

Reactions of Di- and Polynuclear Complexes. 6.¹ Reaction of
 $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe}\}_2\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$
with $[\text{Fe}_3(\text{CO})_{12}]$. Ligand Exchange between Metals: Synthesis
and Characterization of Di- and Trinuclear Iron-Alkyne
Complexes. Crystal Structure of
 $\{[\text{Fe}(\text{CO})_3]_2\{\mu\text{-}(\text{CF}_3)\text{CCC}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]\}$

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The dinuclear complex $[\text{Cp}(\text{CO})\text{Fe}\{\mu\text{-}(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SMe}\}_2\text{Fe}(\text{CO})\text{Cp}]$ (1) reacts in toluene with $[\text{Fe}_3(\text{CO})_{12}]$ to form a chromatographically separable mixture of two cluster compounds, $\{[\text{Fe}(\text{CO})_3]_2\{\mu\text{-}(\text{CF}_3)\text{C}_2(\text{CF}_3)\text{S}\}\}$ (2) and $[\text{Fe}_3\text{Cp}_2(\text{CO})_3(\mu_3\text{-CO})(\mu\text{-CO})(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)]$ (6), together with the di- and trinuclear species $[\text{Fe}(\text{CO})_3]_2\{\text{C}_2\text{F}_2(\text{CF}_3)\text{SMe}\}$ (3), $\{\text{Fe}(\text{CO})_3\}_2\{\mu\text{-SMe}\}\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ (4), and $\{\text{Fe}(\text{CO})_3\}_2\{\mu\text{-}(\text{CF}_3)\text{C}_3[\text{FeCp}(\text{CO})_2]\}$ (5). Cluster 6 is obtained as a mixture of two isomers, 6a and 6b. The same reactants in benzene yield a similar mixture, except that 5 is absent and two isomeric iron dinuclear species $[\text{Cp}(\text{CO})\text{Fe}\{\mu\text{-}(\text{CF}_3)\text{C}_2(\text{CF}_3)\text{SMe}\}\text{Fe}(\text{CO})_3]$ (7a,b) are also obtained. Heating 1 and $\text{Fe}_3(\text{CO})_{12}$ in tetrahydrofuran gives 7a, 7b, and yet a third isomer, 7c. On being heated in toluene, the isomeric complexes 7a and 7c decompose to $[\text{CpFe}(\mu\text{-CO})_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)\text{FeCp}]$ (8). The formation of these derivatives implies ligand-exchange processes between different metal sites. The molecular structures of compounds 2 and 6a have been established by single-crystal X-ray diffraction studies, which were communicated elsewhere. 6a contains a triangular Fe_3 unit μ_3 bridged by CO; one of the Fe-Fe edges is semibridged by a second CO ligand, and the remaining CO ligands are terminally bonded to a single iron atom. The $\text{CF}_3\text{C}_2\text{CF}_3$ alkyne ligands in 6a and 6b each adopt $\mu_3\text{-}\eta^2\text{-}\parallel$ bonding modes but differ in their orientations with respect to the unsymmetrically substituted Fe_3 triangles. Compound 2 has also been shown to contain a $\mu_3\text{-}\eta^2\text{-}\parallel\text{-CF}_3\text{C}_2\text{CF}_3$ unit bridging an Fe_3S triangle. X-ray analysis of 5 reveals the presence of a new ligand, $(\text{CF}_3)\text{CC}=\text{CFeCp}(\text{CO})_2$, which bridges two $\text{Fe}(\text{CO})_3$ units. This new ligand results from abstraction of three fluorine atoms from a CF_3 group. The $\text{Fe}(\text{CO})_3$ units are also linked by an Fe-Fe bond of 2.477 (2) Å. 5 crystallizes in the orthorhombic space group *Pbca* with $a = 13.533$ (4), $b = 14.748$ (4), $c = 20.067$ (3) Å, and $R = 0.041$ for refinement of 280 parameters from 2619 unique observations. The molecular structures of the isomers 7, isomer 6b, and compounds 4 and 8 have been assigned from consideration of their infrared, mass, and NMR spectra (^1H , ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$). The catalytic activity of the trinuclear species 6 in the homogeneous isomerization of straight-chain alkenes is described.

Introduction

There is considerable current interest in transition-metal clusters containing coordinated alkynes, not only because these species can act as potential models for the chemisorption of unsaturated hydrocarbons on metallic surfaces² but also because they represent synthetic challenges.³ In our recent studies we have focused on the ability of thioalkenyl ligands in metal complexes to facilitate cluster synthesis.⁴ We showed that these species react with carbonylcobalt derivatives to give tetranuclear clusters both through condensation of unsaturated species formed by pyrolytic decarbonylation and by ligand exchange between different metallic sites.

