

ligand can accomplish this. Furthermore, the π -accepting empty orbital offers an ulterior mode of bonding that facilitates bridging between the two centers. All of these factors make the formyl ligand a better migrating group than the alkyl ligand. When $R = H$, the migration still occurs, but more slowly;³ even though the hydrogen atom has no electronegative center bonded to it, the spherical

symmetry of its orbital still allows for fair bridging capabilities.

Acknowledgment. We thank Prof. Charles P. Casey for many helpful discussions and we are grateful to the National Science Foundation for financial support through Grant No. CHE-8601434.

A Simple Route to Hexacarbonyldiiron Complexes Containing a Bridging Thiolate and an Organic Bridging Ligand by Means of $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ Intermediates

Dietmar Seyferth,* Gary B. Womack, Colin M. Archer, and John C. Dewan

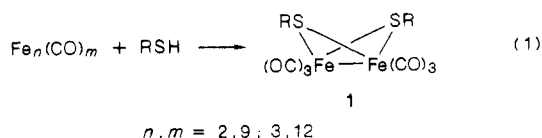
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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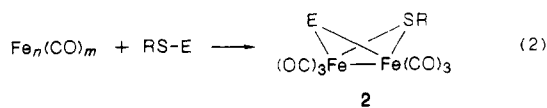
The reaction of thiolate salts, M^+SR^- , with $\text{Fe}_3(\text{CO})_{12}$ in THF at room temperature gives $M[(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]$. These react as nucleophiles at the oxygen of the bridging CO ligand (with $\text{Et}_3\text{O}^+\text{BF}_4^-$) and as nucleophiles at iron (with halides of potentially bridging groups: $\text{RC}(\text{O})\text{Cl}$, $\text{Me}_2\text{NC}(\text{S})\text{Cl}$, allyl chloride, propargylic halides) to give products of type $(\mu\text{-RS})(\mu\text{-organic group})\text{Fe}_2(\text{CO})_6$ in good yield. A less practical route to such products involves the action of 2 molar equiv of LiBEt_3H on $(\mu\text{-CH}_3\text{CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$, followed by addition of the halide electrophile. The reaction of the $[(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]^-$ anions with propargylic halides was shown to proceed by way of an $\text{S}_\text{N}2'$ mechanism. The structures of $[\text{Et}_3\text{NH}](\mu\text{-CO})(\mu\text{-mesitylS})\text{Fe}(\text{CO})_6$, $(\mu\text{-allyl})(\mu\text{-C}_2\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$, and $(\mu\text{-allenyl})(\mu\text{-}(\text{CH}_3)_3\text{CS})\text{Fe}_2(\text{CO})_6$ were determined by X-ray diffraction.

Introduction

Diiron hexacarbonyl complexes containing two bridging thiolate ligands are readily prepared as shown in eq 1.¹



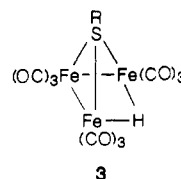
However, dinuclear complexes containing a bridging RS group in conjunction with a different type of bridging ligand are not readily accessible. The reaction shown in eq 2 serves this purpose, and examples are known where



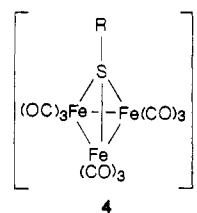
E is $\text{R}'_2\text{P}$,² $\text{CH}_2=\text{CH}$,³ $\text{R}'\text{SC}(\text{S})$,⁴ $\text{R}'\text{OC}(\text{S})$,⁵ $\text{R}'\text{C}(\text{NR}'')$,⁶ and $\text{R}'\text{C}\equiv\text{C}$.⁷ Such reactions generally give only poor-to-moderate product yields, and, furthermore, the starting RS-E compound is not always easily available. We report here the development of a new method of preparation of

complexes of type 2 which does not require the prior synthesis of an RS-E compound, a reaction which is based instead on the reactivity of an intermediate formed by the action of thiolate anions, RS^- , on triiron dodecacarbonyl.

The first report of the reaction between organic thiols and $\text{Fe}_3(\text{CO})_{12}$, by Hieber and Spacu in 1937,⁸ provided examples of the reaction shown in eq 1. Many complexes of type 1 have been reported since that time.¹ Reactions of secondary and tertiary thiols with $\text{Fe}_3(\text{CO})_{12}$ also gave trinuclear complexes of type 3.⁹ Such complexes could



be deprotonated with a tertiary amine, and the resulting anionic species 4 reacted with a variety of electrophiles,



for instance, R_2PCl , R_2AsCl , RPCl_2 , and Cl_2 , to give new $\text{Fe}_3(\text{CO})_9$ cluster complexes.¹⁰ In related work, Takács and

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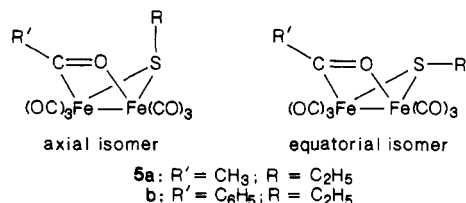
Table I. IR Data for the $[(\mu\text{-E})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ Anions

anion	cation	$\nu(\mu\text{-CO}), \text{cm}^{-1}$	solvent
6	Et_3NH	1743	THF
6	Na	1745 1697	THF
6	Li	1745 1670	THF
7	Ph_4P	1735	CH_2Cl_2
8	Li	1645	THF
8	PPN	1710	THF

Markó reported that sodium thiolates react with $\text{Fe}_3(\text{CO})_{12}$ in refluxing THF to give solutions containing the sodium salt of the type 4 anions.¹¹ It was our attempt to prepare the sodium salt of a type 4 anion by the Takács/Markó procedure which led us into the new area which is the subject of this paper.

Results and Discussion

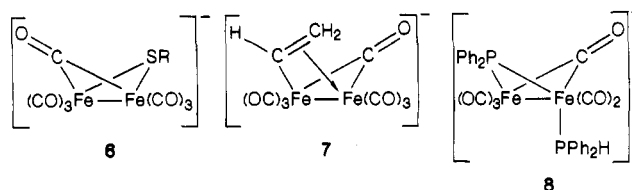
When $\text{Fe}_3(\text{CO})_{12}$ was added to a solution of sodium ethanethiolate (prepared by the action of sodamide on ethanethiol in THF) at room temperature, a vigorous reaction ensued, with brisk gas evolution and formation of a red-brown solution. This was unexpected, since Takács and Markó had not mentioned an initial reaction at room temperature. Nevertheless, examination of the reaction mixture by thin-layer chromatography (TLC) showed that all of the iron carbonyl had been consumed within a few minutes. Accordingly, the mixture was stirred at room temperature for 1 h, and then a slight excess of acetyl chloride was added. After the reaction mixture had been stirred at room temperature, the major product, isolated in 26% yield, was **5a** (a mixture of isomers, 2.2:1 equatorial



Et/axial Et (e-Et/a-Et)), a dinuclear bridging acetyl complex. A trinuclear complex did not appear to have been formed. A similar reaction was found to occur between $\text{C}_2\text{H}_5\text{SLi}$ and $\text{Fe}_3(\text{CO})_{12}$. A red-brown solution was formed at -20°C in THF; addition of acetyl chloride then gave **5a** in 36% yield (e-Et/a-Et = 2.5).

In an attempt to improve the product yield, the intermediate dinuclear anionic species derived from $\text{Fe}_3(\text{CO})_{12}$ was generated by means of an organic base. In this approach, ethanethiol and triethylamine were added to a green THF solution of $\text{Fe}_3(\text{CO})_{12}$ at room temperature. After 5 min all of the triiron dodecacarbonyl had been consumed and a red-brown solution resulted. Stirring was continued for another 10 min, and then an excess of acetyl chloride was added. After a reaction period of 20 h, **5a** was isolated in 52% yield as a 3:1 (e-Et/a-Et) mixture of geometric isomers. Following the same procedure, benzoyl chloride was used as the quenching electrophile and an 83% yield of **5b** was isolated as a 2.3:1 (e-Et/a-Et) mixture of both isomers. (Both **5a** and **5b** had been synthesized earlier in this study by the reaction of the corresponding S-alkyl thioester, $\text{RC}(\text{O})\text{SR}'$, and $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$.)

This new method of generating the dinuclear anionic intermediate is a convenient one which we used to good advantage in our subsequent research. All available evidence indicates that the dinuclear anionic intermediate formed in the $\text{RS}^-/\text{Fe}(\text{CO})_{12}$ reaction is **6**. Similar species with other bridging ligands, **7**¹² and **8**,¹³ have been reported recently. The infrared spectra of all of these species are



characterized by bands in the bridging $\nu(\text{CO})$ region (Table I). The IR spectra of the Na^+ and Li^+ salts of **6** revealed two bands assignable to bridging carbonyl vibrations. In the case of the $[\text{Et}_3\text{NH}]^+[\text{6}]^-$ complex only the higher wavenumber band was observed at 1743 cm^{-1} . The lower frequency bands in the infrared spectra of the sodium and lithium salts of **6** no doubt are due to ion pairing interaction of the metal cation at the $\mu\text{-CO}$ oxygen atom. The higher wavenumber absorption bands, which are independent of the cation, are attributed to the free anion.¹⁴

Although the infrared spectra and all of the reaction chemistry of the species which we assumed to be $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ anions supported this structure, a more conclusive structure proof was desirable. In a search for a crystalline salt we prepared among others, $[\text{Et}_3\text{NH}](\mu\text{-}2,4,6\text{-}(\text{CH}_3)_3\text{C}_6\text{H}_2\text{S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ (**9**). Crystals suitable for X-ray crystallography could be grown from a diethyl ether solution of this salt. The crystalline solid was found to be air-sensitive, and samples decomposed slowly even at -20°C under dry nitrogen. The material was best stored under an atmosphere of carbon monoxide.

The structure of the anion in **9**, as determined by a single-crystal X-ray diffraction study of salt **9**, is shown in Figures 1 and 2. The structure of the anion is indeed one of a dinuclear "butterfly" complex, as we had assumed. The carbonyl and the 2,4,6-trimethylbenzenethiolate bridges each are symmetrical. The Fe-C and Fe-S bond distances of the bridging ligands are not significantly different from those observed in similar $\text{Fe}_2(\text{CO})_6$ complexes with bridging organosulfur ligands or bridging CO ligands.¹⁵⁻¹⁸ The C=O bond distance for the bridging carbonyl in **9** of 1.208 (7) Å is typical of carbonyls bridging a $\text{Fe}_2(\text{CO})_6$ moiety.¹⁷ The distance between the two iron atoms in the anion of salt **9** is relatively short, 2.494 (1) Å, in a comparison with Fe-Fe distances in similar bridged ligands.¹⁵⁻²⁰

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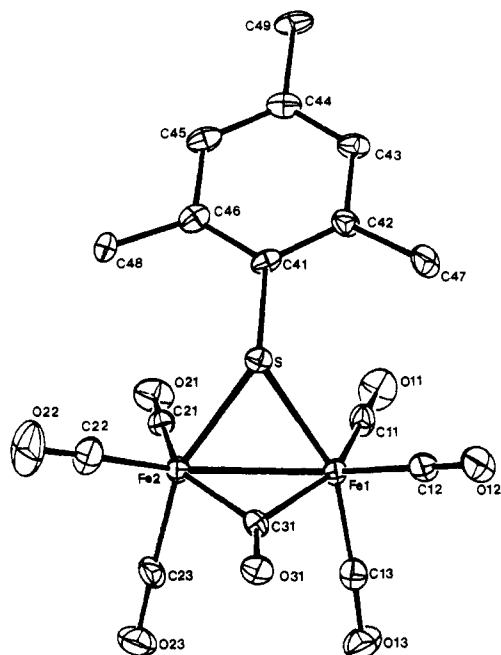


Figure 1. ORTEP representation of the molecular structure of the anion in $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-C}_6\text{H}_2\text{Me}_3\text{S})\text{Fe}_2(\text{CO})_6]$ (**9**) as viewed along a direction perpendicular to the Fe-Fe bond. Probability ellipsoids are drawn at the 30% level.

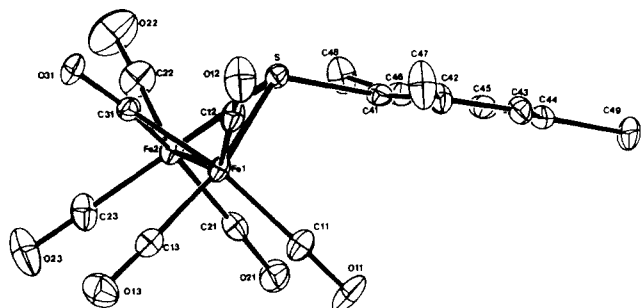
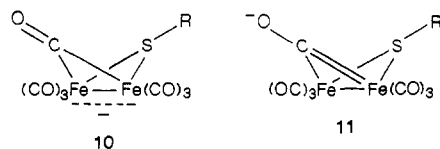


Figure 2. ORTEP representation of the molecular structure of the anion in $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-C}_6\text{H}_2\text{Me}_3\text{S})\text{Fe}_2(\text{CO})_6]$ (**9**) as viewed along a direction that is almost parallel to the Fe-Fe bond. Probability ellipsoids are drawn at the 30% level.

In preliminary communications, we have already shown that the chemistry of the simple anions of type **6** is unexpectedly varied and rich.¹⁸ In this paper we deal with some of the more straightforward chemistry of anions of type **6**. In considering which reactions of anions of type **6** to study and how to interpret the results, it is useful to give thought to the site of the negative charge in the anion. Most likely, this charge will be concentrated at the metal centers and at the oxygen, and we may write the anion as a resonance hybrid, with canonical forms **10** and **11**. In



11 the CO bridge is formally a deprotonated hydroxycarbyne. In terms of reactivity, we may, on the basis of this description of anions of type **6** as **10** ↔ **11**, expect that electrophiles will attack either at iron or at the oxygen atom of the CO bridge.

