian XL-300, or a Varian Gem-300 spectrometer operating at 90, 250, 300, or 300 MHz, respectively. 13C NMR spectra were recorded on a Bruker WH-270, a Varian XL-300, a Varian Gem-300, or a Varian XL-400 spectrometer operating at 67.9, 75.4, 75.5, or 70.5 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan 3200 mass spectrometer operating at 67.9, 75.4, 75.5, or 100.5 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan MAT-731 mass spectrometer operating in the positive ion mode. Masses were correlated using the following isotopes: $^1$H, $^{13}$C, $^{14}$N, $^{16}$O, $^{32}$S, $^{32}$P, and $^{201}$Hg. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory in Herlev, Denmark.

**X-ray Crystallography.** Structure of [(µ-CH$_3$OCH$_2$CH=CH)($\mu$-BuS)Fe$_2$(CO)$_3$]$_2$Hg. A red rod of [(µ-CH$_3$OCH$_2$CH=CH)($\mu$-BuS)Fe$_2$(CO)$_3$]$_2$Hg.
Reactions of $([\mu\cdot CO]/[\mu\cdot RS])Fe_{10}CO_{13}$ with Hg Compounds

Organometallics, Vol. 13, No. 10, 1994 3841

**Table 3. Comparison of Relevant IR, $^1H$ NMR, and $^{13}C$ NMR Spectral Data for (μ-η$^1$;η$^2$-CH=CHC(OH)(μ-t-BuS)Fe$_3$(CO)$_6$(16) and (μ-η$^1$;η$^2$-CD=CHC(OH)(μ-t-BuS)Fe$_3$(CO)$_6$(19)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>X</th>
<th>$\nu_{C=O}$</th>
<th>$\Delta \delta$</th>
<th>$\delta_{H_{\alpha}}$</th>
<th>$\delta_{H_{\beta}}$</th>
<th>$\delta_{H_{\gamma}}$</th>
<th>$\delta_{H_{\delta}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>H$_x$</td>
<td>1692</td>
<td>8.84 (d), $J = 12.21$</td>
<td>3.80 (d), $J = 12.21$, $J' = 5.37$</td>
<td>9.10 (d), $J' = 5.38$</td>
<td>163.10 (d), $J_{CH} = 152.5$</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>D</td>
<td>1694</td>
<td>8.80 (dd), $J = 4.99$</td>
<td>9.10 (d), $J' = 4.29$</td>
<td>162.59 (t), $J_{CH} = 18.0$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $\nu$ values are in cm$^{-1}$, $\delta$ values in ppm, and $J$ values in Hz.

**Scheme 3. Proposed Reaction Course for the Aqueous Acid Hydrolysis of (μ-CH$_3$OCH=CHC)(μ-t-BuS)Fe$_3$(CO)$_6$ (9) To Form (μ-η$^1$;η$^2$-CH=CHC(OH)(μ-t-BuS)Fe$_3$(CO)$_6$ (16)**

CH=C(t-BuS)Fe$_3$(CO)$_6$Hg (which had been grown in pentane/CH$_2$Cl$_2$) having approximate dimensions of 0.156 $\times$ 0.240 $\times$ 0.360 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 25.00$^0$ $< \theta < 29.00$ $^0$, corresponded to a monoclinic cell with dimensions given in Table 4. For $Z = 4$ and $fw = 1078.63$, the calculated density is 1.891 g/cm$^3$. On the basis of the systematic absences of $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at a temperature of 23 $\pm$ 1 °C using the $\omega-2\theta$ scan technique to a maximum $2\theta$ value of 55.0$^0$. $\omega$ scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.37$^0$ with a takeoff angle of 6.0$^0$. Scans of (1.42 + 0.35 tan $\phi$)$^0$ were made at a speed of 16.0$^0$/min (in $\omega$). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of eight rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 31 cm.

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

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

The structure was solved by a combination of the Patterson method and direct methods.$^{17}$ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d(C-H) = 0.95$ Å) and were assigned isotropic thermal parameters which were 20% greater than the $B_{	ext{eq}}$ value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement$^{18}$ was based on 3418 observed reflections ($I > 3\sigma(I)$).