As an extension of this work, we have now examined the reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe}\}_2\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$ with $[\text{Fe}_3(\text{CO})_{12}]$. When this reaction is carried out in toluene, new $\mu_3\text{-}\eta^2\text{-}\parallel$ -alkyne Fe_3C_2 and Fe_2SC_2 five-vertex cluster polyhedra are formed, together with dinuclear iron derivatives $\{[\text{Fe}(\text{CO})_3]_2\{\mu\text{-SMe}\}\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}$ and $\{\text{Fe}(\text{CO})_3\}_2\{\mu\text{-}(\text{CF}_3)\text{CCC}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]\}$. Formation of the last of these complexes reveals an unusual ligand transformation involving interactions at two or more metal sites. When the reaction is conducted in benzene or tetrahydrofuran, some of the above products are obtained, together with new isomeric dinuclear derivatives $[\text{Fe}(\text{CO})_3\{\mu\text{-}(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SMe}\}\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$. This paper describes the details of the synthesis, molecular structure and bonding, and chemical properties of these di- and polynuclear complexes. A preliminary communication of a part of this work has already appeared.⁵

Results and Discussion

Reaction of $[\text{Cp}(\text{CO})\text{Fe}\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe}\}_2\text{Fe}(\text{CO})\text{Cp}]$ (1) with $[\text{Fe}_3(\text{CO})_{12}]$ in Toluene. The reaction of 1 with a large excess of $\text{Fe}_3(\text{CO})_{12}$ in toluene under reflux

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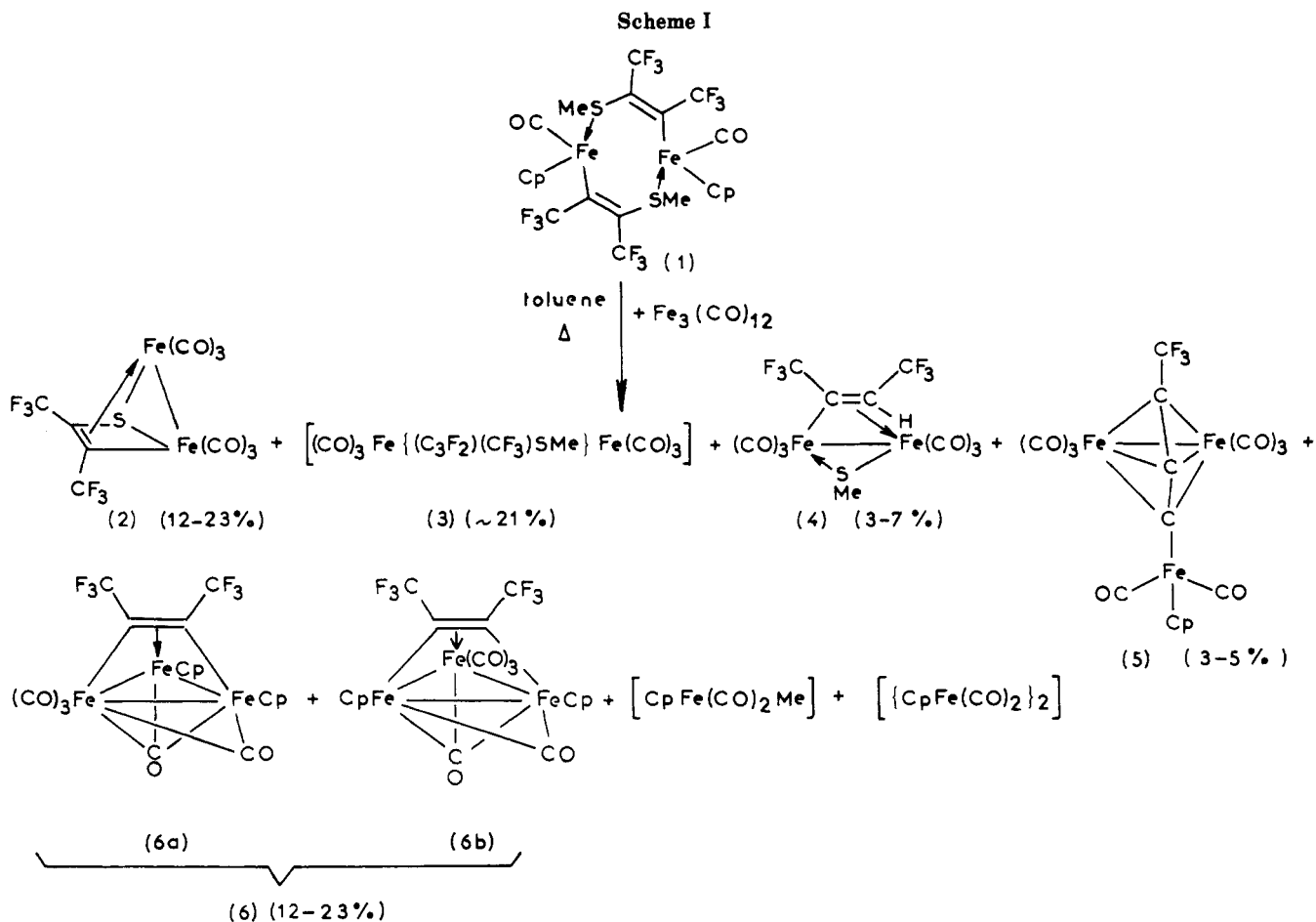
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Scheme I