The formation of the bridging acyl complexes **5** by reaction of anion **6** with acyl chlorides may be rationalized as shown in Scheme I: initial attack at iron, followed by displacement of CO and formation of the acyl bridge be-

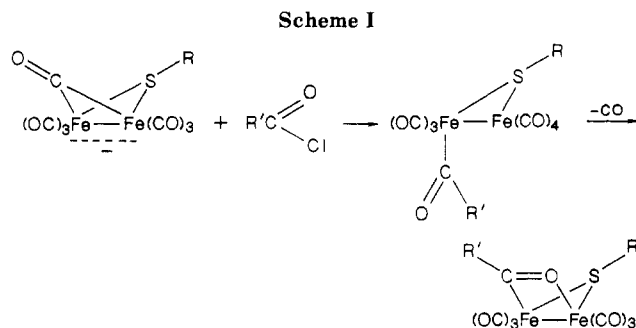


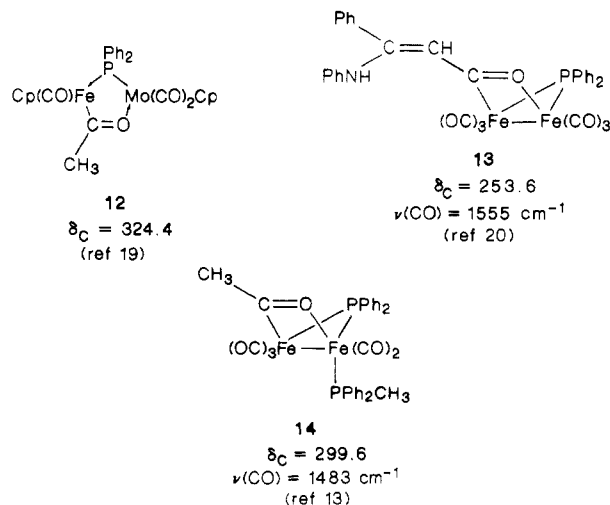
Table II. Some Interatomic Distances (Å) and Angles (deg) for **18**

interatomic distances	bond angles
Fe(1)-Fe(2) = 2.675 (1)	Fe(1)-S-Fe(2) = 73.2 (1)
Fe(1)-S = 2.235 (2)	Fe(1)-C(3)-C(4) = 89.6 (3)
Fe(1)-C(3) = 2.119 (5)	Fe(1)-Fe(2)-S = 53.1 (1)
Fe(1)···C(4) = 2.546 (4)	Fe(1)-Fe(2)-C(5) = 89.9 (1)
Fe(2)-S = 2.251 (2)	Fe(1)-S-C(1) = 86.2 (1)
Fe(2)-C(5) = 2.139 (5)	Fe(2)-Fe(1)-S = 53.7 (1)
Fe(2)···C(4) = 2.445 (4)	Fe(2)-Fe(1)-C(3) = 86.2 (1)
S-C(1) = 1.823 (5)	Fe(2)-S-C(1) = 113.6 (2)
C(1)-C(2) = 1.513 (9)	C(3)-C(4)-C(5) = 126.3 (7)
C(3)-C(4) = 1.426 (8)	C(4)-C(5)-Fe(2) = 84.3 (3)
C(4)-C(5) = 1.414 (8)	
Fe-CO(mean) = 1.784	
C-O(mean) = 1.137	

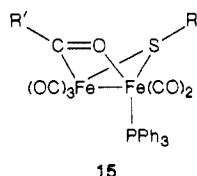
tween the iron atoms. This general sequence has served to explain much of the chemistry observed for anions of type **6** as outlined below.

In later experiments, the anions **6** mostly were generated by the RSH/ Et_3N route described above. Also, the RSLi route was simplified and improved: The slow addition of the *n*-BuLi solution to a THF solution of the thiol and $\text{Fe}_3(\text{CO})_{12}$ at -78°C , followed by warming to room temperature, resulted in the usual color change from green to red-brown. Yields of products derived from **6** generated by either procedure generally were good to excellent.

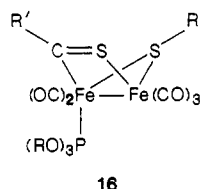
More reactions of anions of type **6** with acyl chlorides were carried out, and a number of complexes of type **5** were prepared (Table II). In some, but not all, reactions, the NMR spectra of the product indicated the presence of both equatorial and axial isomers. The most characteristic spectroscopic features of the products in Table II are the bridging CO frequency of the infrared spectrum, and the ^{13}C NMR resonance due to the acyl carbon atom at very low field (287–306 ppm). ^{13}C resonances in that range are diagnostic for bridging acyl groups, as the literature values for complexes **12**, **13**, and **14** show.



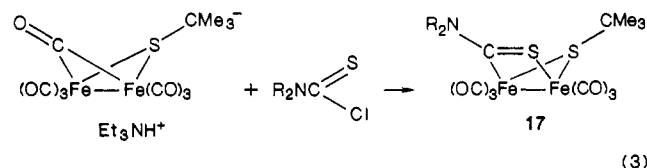
Some of the μ -acyl complexes of type 5 were oils. These were derivatized as their solid, analyzable mono(triphenylphosphine) substitution products 15. The acyl



carbon atom resonances in the ^{13}C NMR spectra of complexes of type 15 were singlets, with no coupling to ^{31}P . For this reason, their structures were assumed to be as written. In support of this assumption is the report that in the ^{13}C NMR spectrum of 16 the thioacyl carbon atom is coupled to phosphorus, ^{31}P ($J = 4.6\text{--}6.1$ Hz).^{5,21}

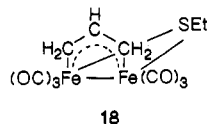


Conceptually, the reaction of anions of type 6 with N,N -dialkylthiocarbamoyl chlorides (eq 3) is closely related to their reaction with acyl halides. Complexes of type 17 ($R = \text{CH}_3, \text{C}_2\text{H}_5$) were prepared in high (>80%) yield. The $\text{C}=\text{S}$ resonances in the ^{13}C NMR spectra were observed at 244.6 ($R = \text{CH}_3$) and 241.7 ppm ($R = \text{C}_2\text{H}_5$).



In view of the results obtained when acyl chlorides and N,N -dialkylthiocarbamoyl chlorides were the electrophiles used (which were rationalized in terms of the sequence shown in Scheme I), it was of interest to carry out reactions of anions of type 6 with wholly organic halides, the organic groups of which were potential bridging ligands.

One such organic species is the allyl group. Accordingly, allyl chloride was added to the $\text{Fe}_3(\text{CO})_{12}/\text{EtSH}/\text{Et}_3\text{N}$ mixture. The same experimental observations were noted as described before; the solution became red and a white precipitate formed. A red, crystalline solid, mp 41–42 °C, was obtained in 80% yield after filtration chromatography of the reaction mixture. This new product was assumed to be a diiron complex with a bridging allyl ligand, 18. The



mass spectrum of this solid, which showed peaks for the parent ion and successive loss of six carbonyl ligands, and the combustion analysis confirmed the elemental composition of 18. The ^{13}C NMR spectrum indicated that the allyl ligand was bound symmetrically in the complex; a signal for the two allyl methylene carbon atoms appeared as a triplet at δ_{C} 20.9 ($J = 154$ Hz). In the ^1H NMR spectrum, the allyl protons were observed as a multiplet of δ 4.76 and two doublets at δ 0.47 ($J(\text{HH}_{\text{anti}}) = 12.6$ Hz)

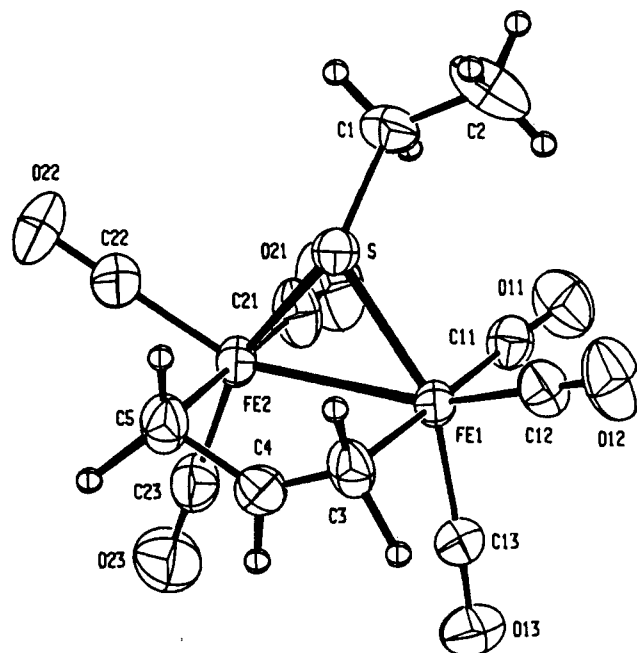


Figure 3. ORTEP representation of the molecular structure of $(\mu\text{-CH}_2\text{CHCH}_2)(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ (18) showing the 40% probability thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms are drawn as arbitrary spheres with $\beta = 1.0$ Å.

and 1.97 ($J(\text{HH}_{\text{syn}}) = 7.5$ Hz) corresponding to the anti and syn hydrogens. The coupling constants for the anti and syn allyl protons compare well with those reported for two dinuclear palladium complexes containing bridging allyl ligands.^{22,23} Transition-metal compounds with μ -allyl functions are not plentiful,²⁴ but X-ray diffraction studies have been accomplished for several compounds with this ligand bridging both bonded^{22,23,25} and nonbonded metal centers.²⁶

Desiring to confirm unambiguously the presence of a μ -allyl ligand, an X-ray diffraction study of 18 was undertaken. Single crystals of 18 suitable for this purpose were grown from methanol solution at -20 °C. The structure determination of 18 confirmed that it was a diiron hexacarbonyl complex with both an ethanethiolate and allyl ligand bridging the two metals (Figure 3 and Table II).

The thiolate ligand is bound slightly asymmetrically across the metals [$\text{Fe}(2)\text{-S} = 2.251$ (2) Å; $\text{Fe}(1)\text{-S} = 2.235$ (2) Å] as in the allyl ligand [$\text{Fe}(1)\text{-C}(3) = 2.119$ (5) Å; $\text{Fe}(2)\text{-C}(5) = 2.139$ (5) Å], although this deviation from symmetry was not great enough to be detected spectroscopically. The plane of the allyl carbon atoms is tilted by 6.53° with respect to the Fe-S-Fe plane with C(4) being tipped slightly toward the latter plane. The carbon-carbon distances of the allyl unit [$\text{C}(3)\text{-C}(4) = 1.426$ (8) Å; $\text{C}(4)\text{-C}(5) = 1.414$ (8) Å] lie between the values reported for single and double carbon-carbon bonds, indicating the ligand is best regarded as a delocalized μ -allyl ligand.

The formation of 18 could have taken place by either an $\text{S}_{\text{N}}2$ or an $\text{S}_{\text{N}}2'$ mechanism. This question of mechanism was examined in the case of propargyl bromide. This

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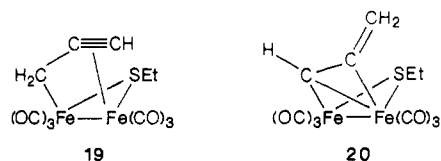
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Table III. Relevant Bond Lengths (Å) and Angles (deg) for 21

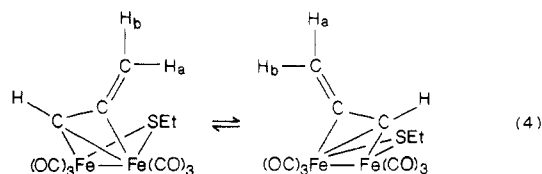
bond lengths	bond angles
Fe(1)–Fe(2) = 2.550 (1)	Fe(1)–C(5)–Fe(2) = 77.5 (2)
Fe(1)–S = 2.250 (2)	Fe(1)–C(5)–C(6) = 124.1 (5)
Fe(1)–C(5) = 1.982 (6)	Fe(1)–Fe(2)–C(5) = 49.4 (2)
Fe(2)–S = 2.283 (2)	Fe(1)–Fe(2)–C(6) = 78.3 (2)
Fe(2)–C(5) = 2.091 (6)	Fe(1)–Fe(2)–S = 55.2 (1)
Fe(2)–C(6) = 2.125 (6)	Fe(1)–S–C(1) = 121.9 (2)
S–C(1) = 1.867 (6)	Fe(2)–Fe(1)–S = 56.4 (1)
C(1)–CH ₃ (mean) = 1.522	Fe(2)–C(5)–C(6) = 72.5 (4)
C(5)–C(6) = 1.363 (9)	Fe(2)–C(6)–C(5) = 69.8 (4)
C(6)–C(7) = 1.335 (9)	Fe(2)–S–C(1) = 119.5 (2)
Fe–CO(mean) = 1.780	C(5)–Fe(1)–S = 83.0 (2)
C–O(mean) = 1.144	C(5)–C(6)–C(7) = 156.7 (7)
	C(5)–Fe(2)–C(6) = 37.7 (2)

electrophile reacted with [Et₃NH][(μ -EtS)(μ -CO)Fe₂(CO)₆] to give a red, crystalline solid in 91% yield. If an S_N2 mechanism were operative, the expected product would be 19. An S_N2' process would be expected to give a μ - σ , π -allenyl complex, 20. The proton NMR spectrum of

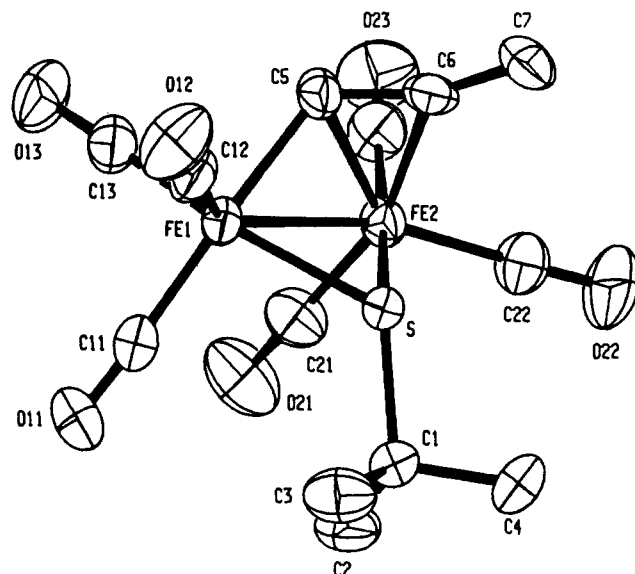


the product favored 20: the methylene protons were equivalent, occurring as a doublet ($J = 4.9$ Hz), due to long-range coupling, at δ 5.30 in the olefin region. The methine proton produced a triplet ($J = 4.9$ Hz) at δ 7.39. The ¹³C NMR spectrum did not provide conclusive information. The carbon signals of the organic ligand appeared at δ_C 93.4 (t, $J = 167$ Hz), 114.9 (d, $J = 162$ Hz), and 176.6 (s) with the expected proton-coupling patterns. The carbon signals of the organic ligand appeared at δ_C 93.4 (t, $J = 167$ Hz), 114.9 (d, $J = 162$ Hz), and 176.6 (s) with the expected proton-coupling patterns.

In 20 the methylene group is not bound to the metals at all, instead the ligand is bound like a bridging σ , π -vinyl group.²⁷ A fluxional process of μ -vinyl ligands by which they change their coordination from one metal to the other as shown in eq 4 has been suggested to explain the dynamic behavior of these ligands.²⁸ Such a process for 20 would equilibrate the two methylene hydrogens as they exchange positions when the ligand flips from one metal to the other (eq 4).