**Table 4. Crystal Data for [(μ-CH$_3$OCH=CHC)(μ-t-BuS)Fe$_3$(CO)$_6$]Hg (6)**

<table>
<thead>
<tr>
<th>empirical formula</th>
<th>C$<em>{30}$H$</em>{58}$O$<em>{14}$S$</em>{2}$Fe$_{4}$Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$fw$</td>
<td>1078.63</td>
</tr>
<tr>
<td>cryst color, habit</td>
<td>red, rod</td>
</tr>
<tr>
<td>cryst dimens (mm)</td>
<td>0.156 $\times$ 0.240 $\times$ 0.360</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
</tr>
<tr>
<td>no. of refls used for unit cell determination</td>
<td>25 (25.0-32.0)</td>
</tr>
<tr>
<td>(2θ range, deg)</td>
<td></td>
</tr>
<tr>
<td>$\omega$-scan peak width at half-height</td>
<td>0.37</td>
</tr>
<tr>
<td>lattice params</td>
<td>[ $a = 15.554(4)$ Å, $b = 12.496(3)$ Å, $c = 19.752(5)$ Å, $\beta = 99.26(2)$°, $V = 3789(2)$ Å$^3$ ]</td>
</tr>
<tr>
<td>space group</td>
<td>$P2_1/c$ (No. 14)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.891 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>2104</td>
</tr>
<tr>
<td>μ(Mo Kα)</td>
<td>56.98 cm$^{-1}$</td>
</tr>
</tbody>
</table>

$^{17}$ Structure solution methods are as follows. PHASE (Patterson Heavy Atom Solution Extractor); Calbrey, J. C. Ph. D. Dissertation, University of Wisconsin at Madison, 1972. DIRDIF (Direct Methods for Difference Structures) – an automatic procedure for phase extension and refinement of difference structure factors; Beurskens, P. T. Technical Report 1998/1; Crystallography Laboratory Toernooiveld: 6525 Ed Nijmegen, The Netherlands.

$^{18}$ Least-squares: function minimized $\sum_{i=1}^{N} [F_{i} - |F_{i}|]^2$, where $\omega = 4F_{o}^2/[F_{o}^2 + (pF_{e}^2)/L_{p}]$, $S$ = scan rate, $C$ = total integrated peak count, $R = \text{ratio of scan time to background counting time}$, $B = \text{total background count}$, $L_{p} = \text{Lorentz-polarization factor}$, and $p = p$ factor.
(I) and 469 variable parameters and converged (largest parameter shift was 0.06 times its ead) with unweighted and weighted agreement factors of $R = 0.036$ and $R^w = 0.047$.

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

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in $F_o^2$ the values for $\Delta f$ and $\Delta f'f''$ were those of Cromer and Waber. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

Structure of ($µ$-CH$_3$OCH$\text{CH}=$C($µ$-Bu$\text{S})F$_2$(CO)$_3$)$\text{H}$ ($9$)

A suitable quality, irregularly shaped red-black crystal of ($µ$-CH$_3$OCH$\text{CH}=$C($µ$-Bu$\text{S})F$_2$(CO)$_3$)$\text{H}$ which had been grown in pentane was mounted on a glass fiber using epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 reflections in the range 22.0° ≤ $2θ$ ≤ 28.8°, which were accurately centered at 22°C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The 1 diffractometry and the lack of systematic absences were consistent with the space groups P1 and P1, the latter of which was ultimately established as the probable one on the basis of the successful refinement of the model and on the location of all hydrogen atoms. A cell reduction failed to show the presence of a higher symmetry cell.

Intensity data in the range $2θ$, $P(\text{Mo Kα}) = 1.535 \text{ g/cm}^3$ 16.831 cm$^{-1}$ of the setting angles of 25 reflections in the range 22.0° ≤ $2θ$ ≤ 28.8°, which were accurately centered at 22°C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The 1 diffractometry and the lack of systematic absences were consistent with the space groups P1 and P1, the latter of which was ultimately established as the probable one on the basis of the successful refinement of the model and on the location of all hydrogen atoms. A cell reduction failed to show the presence of a higher symmetry cell.