Table I. NMR Data for the Complexes (δ)

complex	$^1\text{H}^a$	^{19}F	$^{13}\text{C}^b$
2		-56.23 (q, 3 F, $J_{\text{FF}} = 8.5$), -61.86 (q, 3 F, $J_{\text{FF}} = 8.5$)	206.7, 205.6, 203.0 (CO), 141.5 (q, $=\text{C}(\text{CF}_3)$, $^2J_{\text{CF}} = 40$), 124.7 (q, CF_3 , $J_{\text{CF}} = 275$), 118.7 (q, CF_3 , $J_{\text{CF}} = 276$), 105.6 (q, $=\text{C}(\text{CF}_3)$, $^2J_{\text{CF}} = 49$)
4	2.15 (s, 3 H, SMe), 2.06 (q, 1 H, CH, $J_{\text{F-H}} = 9$)	-48.94 (q, 3 F, $J_{\text{FF}} = 13.5$, -54.75 (dq, 3 F, $J_{\text{FF}} = 13.5$, $J_{\text{F-H}} = 9$)	205.4 (s, br, CO), 128.3 (q, CF_3 , $J_{\text{CF}} = 276$), 124.0 (q, CF_3 , $J_{\text{CF}} = 276$), 75 (qq, $\text{C}=\text{CH}(\text{CF}_3)$, $^2J_{\text{CF}} = 38$, $^3J_{\text{CF}} = 3.7$), 22.0 (s, SCH_3)
5	5.15 (s, 5 H, C_5H_5)	-49.27 (s)	c 210.56 (CpFeCO), 210.23 (s, $\text{Fe}(\text{CO})_3$), 127.8 (q, CF_3 , $J_{\text{CF}} = 267$), 106.9 (s, $\text{FeC}=\text{C}$), 87.2 (s, C_5H_5), 47.5 (s, br, $\text{C}=\text{C}=\text{C}$)
6a (major)	5.07 (s, 5 H, C_5H_5), 4.91 (s, 5 H, C_5H_5)	-49.22 (q, 3 F, $J_{\text{FF}} = 12$), -51.52 (q, 3 F, $J_{\text{F-F}} = 12$)	279.5 (μ_3 -CO), 225.4 (μ -CO), 209.6, 206.7, 204.4 (CO), 170.4 (qq, $=\text{C}(\text{CF}_3)$, $^2J_{\text{CF}} = 36$, $^3J_{\text{CF}} = 2$), 153.3 (qq, $=\text{C}(\text{CF}_3)$, $^2J_{\text{CF}} = 33.5$, $^3J_{\text{CF}} = 2$), 128.4 (q, CF_3 , $J_{\text{CF}} = 276$), 127.5 (q, CF_3 , $J_{\text{CF}} = 276$), 92.8 (s, C_5H_5), 87.8 (s, C_5H_5)
6b (minor)	4.89 (s, 10 H, C_5H_5)	-52.01 (s)	271.3, 239.3 (μ -CO), 210.3 (nCO), 126.5 (q, CF_3 , $J_{\text{CF}} = 278$), 94.1 (s, C_5H_5)
7a	4.93 (s, 5 H, C_5H_5), 2.25 (q, 3 H, Me, $J_{\text{F-H}} = 1.3$)	-51.16 (q, 3 F, $J_{\text{FF}} = 6$), -58.49 (q, br, 3 F, $J_{\text{FF}} = 6$)	d 225.5 (CpFeCO), 209.8, 209.0, 206.0 ($\text{Fe}(\text{CO})_3$), 133.5 (qq, $=\text{C}(\text{CF}_3)$, $^2J_{\text{C-F}} = 39$, $^3J_{\text{CF}} = 2$), 131.5 (q, CF_3 , $J_{\text{CF}} = 272$), 123.3 (q, CF_3 , $J_{\text{CF}} = 277$), 84.7 (s, C_5H_5), 48.3 (q, $=\text{C}(\text{CF}_3)$, $J_{\text{CF}} = 39$), 29.5 (s, SCH_3)
7b	4.88 (s, 5 H, C_5H_5), 1.65 (q, 3 H, Me, $J_{\text{F-H}} = 0.7$)	-49.82 (q, 3 F, $J_{\text{F-F}} = 7.3$), -62.19 (q, br, 3 F, $J_{\text{F-F}} = 7.3$)	239.6 (μ -CO), 211.3, 207.7, 207.4 ($\text{Fe}(\text{CO})_3$), 132.1 (q, CF_3 , $J_{\text{C-F}} = 272$), 127.0 (q, br, $=\text{C}(\text{CF}_3)$, $^2J_{\text{C-F}} = 39.5$), 123.6 (q, CF_3 , $J_{\text{C-F}} = 277$), 84.85 (s, C_5H_5), 57.5 (qq, $=\text{C}(\text{CF}_3)$, $^2J_{\text{C-F}} = 39$, $^3J_{\text{C-F}} = 2$), 22.5 (s, SCH_3)
7c	4.86 (s, 5 H, C_5H_5), 2.25 (q, 3 H, Me, $J_{\text{F-H}} = 1.2$)	-50.15 (q, 3 F, $J_{\text{F-F}} = 7.3$), -58.41 (q, br, 3 F, $J_{\text{F-F}} = 3$)	240.2 (μ -CO), 209.1, 207.9, 207.6 ($\text{Fe}(\text{CO})_3$), 132.2 (q, CF_3 , $J_{\text{F-F}} = 272$), 124.5 (q, br, $=\text{C}(\text{CF}_3)$, $^2J_{\text{C-F}} = 39$), 123.4 (q, CF_3 , $J_{\text{C-F}} = 277$), 84.7 (s, C_5H_5), 51.7 (qq, $=\text{C}(\text{CF}_3)$, $^2J_{\text{C-F}} = 39$, $^3J_{\text{C-F}} = 2$), 29.0 (s, SCH_3)
8	4.75 (s, 10 H, C_5H_5)	-54.48 (s)	266.6 (μ -CO), 129.9 (q, CF_3 , $J_{\text{C-F}} = 270$), 84.5 (s, C_5H_5)