Since the mass spectrum and combustion analysis confirmed that the product had the correct elemental composition, an X-ray diffraction study was carried out in order to resolve the structural question. Crystals suitable for this purpose, however, could not be obtained for the SEt compound. The problem was resolved by adding propargyl bromide instead to the Fe₃(CO)₁₂/Me₃CSH/Et₃N system from which a red, crystalline solid, 21, was

**Figure 4.** ORTEP representation of the molecular structure of (μ , η^2 -CHCCH₂)(μ -Me₃CS)Fe₂(CO)₆ (21) showing the 40% probability thermal ellipsoids and the atom-labeling scheme.**Table IV. ¹³C NMR Data for the μ -Allenyl Complexes^{a,b}**

R'	R	R''	$\delta_C(\text{Fe}_2\text{CR}')$	$\delta_C(\text{FeC}=\text{C})$	$\delta_C(=\text{CR}_2)$
H	H	Et	114.8 (d, $J = 162$ Hz)	176.6	93.4 (t, $J = 167$ Hz)
H	H	CMe ₃	113.2 (d, $J = 162$ Hz)	177.7	95.5 (s, $J = 166$ Hz)
Et ^c	H	CMe ₃	148.6	177.1	94.7 (t, $J = 163$ Hz)
H	Me	CMe ₃	119.6 (d, $J = 166$ Hz)	171.8	115.4

^a Peaks reported in ppm downfield from internal tetramethylsilane. ^b Solvent used was C₆D₆. ^c Solvent used was CD₂Cl₂.

isolated in 92% yield. The ¹H and ¹³C NMR spectra confirmed that the organic ligand in this compound was bound in the same manner as in the SEt derivative. Again the CH₂ protons were equivalent in the ¹H NMR spectrum, appearing as a triplet ($J = 4.4$ Hz) at δ 5.39.

The X-ray diffraction study of 21 proved that the organic group was bound as the μ - σ , π allenyl ligand (Figure 4 and Table III). As in 18, the thiolate ligand bridges the two iron atoms slightly asymmetrically with Fe–S distances of 2.283 (2) and 2.250 (2) Å. Complex 21 has the same basic structural features reported for σ , π -vinyl-bridged Fe₂(CO)₆ systems.²⁹ The Fe–Fe distance of 2.550 (1) Å is significantly shorter than the 2.675 (1) Å distance in 18. This probably reflects the difference in bite sizes of the two organic bridges (i.e., diatomic as opposed to triatomic). The C(6)–C(7) distance of 1.335 (9) Å is a standard carbon–carbon double bond length, while the C(5)–C(6) distance of 1.363 (9) Å is elongated due to π -coordination to Fe(2). This distance is comparable to the C–C bond distance of other μ -vinyl groups.^{27a,b,28b,29}

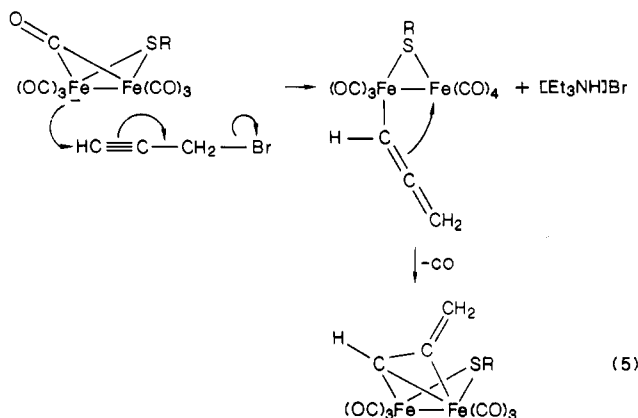
Further proof for an S_N2' mechanism as shown in eq 5 was provided by the reaction of 3-bromo-3-methyl-1-bu-

(27) (a) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546. (b) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (c) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 3474.

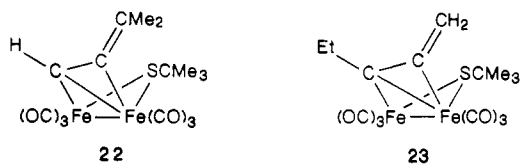
(28) (a) Shapley, J. R.; Richter, S. L.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

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tyne, $\text{HC}\equiv\text{CCMe}_2\text{Br}$, with the $\text{Fe}_3(\text{CO})_{12}/\text{Me}_3\text{CSH}/\text{Et}_3\text{N}$ system. The product, isolated in 95% yield, was **22**. A



similar reaction of $\text{EtC}\equiv\text{CCH}_2\text{Cl}$ produced **23** in 77% yield. These compounds were confirmed to have the μ -allenyl structure by the chemical shifts of their allenyl ligand carbons in the ^{13}C NMR spectra (Table IV) which are in good agreement with the values found for **20** and **21**.



The ^1H NMR spectra of **22** and **23** showed that they too had fluxional allenyl ligands. For **22** the two allenyl methyl groups were equivalent at room temperature, giving rise to a singlet at δ 1.81 (toluene- d_6). The spectrum of **23** showed two broad peaks at δ 2.55 and 5.20, both integrating for two protons, corresponding to the ethyl and allenyl CH_2 groups, respectively. This indicates that the fluxional process for **23** is slower than that for **20**, **21**, and **22** for which the fast-exchange ^1H NMR spectra were obtained at room temperature. A variable-temperature ^1H NMR study of **23** confirmed the dynamic behavior of this compound (Figure 5). As the temperature was lowered, the singlet of the allenyl CH_3 groups broadened until two peaks became observable below -23°C where the methyl groups give rise to two sharp singlets at δ 1.88 and 1.75. The *tert*-butyl group remained a sharp singlet over the entire temperature range at δ 1.07. From these spectra an approximate energy of activation for this fluxional process could be calculated as $\Delta G^\ddagger = 12.4 \text{ kcal mol}^{-1}$, assuming a coalescence temperature of -23°C .³⁰ This ^1H NMR study indicates that the dynamic process depicted in eq 4 is operating in these complexes. It has been suggested recently that μ_2 -acetylide³¹ and μ_2 -acyl³² ligands can also display this type of fluxional behavior.

The μ -allyl and μ -allenyl complexes thus far reported potentially can exist as two isomers with the thiolate alkyl group oriented in either the axial or equatorial position. However, only one isomer could be detected for any of

(30) ΔG^\ddagger was calculated by using the equation

$$\Delta G^\ddagger = 19.14T_c(9.97 + \log T_c/\delta\nu)(\text{J mol}^{-1})$$

where T_c is the coalescence temperature (220 K) and $\delta\nu$ the shift difference (Hz) of the two exchange sites in the limiting low-temperature spectra. See: Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1973; p 243.

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(32) Jensen, C. M.; Chen, Y. J.; Kaesz, H. D. *J. Am. Chem. Soc.* 1984, 106, 4046.

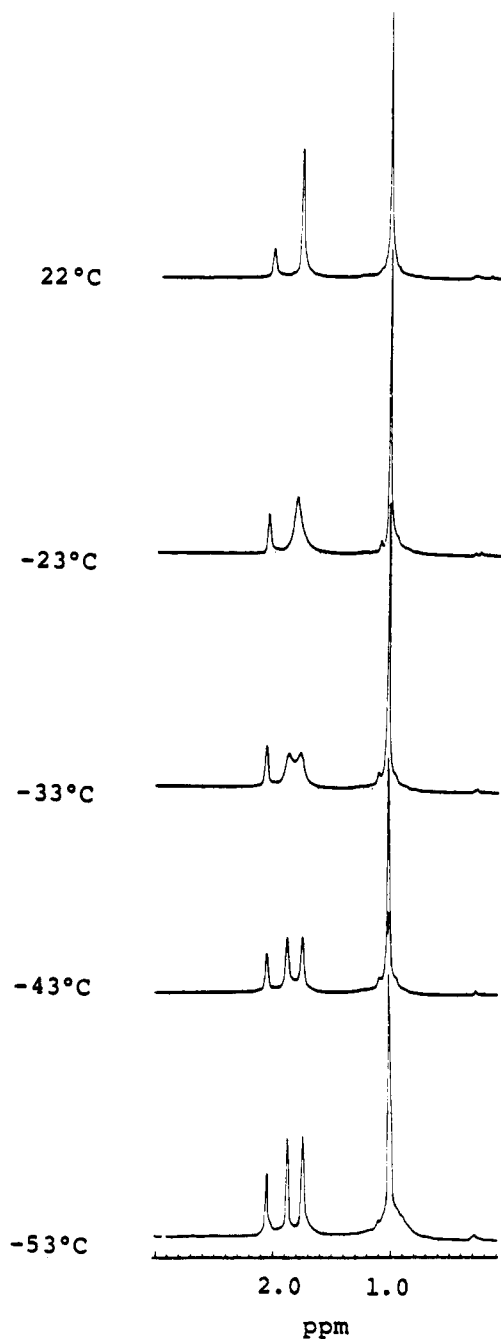
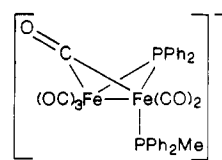


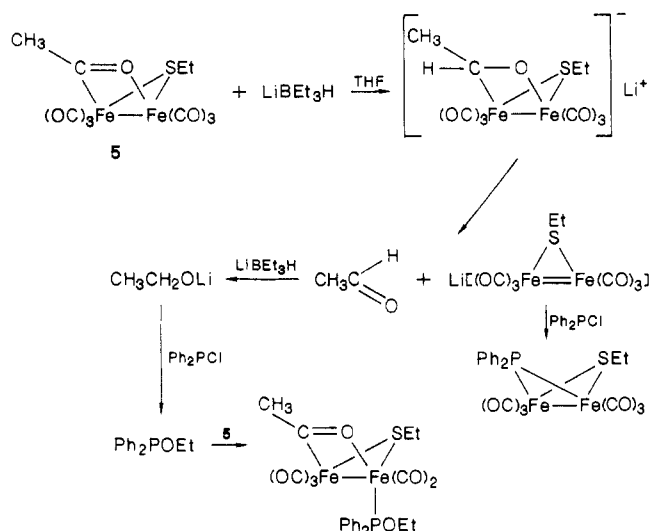
Figure 5. Variable-temperature proton NMR spectra of $(\mu, \eta^2\text{-CHCCMe}_2)(\mu\text{-Me}_3\text{CS})\text{Fe}_2(\text{CO})_6$ (**22**) in toluene- d_6 solution.

these compounds, unlike the μ -acyl complexes for which both possible isomers were observed by NMR spectroscopy. The X-ray crystal structures of **18** and **21** indicate that the μ -allyl and μ -allenyl compounds exist with the thiolate alkyl group in the equatorial position. This also is assumed to be the orientation of the thiolate alkyl groups of the μ -thiocarbonyl complexes.

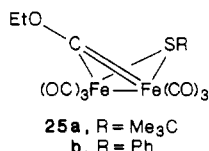
The $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ anions did not react with simple organic halides such as methyl iodide or benzyl chloride, either at room temperature or in refluxing THF. In contrast, the diphenylphosphido-bridged anion **24** was



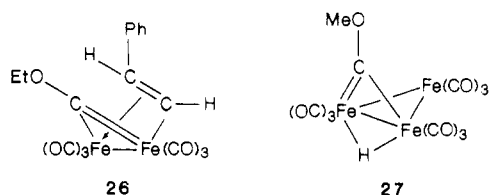
Scheme II



found to react with CH_3I , giving the bridging acetyl complex **14**.¹³ It would appear that **24** is a stronger nucleophile than are the RS-bridged anions **6**. In view of this, the anions $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ ($\text{R} = \text{Me}_3\text{C}$, Ph) were treated with $[\text{Et}_3\text{O}][\text{BF}_4]$, a much stronger electrophile than the organic halides used. In each case ethylation of the bridging CO ligand took place, giving **25**, the bridging



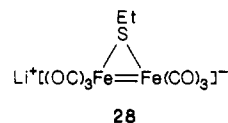
ethoxycarbonyl complexes. There have been prior reports of such alkylation, using reactive alkylating agents, of anions containing bridging CO ligands.³³⁻³⁵ Prepared in this manner were **26**^{33a} and **27**.^{34c}



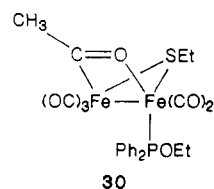
¹³C NMR spectroscopy provided good evidence for the structure of **25**. The carbonyl carbon atom chemical shift was 383.3 ppm for **25a** and 380.0 ppm for **25b**. In comparison δ_{C} (carbonyl C) was 383.8 ppm for **26** and 356.5 ppm for **27**. The reactions of the $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ anions with $[\text{Et}_3\text{O}][\text{BF}_4]$ provide good evidence for the im-

portance of resonance form **11** in which the negative charge is concentrated at the oxygen atom. However, all other reactions of these anions reported here can best be explained in terms of reactions of resonance hybrid **10**, in which the negative charge resides on the iron atoms.

The reactions of bridging acyl complexes of type **5** with lithium triethylborohydride provide another, albeit less practical, route to the $[(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6]$ complexes. When 1 molar equiv of LiBEt_3H was added to one of **5a** at -78°C under a nitrogen atmosphere, a color change from red to brown occurred. In the expectation of an anionic product, possibly **28**, 1 molar equiv of diphenylchlorophosphine was added. Two products were isolated:



the expected one, $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ (**29**), in 55% yield and a dark red oil in 32% yield, which was identified as **30**. The isolation of these two products confirmed the



success of this synthetic method and also revealed the fate of the acetyl ligand and added hydride. The reaction between **5a** and LiBEt_3H apparently proceeded as outlined in Scheme II, but the liberated aldehyde did not remain an innocent byproduct. As it was formed, the acetaldehyde competed with **5a** as an electrophile, reacting with LiBEt_3H to form lithium ethoxide. This diversion of the hydride to a new reactant prevented complete conversion of **5a** to the anion **28**, resulting in only a 55% yield of **29**. However, the unreacted starting material **5a** was not reisolated. Instead the new μ -acetyl complex **30** was obtained in 32% yield, formed in a CO ligand substitution reaction of **5a** by Ph_2POEt . The ethoxyphosphine was formed in situ in the reaction between the generated lithium ethoxide and remaining diphenylchlorophosphine. The isolation of **29** and **30** accounted for 87% of the starting material **5a**, with 64% of the added hydride contained in the ethoxy group of **30**.