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

(24) The cell reduction was performed using a modification of Tracer II by S. L. Lawson. See: Lawson, S. L.; Jacobson, R. A. In The Reduced Cell and Its Crystallographic Applications; Ames Laboratory Reports 15-1141; USEAC: Iowa State University, Ames, IA, April 1965.
employing the o-29 scan technique and using graphite-monochromated Mo Kα radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variations in the intensities of these standards were noted so no correction for decomposition was applied. A total of 6812 unique reflections (h, k, l) was measured and processed in the usual manner using a value of 0.04 for p.39 Of these, 5538 \((F_o^2 > 2\sigma(F_o^2))\) were considered to be observed and were used in subsequent calculations (435 variables).

The structure was solved in the space group \(P1\). The iron positions were obtained from the Patterson map, and all other atoms were obtained by subsequent least-squares and difference-Fourier calculations. Atomic scattering factors for hydrogen30 and the other atoms30 were taken from the usual tabulations; anomalous dispersion terms36 were included in the calculations. All hydrogen atoms were located and were input in the least-squares cycle as fixed contributions in their idealized positions using C–H distances of 0.95 Å. The hydrogen atoms were assigned isotropic thermal parameters of 1 Å\(^2\) greater than the equivalent isotropic value \(B_e\) of their attached carbon atom. All other atoms were refined anisotropically. Absorption corrections were applied to the data using Gaussian integration.

Refinement by full-matrix techniques converged at \(R = 0.038\) and \(R_e = 0.053\). On the final difference-Fourier map, the largest peak was 0.74 e\(\text{Å}^{-3}\); this can be compared to peaks corresponding to carbon atoms on earlier Fourier maps that had intensities of 3.1–6.0 e\(\text{Å}^{-3}\). The alternate space group \(P1\) was rejected, owing to the satisfactory refinement in \(P1\). It should be noted that the crystal structure of \((\mu-\text{CH}_2=\text{CHC})\)(\(\mu-\text{BuS}\))Fe\(_2\)(CO)\(_4\) contains two independent molecules per unit cell, denoted as molecules 1 and 2 in Table 2.

Supplementary material for this structure was submitted with our preliminary communication of a portion of these results39 and was deposited.

**Standard in Situ Preparation of \([\text{Et}_4\text{NH}]\)(\(\mu-\text{RS}\))Fe\(_2\)(CO)\(_4\)l.** A 100-mL Schlenk flask equipped with a rubber septum and a stirbar was charged with 1.51 g (2.98 mmol) of Fe\(_2\)(CO)\(_4\)l and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged successively with 30 mL of THF, 0.42 mL (0.30 g, 3.00 mmol) of triethylamine, and 3.00 mmol of the appropriate thiol. The mixture was stirred for 30 min at room temperature, during which time slow gas evolution and a gradual color change from green to brown-red were observed. The resulting \([\text{Et}_4\text{NH}]\)(\(\mu-\text{RS}\))Fe\(_2\)(CO)\(_4\)l reagent solution then was utilized in situ without further purification.

**Standard in Situ Preparation of \([\text{Li}]\)(\(\mu-\text{OS}\))(\(\mu-\text{RS}\))Fe\(_2\)(CO)\(_4\)l.** A 100-mL Schlenk flask equipped with a rubber septum and a stirbar was charged with 1.51 g (2.98 mmol) of Fe\(_2\)(CO)\(_4\)l and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 mL of THF and 3.00 mmol of the appropriate thiol and cooled to -78 °C in a dry ice/acetone cold bath. Once the flask had been cooled to

---

-78 °C, a hexane solution of n-butyllithium (3.00 mmol) was added slowly by syringe. The deep green reaction mixture was stirred at -78 °C for 30 min. The dry ice/aceton cold bath then was removed and the reaction mixture warmed to room temperature, during which time slow gas evolution and a gradual color change from green to brown-red were observed. The resulting [Li(μ-SiOOCMe3)2Fe]2 reagent solution was stirred for an additional 30 min at room temperature and utilized in situ without further purification.