^aChemical shifts (δ) in ppm measured in CDCl_3 at room temperature unless otherwise stated; J in hertz. ^bHydrogen-1 decoupled. ^cMeasured in CD_2Cl_2 . ^dMeasured at -30°C .

was found to produce a mixture of compounds. These were separated by column chromatography and combined for those with similar R_f factors on silica gel (see Experimental Section) with fractional recrystallization (see Scheme I).

One of the major products of the reaction is the diiron complex 2, which was formulated as $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{CF}_3)\text{-}=\text{C}(\text{CF}_3)\text{S})]$ on the basis of mass, infrared, and NMR

spectral data. Spectroscopic data for all new complexes reported herein are given in Table I and in the Experimental Section. In the mass spectrum of 2 successive loss of CO from the parent ion $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_4\text{F}_6\text{S})]^+$ is observed. In addition, fragments arising from C-F bond scission are also obtained. The calculated isotopic distribution of the parent ion is in excellent agreement with that observed

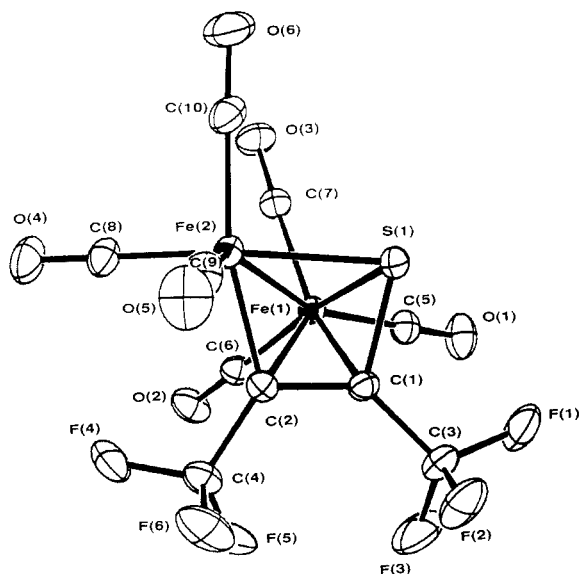


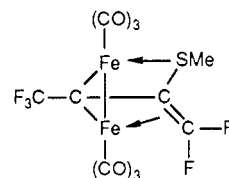
Figure 1. Perspective view of a molecule of $[(\text{Fe}(\text{CO})_3)_2\{\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{S}\}]$ (**2**). Here and in Figures 2 and 3 20% ellipsoids are displayed.