The identification of **30** was confirmed by spectral data and combustion analysis. The ¹³C NMR spectrum contained a peak at δ_{C} 300.3 assigned to the μ -acetyl carbon atom. In the ¹H NMR spectrum of **30** the OCH_2 and SCH_2 proton signals appear as complex multiplets at δ 3.92 and 2.16, respectively, resulting from diastereotopic methylene protons. This is due to the chiral framework of the molecule which is also a characteristic of **5a** and **17**. Only one isomer of **30** was observed by NMR spectroscopy, with the thiolate ethyl group probably in the equatorial position. The δ_{C} 32.0 for the SCH_2 carbon is similar to chemical shifts, δ_{C} 33-34, found for the equatorial SCH_2 carbons in the hexacarbonyl acyl complexes **5**. The Ph_2POEt ligand is probably located on the iron atom to which the acetyl oxygen atom is bonded since the acetyl carbon atom signal in the ¹³C NMR spectrum of **30** is a singlet with no observable P-C coupling.

Since two competitive reactions occurred when LiBEt_3H was added to **5a**, hydride addition to **5a** and to acetaldehyde, the use of 2 equiv of LiBEt_3H was necessary to allow both processes to go to completion. Therefore, in another reaction, 2 equiv of LiBEt_3H were added to **5a** in

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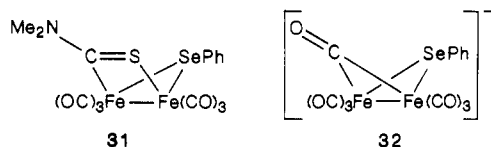
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THF at $-78\text{ }^{\circ}\text{C}$, and after stirring for 20 min, an excess of allyl chloride was added. The solution immediately became red, and the expected **18** was isolated in 82% yield. In the same manner, $(\mu\text{-H}_2\text{C}=\text{C}=\text{CH})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ (**20**), was isolated in 56% yield when propargyl bromide was added to the $2\text{LiBEt}_3\text{H}/\mathbf{5a}$ reaction mixture.

This reaction method for replacing a μ -acyl ligand with another three-electron-donor bridging ligand could also be accomplished with $(\mu\text{-PhCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ (**5b**). The reaction between **5b** and 2 equiv of LiBEt_3H in THF at $-78\text{ }^{\circ}\text{C}$ resulted in a brown solution. Addition of Ph_2PCl to this solution gave $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ in 85% yield. Following the same procedure and using allyl chloride as the electrophile produced **18** in 82% yield. These two reactions indicate that **5b** interacts with LiBEt_3H as **5a** does to form anion **28**. The stability of **28** at temperatures above $-78\text{ }^{\circ}\text{C}$ appears to be limited, however. When a solution of **28**, generated from **5b** and 2 equiv of LiBEt_3H , was removed from the $-78\text{ }^{\circ}\text{C}$ cold bath and stirred for 1 h prior to the addition of Ph_2PCl , the yield of $(\mu\text{-EtS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ was reduced to 33%.

This method for preparing $(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6$ -type complexes, at this point, is not as convenient as using the $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ system. However, as studies of both of these synthetic methods continue, their differences and specialized uses may become more apparent.

Finally, the general $\text{Fe}_3(\text{CO})_{12}/\text{RSH}/\text{Et}_3\text{N}$ procedure may be applied to the synthesis of the selenium analogues. Thus, the addition of PhSeH to a THF solution of $\text{Fe}_3(\text{CO})_{12}$ and triethylamine resulted in the usual color change from green to red (more rapidly than in the case of PhSH). Addition of *N,N*-dimethylthiocarbonyl chloride to the reaction mixture gave **31** in 58% yield. Thus the expected anion **32** had been formed.



Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Reagent grade pentane, dichloromethane, ethanol, and methanol were deoxygenated by bubbling nitrogen through them for 15 min prior to use. Ethanethiol and 2-methylpropanethiol were deoxygenated by bubbling nitrogen through them for 15 min and used as obtained.

Filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. Column chromatography was performed with a 350×25 mm column using silicic acid. All chromatography was done without exclusion of atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at $-20\text{ }^{\circ}\text{C}$.

Infrared spectra were obtained by using a Perkin-Elmer Model 1430 double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a JEOL/FX-90Q or a Bruker 250 NMR spectrometer operating at 90 and 250 MHz, respectively. ^{13}C NMR spectra were obtained by using a JEOL/FX-90Q or Bruker 270 NMR instrument operating at 22.5 and 67.9 MHz, respectively. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained by using a JEOL/FX-90Q instrument operating at 36.2 MHz referencing to external 85% aqueous H_3PO_4 . Mass spectra were obtained with a Finnigan-3200 spectrometer operating at 70 eV. Melting points were determined on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

IR spectra and 70-eV electron-impact mass spectra are given in the supplementary material. Often the product complexes were obtained as an inseparable mixture of isomers (RS group axial or equatorial). As a result, the number of observed bands in the terminal CO region was variable. For instance: $(\mu,\eta^2\text{-CH}_3\text{CO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$: 2081 (s), 2039 (vs), 2009 (s), 1997 (sh), 1972 (s) (cm^{-1} , in pentane) for 3.6:1 e-EtS/a-EtS mixture.

The mass spectra were diagnostic of the doubly bridged $\text{Fe}_2(\text{CO})_6$ complexes, showing (usually, but not always) the molecular ion and then six fragment ions, $\text{M}^+ - n\text{CO}$ ($n = 5, 4, 3, 2, 1, 0$). The $\mu\text{-}\eta^2$ -acyl complexes showed in addition the $(\text{M}^+ - 7\text{CO})$ fragment ion.

The alkanethiolate group of $(\mu\text{-RS})(\mu\text{-E})\text{Fe}_2(\text{CO})_6$ complexes can be oriented in either an equatorial or axial position. For those compounds isolated as a mixture of both geometric isomers a distinction between the equatorial and axial isomers could be made by ^1H NMR spectroscopy. The corresponding resonance signals of the equatorial alkanethiolate ligand are shifted downfield relative to the axial isomer.³⁸

Preparation and Crystal Structure of $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-2,4,6-Me}_3\text{C}_6\text{H}_2\text{S})\text{Fe}_2(\text{CO})_6]$ (9**).** **a. Preparation.** A clean, dry, round-bottomed flask was charged with 2.98 mmol of $\text{Fe}_3(\text{CO})_{12}$ (1.50 g), and the flask was purged with nitrogen for 15 min. Diethyl ether (60 mL) was added to the flask. Then 3.00 mmol of mesitylenethiol (0.457 g) and 3.01 mmol of Et_3N (0.305 g) were added to this solution via syringe. The color of the reaction solution gradually changed from green to red-brown. The solution was stirred at room temperature for 90 min at which time TLC ($\text{SiO}_2/\text{pentane}$) indicated that no unreacted $\text{Fe}_3(\text{CO})_{12}$ remained. The solution was filtered under nitrogen through a pad of Celite, and the filtrate was concentrated by evaporation under a stream of nitrogen to about 40 mL. This solution was placed in a freezer at approximately $-20\text{ }^{\circ}\text{C}$ overnight. Dark red-brown plates crystallized from solution. The solvents were removed by cannula, and the crystals were rinsed with Et_2O (2×10 mL). The compound was dried under vacuum and stored at $-20\text{ }^{\circ}\text{C}$ under an atmosphere of carbon monoxide. The product (mp [under N_2] $119.5\text{ }^{\circ}\text{C}$ dec) was identified as $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-2,4,6-Me}_3\text{C}_6\text{H}_2\text{S})\text{Fe}_2(\text{CO})_6]$ (0.678 g, 1.21 mmol, 40%). ^1H NMR (250 MHz, CDCl_3) [all signals are broad, and no coupling constants could be determined]; δ 1.07 (9 H, $\text{N}[\text{CH}_2\text{CH}_3]_3$), 2.22 (3 H, para- CH_3), 2.59, 2.62 (6 H, ortho- CH_3 's), 2.80 (6 H, $\text{-N}[\text{CH}_2\text{CH}_3]_3$), 6.81, 6.87 (2 H, aromatic H's), 8.75 (very br, 1 H, NH). ^{13}C NMR (67.9 MHz, CDCl_3): δ 9.2 (q, br, $J_{\text{CH}} = 126.6$ Hz, $\text{-N}[\text{CH}_2\text{CH}_3]_3$), 20.6 (q, $J_{\text{CH}} = 126.6$ Hz, one ortho- CH_3), 25.0 (q, $J_{\text{CH}} = 126.5$ Hz, one ortho- CH_3), 47.3 (t, br, $J_{\text{CH}} = 134.1$ Hz, $\text{-N}[\text{CH}_2\text{CH}_3]_3$), 129.0-139.5 (m, aromatic C's), 206.4, 209.2, 216.6 (all s's, carbonyl C's). IR (THF, NaCl): 2078 (m), 2042 (vs), 2036 (vs), 1985 (vs), 1950 (vs), 1925 (vs), 1912 (s), 1749 (m), 1730 (m), 1662 (w) cm^{-1} .

b. Crystal Structure of **9.** A crystal obtained as described above was selected and found suitable for X-ray diffraction studies.

The red-brown crystal was fixed to the tip of a glass fiber and mounted on a Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device. Diffraction data were collected by using $\text{Mo K}\alpha$ radiation at $-65\text{ }^{\circ}\text{C}$. Data collection, reduction, and refinement procedures are detailed elsewhere.³⁶ A semiempirical absorption correction ($\mu = 12.2\text{ cm}^{-1}$ for $\text{Mo K}\alpha$ radiation) was applied. A total of 5879 reflections ($+h,+k,\pm l$) were collected in the range $3^\circ \leq 2\theta \leq 55^\circ$. The 3702 reflections having $F_0 > 2\sigma(F_0)$ were used in the solution and refinement of the structure. Full-matrix least-squares refinement, ignoring H atoms and refining all other atoms anisotropically (298 variables), led to final weighted and unweighted agreement factors of 6.7% and 7.5%, respectively. Computations were performed by using the program system SHELX-76. The largest peak on the final difference-Fourier map was $0.76\text{ e } \text{\AA}^{-3}$.

Crystal Data for **9.** The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.591(6)\text{ \AA}$, $b = 13.330(5)\text{ \AA}$, $c = 15.724(7)\text{ \AA}$, $\beta = 103.75(4)^\circ$, $V = 2563.5\text{ \AA}^3$, $Z = 4$, and $d_{\text{calc}} = 1.454\text{ g/cm}^3$. Atomic coordinates, bond lengths and angles are given in Tables V and VI. An ORTEP representation of the molecular structure of the anion is shown in Figures 1 and 2. A

(38) (a) Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9. (b) King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

Table V. Atomic Coordinates ($\times 10^4$) for the Anion in $[\text{Et}_3\text{NH}][(\mu\text{-CO})(\mu\text{-C}_6\text{H}_2\text{Me}_3\text{S})\text{Fe}_2(\text{CO})_6]^-$ (9)^a

atom	x	y	z
Fe(1)	-873.0 (8)	2200.8 (7)	6952.9 (6)
Fe(2)	351.5 (8)	3379.4 (7)	7966.8 (6)
S	-1464.7 (14)	3722.7 (13)	7357.2 (11)
C(11)	-1500 (6)	1455 (6)	7689 (5)
O(11)	-1858 (5)	989 (4)	8157 (4)
C(12)	-1711 (6)	2105 (6)	5871 (5)
O(12)	-2234 (4)	2074 (5)	5170 (3)
C(13)	69 (6)	1247 (6)	6870 (5)
O(13)	724 (5)	650 (4)	6831 (4)
C(21)	129 (6)	2912 (5)	9000 (5)
O(21)	-9 (4)	2580 (4)	9635 (3)
C(22)	849 (7)	4615 (7)	8105 (6)
O(22)	1202 (6)	5424 (5)	8194 (5)
C(23)	1638 (6)	2817 (6)	8105 (5)
O(23)	2473 (5)	2441 (5)	8171 (4)
C(31)	189 (5)	3144 (5)	6733 (4)
O(31)	575 (4)	3398 (4)	6133 (3)
C(41)	-2460 (6)	3695 (5)	8012 (4)
C(42)	-3477 (6)	3222 (6)	7670 (5)
C(43)	-4279 (6)	3216 (6)	8147 (4)
C(44)	-4104 (6)	3684 (5)	8958 (5)
C(45)	-3129 (6)	4226 (5)	9265 (5)
C(46)	-2294 (6)	4250 (5)	8781 (5)
C(47)	-3775 (6)	2752 (8)	6749 (5)
C(48)	-1318 (6)	4933 (6)	9117 (5)
C(49)	-4976 (6)	3640 (6)	9497 (5)
N	2198 (5)	4222 (4)	5435 (4)
C(51)	2756 (6)	3315 (5)	5168 (5)
C(52)	3061 (7)	2553 (6)	5931 (5)
C(53)	1658 (7)	4837 (5)	4634 (5)
C(54)	667 (7)	4272 (6)	4076 (5)
C(55)	2931 (7)	4865 (6)	6127 (5)
C(56)	3888 (8)	5305 (8)	5816 (7)

^a Estimated standard deviations in the last digit are given in parentheses.

table of final observed and calculated structure factors has been deposited as supplementary material.

Reaction between $\text{Fe}_3(\text{CO})_{12}$, Sodium Ethanethiolate, and Acetyl Chloride. A 300 mL, three-necked, round-bottomed flask equipped with a stir-bar and serum caps was charged with 0.11 g (2.80 mmol) of NaNH_2 (Alfa) and 50 mL of THF under nitrogen. Ethanethiol (Fluka, 0.25 mL, 3.38 mmol) was added and the mixture stirred for 1 h to allow formation of EtSNa . Triiron dodecacarbonyl (1.5 g, 2.98 mmol) then was added as a solid against a flow of nitrogen. Gas evolution immediately was observed, and the green color of the $\text{Fe}_3(\text{CO})_{12}$ was discharged to produce a red-brown solution. After the solution was stirred for 1 h, 0.25 mL (3.50 mmol) of acetyl chloride (Aldrich) was added and the mixture stirred another 20 h. The solvent was removed, leaving a red oil which was taken up in pentane/ CH_2Cl_2 (4/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected, and pentane/ CH_2Cl_2 (4/1, v/v) eluted a red band which gave 0.30 g (0.78 mmol, 26% yield based on $\text{Fe}_3(\text{CO})_{12}$) of a slightly air-sensitive red oil identified as a 2.2:1 (e-Et/a-Et) mixture of isomers of $(\mu, \eta^2\text{-MeCO})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ by comparison of its ^1H NMR spectrum to that of an authentic sample (see next experiment).