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

2R'C≡CH + K₂HgI₂ + 2NaOH $\rightarrow$ H₂O + NaOH

(R'C≡CH)₂Hg + 2KI + 2NaI + 2H₂O (9)

Bis(1-hexynyl)mercury. A dried and degassed 500-mL three-necked round-bottomed flask equipped with an overhead stirrer, an addition funnel, and a gas adapter was cooled to 0 °C in an ice bath. Mercuric chloride (8.22 g, 0.100 mol in 100 mL of ethanol), was added slowly by syringe. The deep green reaction mixture was gaseous and liquid terminal acetylenes can be used, although the reaction mixture was stirred at 0 °C for an additional 2 h. The crude product was filtered, washed with three 50-mL portions of water/ethanol (1/1 v/v), and recrystallized from boiling ethanol to give 13.4 g (74% based on (Et₂S)₂Fe₂(CO)₆). Anal. Calcd for CsH₁₀HgO₂: C, 28.36; H, 2.98. Found: C, 28.27; H, 3.02. 1H NMR (CDCl₃, 250 MHz): δ 7.14 (s, 1H, C=CCH₂N(CH₃)₂), 3.36 (s, 2H, C=CCH₂N(CH₃)₂), 1.15-1.44 (m, 2H, CECCH₂CH₂CH₃), minor isomer), 1.14 (s, 2H, CH₂CH₃, major isomer), 2.22 (s, 1H, C=CCH₂N(CH₃)₂), 3.30 (s, 1H, C=CCH₂N(CH₃)₂), 21.86 (t, JCH = 138.2 Hz, CECCH₂N-, both isomers), 208.24 and 209.51 (both s, terminal CO's, both isomers). Anal. Calcd for CsCCH₂OCH₃: C, 32.92; H, 4.42. Found: C, 32.87; H, 4.54. 13C NMR (CDCl₃, 75.4 MHz): δ 124.8 (s, 13C, CECCH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 138.2 Hz, CECCH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers), 21.86 (t, JCH = 128.8 Hz, CECCH₂CH₂N-, both isomers), 128.8 Hz, CECCH₂CH₂N-, both isomers).
Reactions of [(µ-CO)(µ-RS)Fe₂(CO)₃]⁺ with Hg Compounds

spectrum with that of an authentic sample. Fe(CO)₆ gave 0.35 g (0.81 mmol, 27%) of C₆H₅CO₂H and 0.32 g (0.81 mmol, 27%) from pentane; mp 85.0-87.0 °C. Anal. Calcd for C₂₅H₂₂O₇Fe₂: C, 28.19; H, 1.78; Fe, 20.71; O, 42.35. Found: C, 28.42; H, 1.83; Fe, 20.58. 1H NMR (CDCl₃, 300 MHz): δH 1.23 (t, J = 12.6 Hz, SCH₂CH₃, minor isomer), 1.42 (d, J = 142.6 Hz, CH₂OCH₂CH₂CH₃, major isomer), 7.46 (t, J = 157.2 Hz, CH₂OCH₂CH₂CH₃, C₂H₅), 207.05, 207.42, 210.14, 210.54, and 210.80 (all s, terminal CO's), 221.08 (s, CH₂OCH₂CH₃). Mass spectrum (FD): m/z 1079 (M⁺).

Reaction of [EtsNH][µ-CO][µ-ES]Fe₂(CO)₆] with Bis(3-methoxy-1-propynyl)mercury. To the standard [EtsNH][µ-CO][µ-ES]Fe₂(CO)₆] reagent solution (2.98 mmol) was added (CH₂OCH₂CH₃)₂Hg (1.10 g, 5.24 mmol) as a solid. An immediate reaction with brisk gas evolution and a color change from brown-red to deep red were observed. After the reaction mixture had been stirred for 30 min at room temperature, TLC analysis indicated the formation of two orange-red products which moved in pentane and two orange products which moved closely together in pentane/CH₂Cl₂. The solvent was removed in vacuo to yield a brown-red solid residue which was purified by filtration chromatography. Pentane/CH₂Cl₂ (1/1 v/v) then eluted a dark red band which gave 0.61 g (0.60 mmol, 40%) of [(µ-C₃H₅CH₂CH₂CH₂CH₃)₂Hg (a mixture of two inseparable isomers) as an air-stable, red-black solid after recrystallization from pentane/CH₂Cl₂; mp 171.0-172.0 °C. Anal. Calcd for C₂₅H₂₂O₇Fe₃: C, 28.19; H, 1.78; Fe, 20.71; O, 42.35. Found: C, 28.42; H, 1.83; Fe, 20.58. 1H NMR (CDCl₃, 300 MHz): δH 1.23 (t, J = 12.6 Hz, SCH₂CH₃, minor isomer), 1.42 (d, J = 142.6 Hz, CH₂OCH₂CH₂CH₃, major isomer), 7.46 (t, J = 157.2 Hz, CH₂OCH₂CH₂CH₃, C₂H₅), 207.05, 207.42, 210.14, 210.54, and 210.80 (all s, terminal CO's), 221.08 (s, CH₂OCH₂CH₃). Mass spectrum (FD): m/z 1079 (M⁺).