Reactions of Diiron Nonacarbonyl and Triiron Dodecacarbonyl with S-Alkyl Thiocarboxylates. a. S-Ethyl Thioacetate. A 300-mL, three-necked, round-bottomed flask equipped with serum caps and a magnetic stir-bar was charged with 3.0 g (8.25 mmol) of $\text{Fe}_2(\text{CO})_9$ and flushed with nitrogen. Toluene (60 mL) and 0.63 g (6.0 mmol) of S-ethyl thioacetate were added by syringe, and the reaction mixture was stirred for 48 h. Subsequently, the solvent was removed, and the brown oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor orange band which was not collected. Further elution with pentane/ CH_2Cl_2 (9/1, v/v) moved two dark red bands. The first red band yielded 0.30 g (9.78 mmol, 13% yield based on the thioester) of $(\mu\text{-MeCO})(\mu\text{-EtS})$

Table VI. Bond Lengths (Å) and Bond Angles (deg) in $[(\mu\text{-CO})(\mu\text{-C}_6\text{H}_2\text{Me}_3\text{S})\text{Fe}_2(\text{CO})_6]$ with Estimated Standard Deviations in the Last Digit in Parentheses

Bond Lengths			
Central Diiron Core			
Fe(1)-Fe(2)	2.494 (1)	Fe(1)-S	2.302 (2)
Fe(2)-S	2.306 (2)	Fe(1)-C(31)	1.925 (7)
Fe(2)-C(31)	1.927 (7)	C(31)-O(31)	1.208 (7)
Bridging Thiolate Ligand			
S-C(41)	1.802 (7)	C(41)-C(42)	1.413 (9)
C(42)-C(47)	1.539 (10)	C(42)-C(43)	1.394 (9)
C(43)-C(44)	1.390 (9)	C(44)-C(49)	1.540 (9)
C(44)-C(45)	1.407 (10)	C(45)-C(46)	1.437 (9)
C(46)-C(48)	1.520 (10)	C(41)-C(46)	1.391 (9)
Carbonyl Ligands			
Fe(1)-C(11)	1.840 (7)	C(11)-O(11)	1.134 (8)
Fe(1)-C(12)	1.781 (7)	C(12)-O(12)	1.142 (8)
Fe(1)-C(13)	1.764 (8)	C(13)-O(13)	1.158 (8)
Fe(2)-C(21)	1.823 (8)	C(21)-O(21)	1.143 (8)
Fe(2)-C(22)	1.757 (9)	C(22)-O(22)	1.162 (9)
Fe(2)-C(23)	1.751 (8)	C(23)-O(23)	1.147 (8)
Triethylammonium Cation			
N-C(51)	1.507 (8)	C(51)-C(52)	1.548 (10)
N-C(53)	1.521 (9)	C(53)-C(54)	1.540 (10)
N-C(55)	1.515 (9)	C(55)-C(56)	1.523 (11)
Bond Angles			
The Thiolate-Bridged Anion Involving the Central Diiron Core			
Fe(1)-S-Fe(2)	65.5 (1)	Fe(1)-C(31)-Fe(2)	80.7 (3)
Fe(1)-Fe(2)-S	57.2 (1)	Fe(1)-Fe(2)-C(31)	49.6 (2)
Fe(2)-Fe(1)-S	57.3 (1)	Fe(2)-Fe(1)-C(31)	49.7 (2)
S-Fe(1)-C(31)	76.0 (2)	S-Fe(2)-C(31)	75.9 (2)
Fe(1)-C(31)-O(31)	138.5 (6)	Fe(2)-C(31)-O(31)	140.7 (5)
Involving the Carbonyl Ligands Only			
Fe(1)-C(11)-O(11)	178.0 (7)	Fe(1)-C(12)-O(12)	177.7 (7)
Fe(1)-C(13)-O(13)	177.0 (7)	Fe(2)-C(21)-O(21)	177.2 (7)
Fe(2)-C(22)-O(22)	178.4 (9)	Fe(2)-C(23)-O(23)	178.0 (7)
C(11)-Fe(1)-C(12)	108.5 (3)	C(11)-Fe(1)-C(13)	93.1 (3)
C(12)-Fe(1)-C(13)	97.7 (3)	C(21)-Fe(2)-C(22)	109.7 (4)
C(21)-Fe(2)-C(23)	94.4 (3)	C(22)-Fe(2)-C(23)	95.4 (4)
Involving the Carbonyl Ligands and the Central Core			
Fe(1)-Fe(2)-C(21)	98.7 (2)	Fe(1)-Fe(2)-C(22)	144.8 (3)
Fe(1)-Fe(2)-C(23)	102.9 (3)	Fe(2)-Fe(1)-C(11)	103.3 (2)
Fe(2)-Fe(1)-C(12)	142.4 (2)	Fe(2)-Fe(1)-C(13)	100.2 (2)
C(11)-Fe(1)-C(31)	152.3 (3)	C(12)-Fe(1)-C(31)	98.9 (3)
C(13)-Fe(1)-C(31)	87.1 (3)	C(21)-Fe(2)-C(31)	147.0 (3)
C(22)-Fe(2)-C(31)	103.1 (3)	C(23)-Fe(2)-C(31)	86.0 (3)
S-Fe(1)-C(11)	95.0 (2)	S-Fe(1)-C(12)	99.8 (3)
S-Fe(1)-C(13)	157.3 (2)	S-Fe(2)-C(21)	95.2 (2)
S-Fe(2)-C(22)	98.9 (3)	S-Fe(2)-C(23)	159.0 (2)
Involving the Thiolate Ligand Only			
S-C(41)-C(42)	118.8 (5)	S-C(41)-C(46)	120.3 (6)
C(41)-C(42)-C(43)	120.3 (6)	C(41)-C(42)-C(47)	122.4 (6)
C(41)-C(46)-C(45)	118.1 (7)	C(41)-C(46)-C(48)	124.2 (7)
C(42)-C(41)-C(46)	120.3 (6)	C(42)-C(43)-C(44)	120.9 (7)
C(43)-C(42)-C(47)	117.2 (6)	C(43)-C(44)-C(45)	118.8 (7)
C(43)-C(44)-C(49)	120.6 (7)	C(44)-C(45)-C(46)	121.2 (7)
C(45)-C(44)-C(49)	120.6 (7)	C(45)-C(46)-C(48)	117.6 (6)
Involving the Thiolate Ligand and the Central Core			
Fe(1)-S-C(41)	117.0 (2)	Fe(2)-S-C(41)	121.0 (2)
Triethylammonium Cation			
N-C(51)-C(52)	110.9 (6)	N-C(53)-C(54)	110.5 (6)
N-C(55)-C(56)	112.4 (7)	C(51)-N-C(53)	110.4 (5)
C(51)-N-C(55)	114.1 (6)	C(53)-N-C(55)	111.5 (6)

$\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil identified as a 3.6:1 (e/a) mixture of two isomers. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_7\text{SFe}_2$: C, 31.28; H, 2.10. Found: C, 31.30; H, 2.20. IR (CHCl_3): 1517 (s) (acyl C=O); terminal CO (pentane) 2081 (s), 2039 (vs), 2009 (s), 1997 (s), 1972 (s) cm^{-1} . ^1H NMR (CDCl_3 , 270 MHz): δ 1.37 (t, J = 7.3 Hz, a- CH_3), 1.48 (t, J = 7.3 Hz, e- CH_3), 2.25 (s, CH_3CO , e isomer), 2.31 (s, CH_3CO a isomer), 2.57 (m, SCH_2). ^{13}C NMR (CDCl_3 , 67.9 MHz): δ_{C} 17.9 (q, J = 125 Hz, a- CH_2CH_3), 18.4 (q,

$J = 128$ Hz, e-CH₂CH₃), 26.0 (t, $J = 141$ Hz, a-SCH₂), 33.0 (t, $J = 141$ Hz, e-SCH₂), 46.8 (q, $J = 129$ Hz, CH₃), 47.2 (q, $J = 129$ Hz, CH₃), 207.7, 209.7, 209.9, 211.4, 212.1 (all s, CO), 299.2 (s, acyl CO, e isomer), 301.9 (s, acyl CO, a isomer).

The second red band yielded 0.30 g (9.57 mmol, 10% yield based on thioester) of (μ_3 -EtS)(μ, η^2 -MeCO)Fe₃(CO)₉ as a slightly air-sensitive, red-black solid. After recrystallization from CH₂Cl₂/pentane it had a melting point of 90–92 °C. Anal. Calcd for C₁₃H₉O₁₀SFe₃: C, 29.81; H, 1.54. Found: C, 29.90; H, 1.61. IR (CHCl₃): 1497 (s, acyl C=O); terminal CO (pentane) 2081 (s), 2044 (vs), 2020 (vs), 2000 (vs), 1994 (sh), 1978 (s), 1961 (s), 1954 (m) cm⁻¹. ¹H NMR (CDCl₃, 270 MHz): δ 1.77 (t, $J = 7.3$ Hz, 3 H, CH₃), 2.22 (s, 3 H, CH₃), 3.63 (q, $J = 7.3$ Hz, 2 H, SCH₂). ¹³C NMR (CDCl₃, 67.9 MHz): δ 17.5 (q, $J = 128$ Hz, CH₂CH₃), 41.4 (t, $J = 145$ Hz, SCH₂), 48.3 (q, $J = 127$ Hz, CH₃), 202.4, 206.2, 207.2, 209.0, 213.6, 214.7, 216.3 (all s, CO), 317.5 (s, acyl CO). Mass spectrum: m/z (relative intensity) 496 (M⁺ - CO, 3), 468 (M⁺ - 2CO, 5), 440 (M⁺ - 3CO, 2), 412 (M⁺ - 4CO, 2), 384 (M⁺ - 5CO, 12), 356 (M⁺ - 6CO, 20), 328 (M⁺ - 7CO, 25), 300 (M⁺ - 8CO, 28), 272 (M⁺ - 9CO, 20), 257 (Fe₃CO(SET), 3), 244 (Fe₃Me(SET), 33), 229 (Fe₂SET, 7), 216 (Fe₂(OCMe)SET, 30), 200 (Fe₂S, 56), 188 (Fe₂SET(Me), 14), 173 (Fe₂SET, 12), 168 (Fe₃, 5), 144 (Fe₂S, 100), 112 (Fe₂, 15), 56 (Fe, 87).

b. S-Ethyl Thiobenzoate. A similar reaction using PhC(O)SEt gave a 4.4:1 mixture of the e and a isomers of (μ, η^2 -PhC=O)(μ -EtS)Fe₂(CO)₆ as an air-stable red solid, mp 81–86 °C (from pentane), in 17% yield. Anal. Calcd for C₁₅H₁₀O₇SFe₂: C, 40.40; H, 2.26. Found: C, 40.33; H, 2.29. ¹H NMR (CDCl₃, 270 MHz): δ 1.29 (t, $J = 7.3$ Hz, a-CH₃), 1.50 (t, $J = 7.3$ Hz, e-CH₃), 2.09, 2.29 (both m, a-SCH₂), 2.64 (m, e-SCH₂), 7.3–7.5 (m, Ph). ¹³C NMR (CDCl₃, 67.9 MHz): δ 17.8 (q, $J = 128$ Hz, a-CH₃), 18.3 (q, $J = 127$ Hz, e-CH₃), 26.0 (t, $J = 144$ Hz, a-SCH₂), 33.0 (t, $J = 141$ Hz, e-SCH₂), 126.8 (d, $J = 163$ Hz, Ph), 127.2 (d, $J = 163$ Hz, Ph), 128.3 (d, $J = 163$ Hz, Ph), 128.6 (d, $J = 162$ Hz, Ph), 133.4 (d, $J = 160$ Hz, Ph), 144.5 (s, ipso Ph), 144.8 (s, ipso Ph), 207.7, 209.5, 209.9, 210.3, 211.3, 212.0 (all s, CO), 289.0 (s, acyl CO, e isomer), 291.6 (s, acyl CO, a isomer).

c. S-Ethyl Thiopivalate. A similar reaction using Me₃CC(O)SEt gave (μ, η^2 -Me₃CC=O)(μ -EtS)Fe₂(CO)₆, a red solid, mp 36–38 °C (e isomer only), in 10% yield. Anal. Calcd for C₁₃H₁₄O₇SFe₂: C, 36.65; H, 3.31. Found: C, 36.98; H, 3.40. IR (CHCl₃): 1496 (s, acyl C=O); (pentane) 2082 (s), 2040 (vs), 2010 (s), 1995 (s), 1970 (s) (terminal carbonyls) cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 0.86 (s, 9 H, *tert*-butyl), 1.48 (t, $J = 7.3$ Hz, 3 H, CH₃), 2.58 (m, 2 H, SCH₂). Mass spectrum: m/z (relative intensity) 426 (M⁺, 11), 398 (M⁺ - CO, 7), 370 (M⁺ - 2CO, 13), 342 (M⁺ - 3CO, 40), 314 (M⁺ - 4CO, 32), 286 (M⁺ - 5CO, 43), 258 (M⁺ - 6CO, 100), 230 (M⁺ - 7CO, 31), 200 (Fe₂SC₄H₉, 54), 175 (Fe₂SET, 20), 144 (Fe₂S, 60), 57 (C₄H₉, 19), 56 (Fe, 11).

Reaction between Fe₃(CO)₁₂, Lithium Ethanethiolate, and Acetyl Chloride. A 300-mL, three-necked, round-bottomed flask equipped with a stir-bar and serum caps was charged with 20 mL of THF and 0.22 mL (3.0 mmol) of ethanethiol (Fluka). This solution was cooled to -20 °C, and 1.25 mL (3.0 mmol) of a 2.40 M *n*-butyllithium solution (Alfa) was added and the solution stirred for 1 h to generate the EtSLi. Triiron dodecacarbonyl (1.5 g, 2.98 mmol), dissolved in THF, was cannulated into the EtSLi solution at -20 °C. The mixture became red-brown and was stirred for 1 h. Next, 0.5 mL (7.0 mmol) of acetyl chloride (Aldrich) was added and the reaction mixture removed from the cold bath and stirred for 20 h. Workup as described above for the reaction in which EtSNa was used gave 0.41 g (1.08 mmol, 36% yield based on Fe₃(CO)₁₂) of a slightly air-sensitive red oil identified as a 2.5:1 (e-Et/a-Et) mixture of isomers of (μ, η^2 -MeCO)(μ -EtS)Fe₂(CO)₆ by comparison of its ¹H NMR spectrum to that of an authentic sample.

Reaction between Triiron Dodecacarbonyl, Alkanethiol, and Triethylamine: The Standard *In Situ* Generation of [Et₃NH][(μ -EtS)(μ -CO)Fe₂(CO)₆]. A 100 mL, three-necked, round-bottomed flask equipped with a stir-bar and serum caps was charged with 1.5 g (2.98 mmol) of Fe₃(CO)₁₂ and flushed with nitrogen. Tetrahydrofuran (50 mL) was added by syringe, followed by the addition of 0.25 mL (3.38 mmol) of ethanethiol (Fluka) and 0.48 mL (3.50 mmol) of triethylamine (Aldrich). The solution was stirred for 15 min prior to the addition of any reactants, during which time a color change of green to red-brown occurred.

A similar procedure served well when *t*-BuSH was the alkanethiol used.

Reaction between the Standard Fe₃(CO)₁₂/EtSH/Et₃N Mixture and Acetyl Chloride. The standard Fe₃(CO)₁₂/EtSH/Et₃N reagent solution was prepared as described above; to this mixture was added 0.50 mL (7.0 mmol) of acetyl chloride (Aldrich). The solution was stirred for 20 h during which time it became dark red and a white precipitate formed. The solution was filtered and the solvent removed, leaving a red oil. This was extracted with a 1/1 (v/v) mixture of pentane/CH₂Cl₂ and filtered through a pad of silicic acid. After removal of solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which yielded 0.13 g (0.32 mmol, 11% yield based on Fe₃(CO)₁₂) of (μ -EtS)₂Fe₂(CO)₆ as a red solid.³⁷ Further elution with pentane/CH₂Cl₂ (4/1, v/v) moved a red band which gave 0.60 g (1.56 mmol, 52% yield) of (μ, η^2 -MeCO)(μ -EtS)Fe₂(CO)₆ as a slightly air-sensitive red oil identified as a 3:1 (e-Et/a-Et) mixture of isomers by its ¹H NMR spectrum.

Prepared by using this general procedure were the following (μ, η^2 -RCO)(μ -R'S)Fe₂(CO)₆ complexes.

(μ, η^2 -PhCO)(μ -EtS)Fe₂(CO)₆: 83% yield; red solid; mp 81–86 °C, 2.3:1 e-Et/a-Et isomer mixture.

(μ, η^2 -PhCO)(μ -Me₃CS)Fe₂(CO)₆: 70% yield; red solid; mp 68.5–69.0 °C, a, e-Me₃C isomer mixture (by ¹³C NMR). Anal. Calcd for C₁₇H₁₄O₇SFe₂: C, 43.08; H, 2.98. Found: C, 43.02; H, 3.04. ¹H NMR (90 MHz, CD₂Cl₂): δ 1.26 (br s, 9 H, C(CH₃)₃), 7.35–7.69 (m, 5 H, phenyl). ¹³C NMR (67.9 MHz, CDCl₃): δ 34.3 (q, $J_{CH} = 128.0$ Hz, -SC(CH₃)₃, a isomer), 34.9 (q, $J_{CH} = 128.2$ Hz, -SC(CH₃)₃, e isomer) 127.4, 128.3, 128.5, 133.2, 133.4 (m, phenyl ring C's), 143.9 (s, ipso phenyl carbon), 207.0, 207.2, 209.3, 209.4, 210.2, 210.5, 211.2, 211.5, 212.2 (all s, carbonyl C's), 287.9 (s, C₆H₅C[O] e isomer), 288.8 (s, C₆H₅C[O] a isomer).

(μ, η^2 -PhCO)(μ -PhS)Fe₂(CO)₆: 70% yield; mp 102–103 °C, a,e-Ph isomer mixture (by ¹³C NMR). Anal. Calcd for C₁₉H₁₀O₇SFe₂: C, 46.20; H, 2.04. Found: C, 46.26; H, 2.14. ¹H NMR (90 MHz, CD₂Cl₂): δ 7.00–7.70 (m, phenyl ring H's). ¹³C NMR (67.9 MHz, CDCl₃): δ 126.4–134.0 (m, phenyl ring carbons), 207.2, 208.3, 208.7, 209.8, 211.4, 212.0 (all s, carbonyl carbons), 289.9 (s, C₆H₅C[O] e isomer), 291.4 (s, C₆H₅C[O] a isomer).

(μ, η^2 -Me₂CHCO)(μ -EtS)Fe₂(CO)₆: 45% yield; red oil; ¹H NMR (250 MHz, CD₂Cl₂): δ 0.76–1.57 (complex region, 9 H, all methyl H's), 2.14–2.82 (complex region, 3 H, [CH₃]₂CH- and CH₃CH₂S-). ¹³C NMR (67.9 MHz, CDCl₃): δ 17.5, 17.8, 18.7, 19.6 (complex m, all methyl C's), 33.7, 34.0 (two t's, $J_{CH} = 140.8$ Hz, -SCH₂CH₃, isomers), 57.8, 58.5 (both d's, $J_{CH} = 131.0$ Hz, [CH₃]₂CHC[O], isomers), 209.5, 209.8, 210.3, 214.5 (all s's, carbonyl C's), 307.6 (s, [CH₃]₂CHC[O]-).

Triphenylphosphine derivative (μ, η^2 -Me₂CHCO)(μ -EtS)-Fe₂(CO)₆(Ph₃P): red solid; mp 120.5–122.0 °C. Anal. Calcd for C₂₉H₂₇O₆SPFe₂: C, 53.90; H, 4.21. Found: C, 53.32; H, 4.19. ¹H NMR (90 MHz, CD₂Cl₂): δ 0.62–1.48 (complex m, 9 H, all methyl H's), 1.87–2.34 (complex m, 2 H, -SCH₂CH₃), 2.61–2.84 (septet, $J_{HH} = 1.70$ Hz, 1 H, [CH₃]₂CH-), 7.33–7.73 (m, 15 H, Ph). ¹³C NMR (67.9 MHz, CD₂Cl₂): δ 17.5, 17.9, 18 (3 overlapping q's, J_{CH} 's approximately 127 Hz, methyl C's), 31.6, 32.0 (t's, J_{CH} 's approximately 127 Hz, -SCH₂CH₃ both isomers), 57.3 (d, $J_{CH} = 130.3$ Hz, -CH[CH₃]₂), 128.7–134.2 (m, aromatic C's), 211.2, 211.4, 214.4, 216.2, 218.6 (all s's, carbonyl C's) 305.2 (s, [CH₃]₂CHC[O]).

(μ, η^2 -2-Naphthyl-CO)(μ -EtS)Fe₂(CO)₆: 78% yield; red, glassy solid. ¹H NMR (90 MHz, CD₂Cl₂): δ 1.31 (t, $J_{HH} = 7.2$ Hz, a isomer, -SCH₂CH₃), 1.54 (t, $J_{HH} = 7.6$ Hz, e isomer, -SCH₂CH₃), 1.82–2.98 (complex m, 2 H, both isomers -SCH₂CH₃), 7.20–8.30 (m, 7 H, aromatic H's). ¹³C NMR (67.9 MHz, CDCl₃): δ 17.9 (q, $J_{CH} = 126.5$ Hz, a isomer, -SCH₂CH₃), 18.4 (q, $J_{CH} = 128.1$ Hz, e isomer, -SCH₂CH₃), 26.0 (t, $J_{CH} = 142.8$ Hz, a isomer -SCH₂CH₃), 33.0 (t, $J_{CH} = 140.4$ Hz, e isomer, -SCH₂CH₃), 120.0–142.0 (m, aromatic C's), 207.8, 209.1, 209.6, 210.2, 210.6, 211.6, 212.2 (all s's, carbonyl C's), 288.0, 290.4 (both s, C₁₀H₇C[O] two isomers not assignable).

Triphenylphosphine derivative (μ, η^2 -2-C₁₀H₇-CO)(μ -EtS)-Fe₂(CO)₆(Ph₃P): red solid; mp 161–162 °C. Anal. Calcd for C₃₆H₂₇O₆SPFe₂: C, 59.21; H, 3.73. Found: C, 59.15; H, 3.79. ¹H NMR (250 MHz, CD₂Cl₂): δ 1.21 (t, $J_{HH} = 7.2$ Hz, 3 H, -SCH₂CH₃), 2.18–2.44 (m, 2 H, -SCH₂CH₃), 7.23–8.09 (m, 22 H, Ph). ¹³C NMR (67.9 MHz, CDCl₃): δ 17.9 (q, $J_{CH} = 143.3$ Hz,

-SCH₂CH₃), 31.4 (t, $J_{\text{CH}} = 139.6$ Hz, -SCH₂CH₃), 126.5–133.7 (m, aromatic C's), 211.2, 211.7, 212.6, 214.0 (br), 217.2, 217.3 (all s's, carbonyl C's), 288.16 (s, C₁₀H₇C[O]). ³¹P NMR (36.2 MHz, CD₂Cl₂): δ_{P} 55.0.

(μ , η^2 -*p*-CH₃C₆H₄CO)(μ -Me₃CS)Fe₂(CO)₆: 75% yield; red oil. ¹H NMR (90 MHz, CD₂Cl₂): δ 1.30 (s, a isomer, -SC[CH₃]₃), 1.57 (s, e isomer, -SC[CH₃]₃), 2.39 (s, 3 H, -C₆H₄CH₃), 7.10–7.60 (m, 4 H, aromatic). ¹³C NMR (67.9 MHz, CDCl₃): δ_{C} 21.5 (q, $J_{\text{CH}} = 127.5$ Hz, -C₆H₄CH₃), 34.3 (q, $J_{\text{CH}} = 126.7$ Hz, a isomer, -SC[CH₃]₃), 34.9 (q, $J_{\text{CH}} = 126.3$ Hz, e isomer, -SC[CH₃]₃), 48.7, 49.2 (both s, both isomers, -SC[CH₃]₃), 127.4–144.3 (m, aromatic C's), 207.1, 211.4, 211.6, 216.5, 217.7 (all s, carbonyl carbons), 286.7 (s, CH₃C₆H₄C[O]-).

Triphenylphosphine derivative (μ , η^2 -*p*-CH₃C₆H₄CO)(μ -Me₃CS)Fe₂(CO)₆(Ph₃P): red solid; mp 155–157 °C. Anal. Calcd for C₃₅H₃₁O₆SPFe₂: C, 58.20; H, 4.33. Found: C, 58.01; H, 4.32. ¹H NMR (90 MHz, CD₂Cl₂): δ 1.20 (s, 9 H, -SC[CH₃]₃), 2.35 (s, 3 H, -C₆H₄CH₃), 7.18–7.75 (m, 19 H, aromatic H's). ¹³C NMR (67.9 MHz, CD₂Cl₂): δ_{C} 21.7 (q, $J_{\text{CH}} = 125.7$ Hz, -C₆H₄CH₃), 34.3 (q, $J_{\text{CH}} = 126.7$ Hz, -SC[CH₃]₃), 49.3 (s, -SC[CH₃]₃), 127.4–144.4 (m, aromatic C's), 211.5, 212.7, 215.8, 217.6, 218.4 (all s's carbonyl C's), 287.4 (s, CH₃C₆H₄CO). ³¹P NMR (36.21 MHz, CD₂Cl₂): δ_{P} 36.2.

Reaction of [Et₃NH][(μ -CO)(μ -Me₃CS)Fe₂(CO)₆] with *N,N*-Dialkylthiocarbamoyl Chlorides. a. Me₂NC(S)Cl. The anion was generated in 50 mL of THF using 0.51 g of Fe₃(CO)₁₂ (1.02 mmol), 0.10 g of Et₃N (1.00 mmol), and 0.09 g of (CH₃)₃CSH (1.01 mmol). After the green to red-brown color change had occurred, 0.27 g of *N,N*-dimethylthiocarbamoyl chloride (Sigma, 2.17 mmol) was added to the stirred solution. Gas evolution and an immediate color change to bright red were observed. The reaction mixture was stirred at room temperature for 30 min, and then the solvent was removed in vacuo to give a red tarry residue. This was taken up in 50/50 pentane/CH₂Cl₂ (v/v) and chromatographed on a column of Grade III alumina (250 × 25 mm). Elution with 80/20 pentane/CH₂Cl₂ (v/v) yielded a red band which gave a red, air-stable, crystalline solid which could be recrystallized from pentane (mp 99.5–100.2 °C). This was identified as (μ , η^2 -Me₂NC=S)(μ -Me₃CS)Fe₂(CO)₆ (0.40 g, 0.87 mmol, 85%). Anal. Calcd for C₁₃H₁₅O₆NS₂Fe₂: C, 34.16; H, 3.31; N, 3.06. Found: C, 34.16; H, 3.09; N, 3.09. ¹H NMR (90 MHz, CDCl₃): δ 1.50 (s, 9 H, -SC(CH₃)₃), 3.21 (a, 2 H, -NCH₃ endo), 3.48 (s, 3 H, -NCH₃ exo). ¹³C NMR (67.9 MHz, CDCl₃): δ_{C} 34.1 (q, $J_{\text{CH}} = 127.2$ Hz, -SC(CH₃)₃), 44.2 (q, $J_{\text{CH}} = 139.8$ Hz, -NCH₃ endo), 46.7 (q, $J_{\text{CH}} = 140.1$ Hz, -NCH₃ exo), 50.5 (s, -SC(CH₃)₃), 210.4, 210.6 (br), 210.9, 213.3 (all s's, carbonyl C's), 244.6 (s, S=C=N-).

b. Et₂NC(S)Cl. The same procedure gave (μ , η^2 -Et₂NC=S)(μ -Me₃CS)Fe₂(CO)₆, a red solid, mp 71.8–72.5 °C (from pentane), in 83% yield. Anal. Calcd for C₁₅H₁₉O₆NS₂Fe₂: C, 37.14; H, 3.95. Found: C, 37.51; H, 4.15. ¹H NMR (90 MHz, CDCl₃): δ 1.26 (t, 3 H, $J_{\text{HH}} = 7.08$ Hz, -NCH₂CH₃ endo), 1.44 (t, 3 H, $J_{\text{HH}} = 7.08$ Hz, -NCH₂CH₃ exo), 1.65 (s, 9 H, -SC(CH₃)₃), 3.30–4.42 (complex m, 4 H, -N(CH₂CH₃)₂). ¹³C NMR (67.9 MHz, CDCl₃): δ_{C} 11.5 (q, $J_{\text{CH}} = 128.1$ Hz, -NCH₂CH₃ endo), 13.9 (q, $J_{\text{CH}} = 127.9$ Hz, -NCH₂CH₃ exo), 34.0 (q, $J_{\text{CH}} = 127.3$ Hz, -SC(CH₃)₃), 48.2 (t, $J_{\text{CH}} = 138.8$ Hz, -NCH₂CH₃ endo), 50.2 (s, -SC(CH₃)₃), 51.0 (t, $J_{\text{CH}} = 138.9$ Hz, -NCH₂CH₃ exo), 207.7–213.8 (unresolved s's, carbonyl C's), 241.7 (s, S=CNEt).