Reaction of [EtsNH][µ-CO][µ-t-BuS]Fe₂(CO)₆] with Bis(3-dimethylamino-1-propynyl)mercury. The standard [EtsNH][µ-CO][µ-t-BuS]Fe₂(CO)₆] reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, ((CH₃)₂NCH₂CH₂CH₂CH₃)₂Hg (0.92 g, 2.51 mmol) was added as a solid. Brisk gas evolution was observed along with a gradual color change to deep brown-red. After the reaction mixture had been stirred for 19 h at room temperature, TLC analysis indicated the formation of an orange and a rose product which moved in pentane and two orange products which moved closely together in pentane/CH₂Cl₂. The solvent was removed in vacuo to yield a brown oil which was purified by filtration chromatography. Pentane eluted an orange band which gave 0.28 g (0.69 mmol, 44% based on [(µ-CH₃CH₂CH₂CH₂CH₃)₂Hg (a mixture of two inseparable isomers) as an air-stable, red-black solid after recrystallization from pentane/CH₂Cl₂; mp 171.0-172.0 °C. Anal. Calcd for C₂₅H₂₂O₇Fe₃: C, 28.19; H, 1.78; Fe, 20.71; O, 42.35. Found: C, 28.42; H, 1.83; Fe, 20.58. 1H NMR (CDCl₃, 300 MHz): δH 1.23 (t, J = 12.6 Hz, SCH₂CH₃, minor isomer), 1.42 (d, J = 142.6 Hz, CH₂OCH₂CH₂CH₃, major isomer), 7.46 (t, J = 157.2 Hz, CH₂OCH₂CH₂CH₃, C₂H₅), 207.05, 207.42, 210.14, 210.54, and 210.80 (all s, terminal CO's), 221.08 (s, CH₂OCH₂CH₃). Mass spectrum (FD): m/z 1079 (M⁺).

(q, J\textsubscript{CH} = 138.5 Hz, N(CH\textsubscript{3}), minor isomer), 48.81 (s, SC(CH\textsubscript{3})\textsubscript{3}, both isomers), 129.09 (d, J\textsubscript{CH} = 160.1 Hz, (CH\textsubscript{3})\textsubscript{2}NCH=CHC, major isomer), 158.71 (d, J\textsubscript{CH} = 170.5 Hz, N(CH\textsubscript{3})=CHC, major isomer), 160.36 (d, J\textsubscript{CH} = 173.2 Hz, (CH\textsubscript{3})\textsubscript{2}NCH=CHC, minor isomer), 211.77, 212.25, 213.20, and 214.45 (all s, terminal CO\textsubscript{s}, both isomers), 364.57 (s, carbonye C, minor isomer), 375.32 (s, carbonye C, major isomer).

**Reaction of [Et\textsubscript{3}NH][\mu-\text{CO}]\mu-\text{EtS})Fe\textsubscript{2}(CO)\textsubscript{6} with Bis-(3-dimethylamino)-1-propynyl)mercury**

The standard [Et\textsubscript{3}NH][\mu-\text{CO}]\mu-\text{EtS})Fe\textsubscript{2}(CO)\textsubscript{6} reagent solution (1.98 mmol) was generated at room temperature. Against a positive flow of nitrogen, ((CH\textsubscript{3})\textsubscript{2}NCH=CHC)\textsubscript{2}Hg (1.28 g, 3.50 mmol) was added as a solid.

Gas evolution was observed along with a gradual color change to brown-red. After the reaction mixture had been stirred for 1.5 h at room temperature, TLC analysis indicated an orange product which moved in pentane and green and orange-red products which moved in pentane/CH\textsubscript{2}Cl\textsubscript{2}. The solvent was removed in vacuo to yield a brown-red residue which was purified by filtration chromatography.