Reaction between the Standard Fe₃(CO)₁₂/EtSH/Et₃N Mixture and Allyl Chloride. The standard Fe₃(CO)₁₂/EtSH/Et₃N reagent solution was prepared, and to this was added 1.0 mL (12.2 mmol) of allyl chloride (Aldrich). The solution was stirred for 20 h, during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This was taken up in pentane and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which yielded 0.13 g (0.32 mmol, 11% yield based on Fe₃(CO)₁₂) of (μ -EtS)₂Fe₂(CO)₆. Further elution with pentane moved a second orange band which gave 0.91 g (2.38 mmol, 80% yield) of (μ -CH₂CHCH₂)(μ -EtS)Fe₂(CO)₆ as an air-stable, red solid, mp 41–42 °C (from MeOH) (crystals from this source were used in the X-ray diffraction study). Anal. Calcd for C₁₁H₁₀O₆SFe₂: C, 34.59; H, 2.64. Found: C, 34.65; H, 2.74. ¹H NMR (CDCl₃, 250 MHz): δ

0.47 (d, $J = 12.6$ Hz, 2 H, FeCH₂ anti), 1.29 (t, $J = 7.4$ Hz, 3 H, CH₃), 1.97 (d, $J = 7.5$ Hz, 2 H, FeCH₂ syn), 2.47 (q, $J = 7.4$ Hz, 2 H, SCH₂), 4.76 (m, 1 H, CH). ¹³C NMR (C₆D₆, 67.9 MHz): δ_{C} 18.1 (q, $J = 130$ Hz, CH₃), 20.9 (t, $J = 154$ Hz, FeCH₂), 32.7 (t, $J = 141$ Hz, SCH₂), 88.5 (d, $J = 158$ Hz, CH), 211.2 (s, CO). Mass spectrum: m/z (relative intensity) 382 (M⁺, 5), 354 (M⁺ - CO, 6), 326 (M⁺ - 2CO, 36), 298 (M⁺ - 3CO, 11), 270 (M⁺ - 4CO, 19), 242 (M⁺ - 5CO, 22), 214 (M⁺ - 6CO, 67), 186 (Fe₂SC₃H₆, 70), 144 (Fe₂S, 100), 56 (Fe, 29). IR (CHCl₃): 3000 (w), 2979 (w), 2940 (m), 1495 (m), 1454 (m), 1378 (m), 1210 (m), 1153 (m), 867 (w), 623 (s), 599 (s), 512 (m) cm⁻¹; terminal carbonyl region (pentane) 2060 (s), 2022 (s), 1984 (vs) cm⁻¹.

Reaction between the Standard Fe₃(CO)₁₂/EtSH/Et₃N Mixture and Propargyl Bromide. The standard Fe₃(CO)₁₂/EtSH/Et₃N reagent solution was prepared; to this mixture was added 1.0 mL (13.3 mmol) of propargyl bromide (Aldrich). The solution was stirred for 20 h, during which time it became red and a white precipitate formed. The solution was filtered and the solvent removed leaving a red oil. This was taken up in pentane and filtered through a pad of silicic acid. After removal of the solvent, the material remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a minor yellow band which was not collected. Further elution with pentane moved a second orange band which yielded 1.03 g (2.71 mmol, 91% yield) of (μ - η^1 , η^2 -H₂C=C=CH)(μ -EtS)Fe₂(CO)₆ as an air-stable, red solid, mp 39–41 °C, after crystallization from methanol. Anal. Calcd for C₁₁H₈O₆SFe₂: C, 34.77; H, 2.12. Found: C, 34.70; H, 2.30. IR (CHCl₃): 3004 (m), 2985 (m), 2945 (m), 2882 (w), 1754 (m) ν (C=C), 1700 (w), 1457 (m), 1427 (m), 1382 (m), 1258 (m), 1165 (w), 1038 (w), 1010 (w), 974 (w), 897 (w), 847 (m), 628 (s), 612 (s), 580 (sh), 560 (m) cm⁻¹; terminal carbonyl region (pentane) 2072 (s), 2039 (s), 2000 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 250 MHz): δ 1.29 (t, $J = 7.4$ Hz, 3 H, CH₃), 2.37 (q, $J = 7.4$ Hz, 2 H, SCH₂), 5.30 (d, $J = 4.9$ Hz, 2 H, =CH₂), 7.39 (t, $J = 4.9$ Hz, 1 H, Fe₂CH). ¹³C NMR (C₆D₆, 67.9 MHz): δ_{C} 17.7 (q, $J = 129$ Hz, CH₃), 34.7 (t, $J = 142$ Hz, SCH₂), 93.4 (t, $J = 167$ Hz, =CH₂), 114.8 (d, $J = 162$ Hz, Fe₂CH), 176.6 (s, FeC=), 209.6 (s, CO). Mass spectrum: m/z (relative intensity) 380 (M⁺, 7), 352 (M⁺ - CO, 26), 324 (M⁺ - 2CO, 45), 296 (M⁺ - 3CO, 25), 268 (M⁺ - 4CO, 27), 240 (M⁺ - 5CO, 24), 212 (M⁺ - 6CO, 86), 184 (Fe₂SC₃H₄, 100), 183 (Fe₂SC₃H₃, 32), 144 (Fe₂S, 76), 112 (Fe₂, 7), 56 (Fe, 14).

A similar reaction was carried out by using the Fe₃(CO)₁₂/Me₃CSH/Et₃N reagent. The red oil which was produced was purified by filtration chromatography (silicic acid/petroleum ether). Petroleum ether eluted a red band which gave 1.12 g (2.75 mmol, 92% yield) of (μ - η^1 , η^2 -H₂C=C=CH)(μ -Me₃CS)Fe₂(CO)₆ as a slightly air-sensitive, red solid, mp 56–58 °C, after crystallization from pentane. Anal. Calcd for C₁₃H₁₂O₆SFe₂: C, 38.27; H, 2.96. Found: C, 38.20; H, 3.01. IR (CHCl₃): 2970 (m), 2947 (m), 2930 (m), 2905 (w), 2868 (w), 1750 (m) (C=C), 1695 (w), 1471 (w), 1458 (m), 1421 (w), 1394 (w), 1367 (s), 1154 (s), 1032 (w), 1017 (w), 1006 (w), 890 (w), 842 (m), 614 (s), 598 (s), 496 (s) cm⁻¹; terminal carbonyl region (pentane) 2054 (s), 2040 (vs), 2002 (vs), 1998 (vs) cm⁻¹. ¹H NMR (acetone-*d*₆, 90 MHz): δ 1.38 (s, 9 H, *tert*-butyl CH₃), 5.39 (d, $J = 4.4$ Hz, 2 H, =CH₂), 7.39 (t, $J = 4.4$ Hz, 1 H, Fe₂CH). ¹³C NMR (C₆D₆, 67.9 MHz): δ_{C} 33.0 (q, $J = 129$ Hz, CH₃), 48.2 (s, CMe₃), 95.5 (t, $J = 166$ Hz, =CH₂), 113.2 (d, $J = 162$ Hz, Fe₂CH), 177.7 (s, FeC=), 210.2 (s, CO).

Reaction between the Standard Fe₃(CO)₁₂/Me₃CSH/Et₃N Mixture and 3-Bromo-3-methyl-1-butyne. The standard Fe₃(CO)₁₂/Me₃CSH/Et₃N reagent solution was prepared; to this was added 1.1 g (7.5 mmol) of 3-bromo-3-methyl-1-butyne. The solution was stirred for 4.5 h, during which time it became bright red and a white precipitate formed. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 1.23 g (2.83 mmol, 95% yield) of (μ - η^1 , η^2 -Me₂C=C=CH)(μ -Me₃CS)Fe₂(CO)₆ as a slightly air-sensitive, red solid, mp 46–47 °C, after crystallization from ethanol. Anal. Calcd for C₁₅H₁₆O₆SFe₂: C, 41.32; H, 3.70. Found: C, 41.10; H, 3.77. IR (CHCl₃): 2983 (m), 2939 (m), 2918 (m), 2873 (m), 1755 (w), ν (C=C), 1462 (m), 1400 (w), 1371 (s), 1159 (s), 1022 (w), 999 (m), 879 (m), 642 (m), 605 (s), 564 (s), 500 (s) cm⁻¹; terminal carbonyl region (pentane) 2072 (s), 2039 (vs), 2000 (vs), 1993 (sh) cm⁻¹. ¹H NMR (CD₂Cl₂, 250 MHz): δ 1.34 (s, 9 H, *tert*-butyl CH₃), 1.96 (s, 6 H, =CCH₃), 7.36 (s, 1 H, Fe₂CH). ¹³C NMR (C₆D₆, 22.5 MHz): δ_{C} 25.7 (q, $J = 128$

H_z, =CCH₃), 32.7 (q, *J* = 127 Hz, *tert*-butyl CH₃), 47.4 (s, CMe₃), 115.4 (s, =CMe₂), 119.6 (d, *J* = 161 Hz, Fe₂CH), 171.8 (s, C=CMe₂), 211.0 (s, CO).

Reaction between the Standard Fe₃(CO)₁₂/Me₃CSH/Et₃N Mixture and 1-Chloro-2-pentyne. The standard Fe₃(CO)₁₂/Me₃CSH/Et₃N reagent was prepared. To this was added 0.35 g (3.41 mmol) of 1-chloro-2-pentyne. The solution was stirred for 4 h, during which time the solution became red and a white precipitate formed. After removal of the solvent, the red oil remaining was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 1.01 g (2.31 mmol, 77% yield) of (μ-η¹,η²-H₂C=C=CET)(μ-Me₃CS)Fe₂(CO)₆ as an air-stable, red solid, mp 54–56 °C, after crystallization from ethanol. Anal. Calcd for C₁₅H₁₆O₆SFe₂: C, 41.32; H, 3.70. Found: C, 41.15; H, 3.87. IR (CHCl₃): 2977 (s), 2937 (m), 2907 (m), 2876 (m), 1731 (m), 1695 (w), 1457 (m), 1428 (w), 1396 (w), 1367 (m), 1154 (s), 1088 (w), 1040 (w), 1016 (m), 971 (w), 891 (m), 843 (m), 631 (s), 570 (vs), 493 (s) cm⁻¹; terminal carbonyl region (pentane) 2063 (s), 2034 (vs), 1994 (vs), 1986 (s) cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 1.26 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.36 (s, 9 H, Me₃C), 2.55 (br, 2 H, CH₂), 5.20 (br, 2 H, =CH₂). ¹³C NMR (CD₂Cl₂, 67.9 MHz): δ_C 16.8 (q, *J* = 128 Hz, CH₃), 33.4 (q, *J* = 127 Hz, *tert*-butyl CH₃), 45.0 (t, *J* = 132 Hz, CH₂), 49.3 (s, CMe₃), 94.7 (t, *J* = 163 Hz, =CH₂), 148.6 (s, Fe₂CET), 177.1 (s, FeC=), 210.6 (s, CO).

Reaction between (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆, 1 Equiv of LiBEt₃H, and Diphenylchlorophosphine. A 250-mL, round-bottomed flask containing 0.85 g (2.21 mmol) of (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆ was equipped with a stir-bar and a serum cap and flushed with nitrogen. THF (50 mL) was added and the red solution cooled to -78 °C; then 2.21 mL (2.21 mmol) of a 1.0 M LiBEt₃H solution in THF was added by syringe. The solution became brown and was stirred for 30 min. Diphenylchlorophosphine (0.40 mL, 2.21 mmol, Strem) was added and the solution removed from the cold bath. The reaction mixture was stirred for 20 h during which time it became dark red. The solvent was removed on a rotary evaporatory leaving a red oil which was extracted with pentane/CH₂Cl₂ (1/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which then was subjected to filtration chromatography (silicic acid/pentane). Pentane/CH₂Cl₂ (9/1, v/v) eluted an orange band which gave 0.64 g (1.22 mmol, 55% yield) of (μ-Ph₂P)(μ-EtS)Fe₂(CO)₆ identified by comparison of its melting point and ³¹P NMR spectrum with those of an authentic sample.³⁹ A second dark red band was eluted from the column with a 3/1 (v/v) pentane/CH₂Cl₂ mixture giving 0.41 g (0.70 mmol, 32% yield) of (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆PPH₂OEt as a dark red, air-stable oil. Anal. Calcd for C₂₃H₂₃O₇SPFe₂: C, 47.13; H, 3.96. Found: C, 47.49; H, 4.13. IR (CHCl₃): ν(C=O) 1502 (s); terminal carbonyl region (pentane) 2040 (vs), 2023 (m), 1983 (vs), 1958 (s), 1939 (m) cm⁻¹. ¹H NMR (CD₂Cl₂, 250 MHz): δ 1.23 (t, *J* = 7.4 Hz, 3 H, CH₃), 1.33 (t, *J* = 7.0 Hz, 3 H, CH₃), 2.16 (m, 2 H, SCH₂), 2.19 (s, 3 H, acyl CH₃), 3.92 (m, 2 H, OCH₂), 7.48 and 7.72 (both m, 10 H, Ph). ¹³C NMR (CD₂Cl₂, 67.9 MHz): δ_C 16.7 (q, *J* = 128 Hz, CH₃), 18.2 (q, *J* = 128 Hz, CH₃), 32.0 (t, *J* = 140 Hz, SCH₂), 47.2 (q, *J* = 128 Hz, acyl CH₃), 63.6 (t, *J* = 142 Hz, OCH₂), 127–132 (Ph), 138.7 (d, *J*(P-C) = 48 Hz, ipso Ph), 210–218.5 (FeCO), 300.3 (s, acyl CO). ³¹P{¹H} NMR (CDCl₃, 36.2 MHz): δ_P 153.6 (s).

Reaction between (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆ and LiBEt₃H. Allyl Chloride Quench. By syringe, 2.0 mL (2.20 mmol) of a 1.0 M LiBEt₃H solution in THF (Aldrich) was added to a -78 °C THF (50 mL) solution of 0.38 g (0.99 mmol) of (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆. The mixture became brown and was stirred for 20 min prior to addition of 0.50 mL (6.13 mmol) of allyl chloride (Aldrich). The solution immediately became red and was removed from the cold bath and stirred for 2 h. Removal of the solvent left a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.31 g (0.807 mmol, 82% yield) of (μ-CH₂CHCH₂)(μ-EtS)Fe₂(CO)₆ as an air-stable, red solid, mp 40–42 °C, after crystallization from methanol. It was identified by comparison of its ¹H NMR spectrum to that of an authentic sample (see above).

Table VII. Crystal Data for Compounds 18 and 21

18	
<i>a</i> = 13.400 (2) Å	space group <i>Pn</i> 2 ₁ <i>a</i>
<i>b</i> = 6.958 (1) Å	<i>Z</i> = 4
<i>c</i> = 15.970 (2) Å	mol wt = 381.96 g
<i>V</i> = 1489.0 Å ³	ρ(calcd) = 1.704 g cm ⁻³
	μ = 20.70 cm ⁻¹ (absorptn correctn not applied)
21	
<i>a</i> = 8.455 (1) Å	<i>V</i> = 848.9 Å ³
<i>b</i> = 9.478 (1) Å	space group <i>P</i> 1̄
<i>c</i> = 10.926 (2) Å	<i>Z</i> = 2
α = 90.95 (1)°	mol wt = 207.99 g
β = 97.44 (1)°	ρ(calcd) = 1.596 g cm ⁻³
γ = 101.81 (1)°	μ = 18.18 cm ⁻¹ (absorptn correctn not applied)

Propargyl Bromide Quench. The same procedure was used in the reaction of 2.82 mmol of 1.0 M LiBEt₃H in THF with 1.41 mmol of (μ,η²-MeCO)(μ-EtS)Fe₂(CO)₆ in 50 mL of THF. Addition of 9.3 mmol of propargyl bromide resulted in formation of a red solution. Workup gave 0.30 g (0.79 mmol, 56%) of (μ-η¹,η²-CH₂=C=CH)(μ-EtS)Fe₂(CO)₆ as a red solid, mp 39–41 °C (from MeOH), whose spectroscopic properties were identical with those of an authentic sample (see above).

Reaction between (μ,η²-PhCO)(μ-EtS)Fe₂(CO)₆ and LiBEt₃H. Allyl Chloride Quench. By syringe, 0.90 mL (0.90 mmol) of a 1.0 M LiBEt₃H solution (Aldrich) was added to a -78 °C THF (30 mL) solution of 0.20 g (0.448 mmol) of (μ,η²-PhCO)(μ-EtS)Fe₂(CO)₆. The mixture became brown and was stirred for 30 min prior to addition of 0.50 mL (6.13 mmol) of allyl chloride (Aldrich). The solution immediately became red and was removed from the cold bath and stirred for 1 h. Removal of the solvent left a red oil which was taken up in pentane/CH₂Cl₂ (9/1, v/v) and filtered through a pad of silicic acid. The red filtrate yielded a red oil which was subjected to filtration chromatography (silicic acid/pentane). Pentane eluted a red band which gave 0.14 g (0.366 mmol, 82% yield) of (μ-CH₂CHCH₂)(μ-EtS)Fe₂(CO)₆ as a red air-stable solid, mp 40–42 °C, after recrystallization from methanol.

Reaction between the Anion Formed by the Reaction of C₆H₅SeH, Fe₃(CO)₁₂, and NEt₃ with *N,N*-Dimethylthiocarbamoyl Chloride. A solution of 2.98 mmol of Fe₃(CO)₁₂ (1.50 g) and 3.01 mmol of NEt₃ (0.30 g) in THF (50 mL) was prepared. To this solution was added 3.03 mmol of C₆H₅SeH (Alfa, 0.48 g) dropwise via syringe at room temperature. An immediate color change from green to dark red was observed. After 15 min, 3.27 mmol of Me₂NC(S)Cl (Sigma, 0.40 g) was added to the stirred reaction mixture as a solid against a positive flow of nitrogen. After 1 h at room temperature the color of the reaction mixture was cherry red. The solvents were removed in vacuo. The resulting residue was taken up in 70/30 pentane/Et₂O (v/v) and subjected to silicic acid filtration chromatography in a 350-mL glass-fritted funnel. Pentane eluted a broad red band which gave a red oily residue. This residue was redissolved in 70/30 pentane/Et₂O (v/v) and rechromatographed in the same manner as before. A minor red-orange band which eluted first by using pentane as an eluent was discarded. Further elution with pentane yielded a bright red band which gave a red crystalline compound (mp 123–124 °C). This was identified as (μ-Me₂NC=S)(μ-PhSe)Fe₂(CO)₆ (9.91 g, 1.74 mmol, 58%). Anal. Calcd for C₁₅H₁₁O₆NSSeFe₂: C, 34.39; H, 2.12. Found: C, 34.68; H, 2.17. IR (CCl₄, NaCl): 3078 (vw), 2936 (w), 2861 (vw), 2068 (s), 2026 (vs), 2002 (vs), 1987 (s), 1964 (s), 1581 (w), 1510 (m, br), 1478 (w), 1439 (w), 1390 (m), 1233 (vs), 1183 (vw), 1136 (w, br), 1071 (vw), 1042 (vw), 1023 (w), 1002 (w), 922 (w), 692 (m), 667 (vw), 620 (m), 605 (m), 580 (m), 564 (m) cm⁻¹. ¹H NMR (300 MHz, acetone-*d*₆): δ 3.36 (s, 3 H, endo-NCH₃), 3.71 (s, 3 H, exo-NCH₃), 7.33–7.63 (m, 5 H, phenyl H's). ¹³C NMR (67.9 MHz, acetone-*d*₆): δ_C 44.8 (q, *J*_{CH} = 137.8 Hz, exo-NCH₃), 47.6 (q, *J*_{CH} = 139.9 Hz, endo-NCH₃), 128.8–135.2 (m, phenyl C's), 210.4, 211.9, 212.8 (all s, carbonyl C's), 240.0 (s, Me₂NC[S]-).

Crystal and Molecular Structure of (μ-Allyl)(μ-ethanethiolato)hexacarbonyldiiron (18) and (μ-η¹,η²-Allenyl)(μ-2,2-dimethylethanethiolato)hexacarbonyldiiron (21). Compound 18 crystallizes in the space group *Pn*2₁*a*. Data in the range

(39) Seyferth, D.; Womack, G. B.; Archer, C. M.; Brewer, K. S., to be published.

Table VIII. Final Positional Parameters for 18 and 21^a

atom	x	y	z
18			
Fe(1)	0.18677 (4)	0.0000	0.15701 (3)
Fe(2)	0.25864 (4)	-0.0075 (2)	0.00075 (3)
S	0.26187 (8)	0.2424 (3)	0.09021 (7)
C(1)	0.3862 (4)	0.2971 (10)	0.1299 (4)
C(2)	0.3797 (7)	0.3994 (13)	0.2133 (5)
C(3)	0.0534 (4)	0.1082 (9)	0.1035 (3)
C(4)	0.0792 (3)	0.0202 (12)	0.0258 (3)
C(5)	0.1220 (4)	0.1129 (10)	-0.0443 (3)
C(11)	0.2991 (4)	-0.0777 (8)	0.2070 (3)
O(11)	0.3676 (4)	-0.1208 (7)	0.2445 (3)
C(12)	0.1398 (4)	0.1140 (10)	0.2489 (3)
O(12)	0.1094 (3)	0.1861 (10)	0.3066 (3)
C(13)	0.1298 (4)	-0.2340 (9)	0.1664 (3)
O(13)	0.0940 (4)	-0.3797 (7)	0.1704 (3)
C(21)	0.3713 (5)	-0.1113 (10)	0.0384 (3)
O(21)	0.4448 (4)	-0.1812 (11)	0.0563 (3)
C(22)	0.3115 (4)	0.1056 (11)	-0.0879 (4)
O(22)	0.3441 (4)	0.1842 (10)	-0.1450 (3)
C(23)	0.2258 (4)	-0.2345 (10)	-0.0426 (3)
O(23)	0.2052 (4)	-0.3810 (8)	-0.0714 (3)
H(11)	0.4209 (4)	0.3759 (10)	0.0910 (4)
H(12)	0.4219 (4)	0.1804 (10)	0.1377 (4)
H(21)	0.4437 (7)	0.4476 (13)	0.2281 (5)
H(22)	0.3688 (7)	0.3080 (13)	0.2539 (5)
H(23)	0.3332 (7)	0.5024 (13)	0.2114 (5)
H(31)	-0.0034	0.0001	0.1355
H(32)	0.0506	0.2609	0.0983
H(41)	0.0550	-0.1100	0.0181
H(51)	0.1073	0.0116	-0.1073
H(52)	0.1266	0.2655	-0.0391
21			
Fe(1)	0.66290 (11)	0.73388 (9)	0.33808 (8)
Fe(2)	0.95221 (11)	0.74811 (10)	0.28870 (8)
S	0.72078 (19)	0.67004 (16)	0.15235 (14)
C(11)	0.5706 (10)	0.8816 (8)	0.2898 (6)
O(11)	0.5058 (8)	0.9746 (6)	0.2628 (5)
C(12)	0.4821 (9)	0.6012 (8)	0.3422 (6)
O(12)	0.3697 (7)	0.5130 (7)	0.3480 (5)
C(13)	0.6798 (9)	0.7989 (8)	0.4948 (7)
O(13)	0.6880 (8)	0.8404 (6)	0.5943 (5)
C(21)	0.9514 (9)	0.9350 (8)	0.2892 (7)
O(21)	0.9618 (7)	1.0585 (6)	0.2934 (6)
C(22)	1.0799 (9)	0.7149 (9)	0.1777 (8)
O(22)	1.1550 (8)	0.6862 (7)	0.1064 (6)
C(23)	1.1132 (9)	0.7804 (8)	0.4120 (7)
O(23)	1.2234 (8)	0.8026 (7)	0.4883 (6)
C(1)	0.6811 (8)	0.7747 (7)	0.0125 (6)
C(2)	0.7521 (10)	0.9347 (7)	0.0254 (7)
C(3)	0.4959 (9)	0.7402 (8)	-0.0217 (7)
C(4)	0.7586 (11)	0.7045 (9)	-0.0850 (7)
C(5)	0.8135 (8)	0.6074 (6)	0.3986 (6)
C(6)	0.8796 (8)	0.5258 (7)	0.3235 (6)
C(7)	0.9075 (11)	0.4052 (8)	0.2737 (7)
H(21)	0.7035 (10)	0.9774 (7)	0.0861 (7)
H(22)	0.7310 (10)	0.9771 (7)	-0.0516 (7)
H(23)	0.8665 (10)	0.9502 (7)	0.0499 (7)
H(31)	0.4475 (9)	0.7836 (8)	0.0387 (7)
H(32)	0.4568 (9)	0.6387 (8)	-0.0251 (7)
H(33)	0.4681 (9)	0.7771 (8)	-0.1002 (7)
H(41)	0.7134 (11)	0.6039 (9)	-0.0928 (7)
H(42)	0.8730 (11)	0.7196 (9)	-0.0607 (7)
H(43)	0.7376 (11)	0.7466 (9)	-0.1622 (7)

^a Numbers in parentheses are errors in the last significant digit(s).

$3^\circ < 2\theta < 55^\circ$ ($+h,+k,+l$) were collected by using Mo K α radiation on a Enraf-Nonius CAD4F-11 diffractometer. Data collection and reduction procedures have been described in detail elsewhere.³⁶ The structure was solved by direct-methods using MULTAN78

and refined by full-matrix least-squares techniques using SHELX-76. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the ethyl group were placed in calculated positions (C-H = 0.95 Å; H-C-H = 109.5°) and were constrained to ride on the carbon atom to which they are bonded. Hydrogen atoms of the allyl group were located in a difference Fourier map and were included in the refinement as invariants with $U = 0.10$ Å². Final residual indices are $R_1 = 0.034$ and $R_2 = 0.037$ for 1469 observed reflections [$F_o > 4\sigma(F_o)$] and 185 variables.

Data in the range $3^\circ < 2\theta < 55^\circ$ ($+h,\pm k,\pm l$) were collected for compound 21, space group $P\bar{1}$, using Mo K α radiation.³⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the *tert*-butyl group were placed in calculated positions and were constrained to ride on the carbon atoms to which they are bound. Hydrogen atoms of the allenyl group could not be located in difference Fourier maps and have been ignored. Final residual indices are $R_1 = 0.048$ and $R_2 = 0.055$ for 2058 observed reflections [$F_o > 4\sigma(F_o)$] and 200 variables.

Crystal data for compounds 18 and 21 are given in Table VII and final positional parameters for 18 and 21 in Table VIII. Tables of final observed and calculated structure factors for 18 and 21 have been deposited with the preliminary communication in which some of these results were reported.^{18a}

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Registry No. 5a (equatorial isomer), 93530-39-3; 5a (axial isomer), 93603-00-0; 5b (equatorial isomer), 93530-31-5; 5b (axial isomer), 93602-99-4; 9, 117709-46-3; 15 (R' = Me₂CH, R = Et), 117709-50-9; 15 (R' = C₁₀H₇, R = Et), 117709-52-1; 15 (R' = *p*-CH₃C₆H₄, R = Me₃C), 117709-54-3; 17 (R = Me), 117733-96-7; 17 (R = Et), 117733-97-8; 18, 93530-32-6; 20, 93530-33-7; 21, 93530-34-8; 22, 93530-35-9; 23, 93530-36-0; 30, 117687-76-0; 31, 117709-55-4; Fe₃(CO)₁₂, 17685-52-8; (μ_3 -EtS)(μ,η^2 -MeCO)Fe₃(CO)₉, 117709-48-5; PhC(O)SEt, 1484-17-9; Fe₂(CO)₉, 15321-51-4; Me₃CC(O)SEt, 22872-50-0; (μ,η^2 -Me₃CC=O)(μ -EtS)Fe₂(CO)₆, 117773-45-2; (μ -EtS)₂Fe₂(CO)₆, 28829-01-8; (μ,η^2 -PhCO)(μ -Me₃CS)Fe₂(CO)₆ (axial isomer), 118013-31-3; (μ,η^2 -PhCO)(μ -Me₃CS)Fe₂(CO)₆ (equatorial isomer), 117773-46-3; (μ,η^2 -PhCO)(μ -PhS)Fe₂(CO)₆ (axial isomer), 117709-49-6; (μ,η^2 -PhCO)(μ -PhS)Fe₂(CO)₆ (equatorial isomer), 117773-47-4; (μ,η^2 -Me₂CHCO)(μ -EtS)Fe₂(CO)₆ (axial isomer), 117773-44-1; (μ,η^2 -2-naphthyl-CO)(μ -EtS)Fe₂(CO)₆, 117709-51-0; (μ,η^2 -2-naphthyl-CO)(μ -EtS)Fe₂(CO)₆ (equatorial isomer), 117773-48-5; (μ,η^2 -*p*-CH₃C₆H₄CO)(μ -Me₃CS)Fe₂(CO)₆ (axial isomer), 117709-53-2; (μ,η^2 -*p*-CH₃C₆H₄CO)(μ -Me₃CS)Fe₂(CO)₆ (equatorial isomer), 117773-49-6; (CH₃)₃CSH, 75-66-1; LiEt₃H, 22560-16-3; (μ -Ph₂P)(μ -EtS)Fe₂(CO)₆, 93564-55-7; C₆H₅SeH, 645-96-5; Me₂NC(S)Cl, 16420-13-6; Et₂NC(S)Cl, 88-11-9; mesitylenethiol, 1541-10-2; ethanethiol, 75-08-1; S-ethyl thioacetate, 625-60-5; allyl chloride, 107-05-1; propargyl bromide, 106-96-7; 3-bromo-3-methyl-1-butene, 6214-31-9; 1-chloro-2-pentyne, 22592-15-0; diphenylchlorophosphine, 1079-66-9; (μ,η^2 -Me₂CHCO)(μ -EtS)Fe₂(CO)₆ (equatorial isomer), 117709-47-4.

Supplementary Material Available: A table of final positional and thermal parameters for 9 and IR and mass spectral data (7 pages); a listing of final observed and calculated structure factors for compound 9 (16 pages). Ordering information is given on any current masthead page.