Pentane eluted an orange band which after removal of the solvent gave 0.14 g (0.35 mmol, 35% based on S) of (\mu-\text{PhS})\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{6}.\textsuperscript{32} Further elution with pentane/CH\textsubscript{2}Cl\textsubscript{2} (1/1 v/v) yielded a dark red band which was shown by TLC to be a mixture of two products. This residue was recrystomorphatographed on a 450 x 25 mm medium-pressure column using Sigma 230–400 mesh silica gel. Pentane/CH\textsubscript{2}Cl\textsubscript{2} (1/1 v/v) gave a dark red band which yielded 0.56 g (1.48 mmol, 75%) of (\mu-\text{PhS})\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{6}.

**Reaction of [Et\textsubscript{3}NH][\mu-\text{CO}]\mu-(t-BuS)Fe\textsubscript{2}(CO)\textsubscript{6} with 3-Methoxy-1-bromopropylene**

The standard [Et\textsubscript{3}NH][\mu-\text{CO}]\mu-(t-BuS)Fe\textsubscript{2}(CO)\textsubscript{6} reagent solution (2.98 mmol) was generated at room temperature. CH\textsubscript{3}OCH\textsubscript{2}C=CHBr (0.60 g, 4.05 mmol) was added as a solid. Gas evolution was observed along with a gradual color change to brown-red. After the reaction mixture had been stirred for 30 min at room temperature, TLC analysis indicated the formation of three orange-red products which moved in pentane. The solvent was removed in vacuo to yield a red oil which was purified by filtration chromatography.

Pentane eluted an orange band which gave 0.10 g (0.22 mmol, 15% based on S) of (\mu-(t-BuS))Fe\textsubscript{2}(CO)\textsubscript{6}, identified by comparison of its \textsuperscript{1}H NMR spectrum with that of an authentic sample.\textsuperscript{31} Further elution with pentane/CH\textsubscript{2}Cl\textsubscript{2} (9/1 v/v) yielded a dark red band which gave 0.32 g (0.72 mmol, 24%) of (\mu-(t-BuS))Fe\textsubscript{2}(CO)\textsubscript{6} as an air-stable red-brown solid, identified by comparison of its \textsuperscript{1}H NMR spectrum with that of an authentic sample.\textsuperscript{31} Continued elution with pentane/CH\textsubscript{2}Cl\textsubscript{2} (9/1 v/v) yielded a dark red band which gave 0.56 g (1.29 mmol, 43%) of (\mu-(t-BuS))Fe\textsubscript{2}(CO)\textsubscript{6} (12; a mixture of two inseparable isomers) as an almost air-stable red-brown solid.

**Reaction of [Et\textsubscript{3}NH][\mu-\text{CO}]\mu-(t-BuS)Fe\textsubscript{2}(CO)\textsubscript{6} with Aqueous Hydrochloric Acid.** A 100-mL Schlenk flask
Reactions of \([\mu-CO](\mu-RS)Fe_2CO_3\)^2+ with Hg Compounds

equipped with a stirbar and a rubber septum was charged with \((\mu-CH_3OCH-CH(C=CH-C(OH)H_2)Bu)Fe_2CO_3\) (0.31 g, 0.70 mmol) and degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 20 mL of THF. Aqueous hydrochloric acid (6.0 mL of a 0.12 M HCl solution in H_2O, 0.72 mmol) was added by syringe at room temperature. The flask was equipped with a stirbar and a rubber septum was charged with 0.72 mmol) was added by syringe at room temperature. The flask was then charged with 5 mL of ethanol (90%). In a 50-mL Erlenmeyer flask was charged (2,4-dinitrophenyl)hydrazine (0.11 g, 0.56 mmol), and water (95%) was added as well, which produced an orange-yellow solution. Against a strong purge of nitrogen, the 2,4-DNPH solution was added dropwise to the stirred solution of \((\mu-CO)(\mu-CH_3OCH-CH(C=CH-C(OH)H_2)Bu)Fe_2CO_3\) in the 100-mL Schlenk flask. After 20 drops had been added, the solution turned from deep red-orange to bright red-pink. When all of the 2,4-DNPH solution had been added, the solution was stirred at room temperature for 1 h. The solution then was placed in the refrigerator overnight to allow the product to precipitate. The bright orange power was filtered, washed with ethanol, and dried in vacuo to give 0.31 g (0.52 mmol, 98%) of the corresponding 2,4-dinitrophenylhydrazine \((\mu-CO)(\mu-CH_3OCH-CH(C=CH-C(OH)H_2)Bu)Fe_2CO_3\) as an air-stable solid, mp 150.0 °C dec. The carbon and hydrogen combustion analysis gave a correct analysis for the dihydrate (confirmed by v_H at 3700 cm⁻¹ (m, br) in the IR spectrum). Anal. Cals. for C_{19}H_{20}Fe_2N_4O_12S: C, 35.65; H, 3.15. Found: C, 35.75; H, 2.73. \(^1\)H NMR (CDCl_3, 300 MHz): δ_H = 1.42 (s, 9H, SC(CH_3)_3), 1.55 (s, br, -4H, dihydrate), 4.37 (dd, J_H-H = 13.35 Hz, J_H-H = 1.70 Hz, 1H, CH=C=CH(C=H)=), 7.30 (d, J_H-H = 7.28 Hz, 1H, CH=C=CH(C=H)=). 13C NMR (CDCl_3, 75.4 MHz): δ_C = 127.39 (s, J_C-H = 174.9 Hz, 1H, CH=C=CH(C=H)=), 171.5 Hz, 1H, CH=C=CH(C=H)=), 169 (HSEF=CH=C(=O), C), 145 (HSEF=CH=C(=O), C), 163.03 (s, J_C-C = 2720 Hz, CH=CH(C=O)(H)H_2)Bu)Fe_2CO_3\) (17) as an air-stable
Organometallics, Vol. 13, No. 10, 1994

129.38 (s, C3), 129.98 (d, JCH = 170.5 Hz, C3), 138.18 (s, C4),
144.47 (s, C3), 151.54 (d, JCH = 154.0 Hz, CH=CHCH(=N)),
153.80 (d, JCH = 150.9 Hz, CH=CHCH(=N)), 208.89 (s,
terminal CO's).

Reaction of [Et3NH][μ-CO](μ-EtS)Fe2(CO)6 with Phenylpropargyaldehyde. The standard [Et3NH][μ-CO](μ-EtS)-
Fe2(CO)6 reagent solution (2.97 mmol) was generated at room
temperature. Phenylpropargyaldehyde, C6H5C=CHC(O)H (0.40
mL, 0.43 g, 3.27 mmol) was added by syringe. After 21 h, the
reaction mixture was bright red and TLC analysis showed the
formation of two orange-red products. The solvent was
removed in vacuo to give a red-brown oily solid which was
purified by filtration chromatography. Pentane eluted an
orange band which gave 0.072 g (0.18 mmol, 11% based on S)
of (μ-EtS)2Fe2(CO)6, identified by comparison of its 1H NMR
spectrum with that of an authentic sample.30 Further elution
with pentane/CH2Cl2 (4/1 v/v) gave 0.78 g (1.65 mmol, 56%) of
(μ-η1:η2-C6H5C=CHC(O)H)(μ-EtS)Fe2(CO)6 (18) as an air-stable
red-black solid, mp 118.0–119.0 °C, after recrystallization from
Found: C, 43.28; H, 2.73. IR (CCl4, cm⁻¹): 3080 (vw), 3060
(vw), 2970 (w), 2935 (w), 2870 (vw), 2835 (w), 2780 (w),
2720 (v), 1862 (vs, νC=CC=CH), 1483 (w), 1464 (w), 1442 (m),
1408 (w), 1380 (w), 1343 (m), 1313 (vw), 1257 (m), 1146 (s),
1090 (s), 1048 (vw), 1030 (vw), 996 (vw), 975 (vw), 890 (w),
850 (w), 712 (s), 693 (m), 646 (s), 619 (vs), 610 (vs), 551 (m).
IR for terminal carbonyl region (CCl4, cm⁻¹): 2080 (m), 2060
(vs), 2020 (vs), 2015 (vs), 2005 (vs), 1975 (sh).

Acknowledgment. We at MIT are grateful to the
National Science Foundation for support for the pre-
parative work carried out at MIT. We at the University
of Alberta thank the Natural Sciences and Engineering
Research Council of Canada and the University of
Alberta for financial support. Thanks are due also to
Professor M. I. Bruce for useful suggestions concerning
reaction mechanisms.

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