experimentally. Infrared spectra display four absorptions between 2098 and 2025 cm^{-1} , which are assigned to terminal carbonyl stretches and are consistent with formulation of **2** as a binuclear species with two $\text{Fe}(\text{CO})_3$ fragments bridged by heteroatoms. The ^1H NMR spectrum of **2** is characterized by the lack of any resonances, thus confirming the cleavage of the S-Me bond in the parent thiolate ligand. The ^{19}F NMR spectrum exhibits two quartets, and the F-F coupling (8.5 Hz) suggests that the CF_3 groups have a cis configuration. The structure of **2** has been confirmed by an X-ray diffraction study (Figure 1). The structural results have been reported in a preliminary communication⁵ and therefore will not be discussed here in detail.

The molecule of **2** contains a triangular heteroatomic cluster of one sulfur and two iron atoms. Each iron atom carries three terminally bound CO ligands. The hexafluorobut-2-yne ligand interacts with all three atoms of the Fe_2S triangle: it is σ -bonded to the atoms Fe(2) and S and π -bonded to Fe(1) through the C(1)-C(2) bond. The S(1)-C(1)-C(2)-Fe(2) torsion angle $[-3.8(2)^\circ]$ is indicative of a $\mu_3\text{-}\eta^2\text{-}\pi$ attachment of the alkyne to the Fe_2S triangle. The length of the C(1)-C(2) bond [1.406(5) Å] suggests that the alkyne acts as a four-electron donor to the triatomic unit. This formulation of compound **2** has precedents in the literature. Indeed, an example of an iron complex containing a thiokecarbonyl ligand, $\text{RC}=\text{CR}(\text{S})$, has been previously described by Schrauzer et al.^{6a} These authors synthesized $[\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5)_2\text{C}_2\text{S}]$ by thermal and photochemical reaction of (1,2-dithiolato)nickel complexes, $\{(\text{C}_6\text{H}_5)_2\text{C}_2(\text{SMe})_2\text{Ni}\}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]$, or 1,2,3-thiadiazoles with $\text{Fe}(\text{CO})_5$; a diiron adduct, $\{(\text{C}_6\text{H}_5)_2\text{C}_2(\text{SMe})_2\}\text{Fe}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2\}$, was proposed as an intermediate in the formation of the thiokecarbonyl complex.^{6b} A similar oxo compound has also been recently obtained by reacting benzoyl chloride with $\text{Na}_2\text{Fe}(\text{CO})_4$.^{6c} It appears that complex **2** is obtained by a different mechanism. We can rationalize the formation of **2** by invoking a cleavage of the S-CH₃ bond in **1** at elevated temperature and subsequent reaction of the thiokecarbonyl unit thus formed with $\text{Fe}_2(\text{CO})_6$

fragments. In support of this view we note the formation of the alkyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Me}$, which results from the reaction of the electron-deficient $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ entity with the methyl group expelled from **1** in the initial S-CH₃ bond scission. Such a mechanistic pathway involves an exchange of ligands from iron sites in **1** to the $\text{Fe}_2(\text{CO})_6$ moiety.

The product **3** has been characterized as $[(\text{OC})_3\text{Fe}\{\text{C}_3\text{F}_2(\text{CF}_3)(\text{SMe})\}\text{Fe}(\text{CO})_3]$ from microanalytical and spectroscopic data since single crystals suitable for X-ray diffraction could not be obtained. The ^{19}F and ^{13}C NMR spectra were both extremely complicated and not especially informative. In the mass spectrum of **3** peaks higher than 470 did not occur and the stepwise loss of six carbonyls was observed: the compound is then formulated as $\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_6)(\text{SMe})$. From the data available at this stage a definitive structure cannot be assigned to this compound. From the ^{13}C NMR data, the most likely geometry is



Complex **4** was obtained in low yield in the reaction (Scheme I) and was identified by elemental analysis and mass, infrared, and NMR spectra. The mass spectra of this product show the parent ion M^+ and the successive loss of six carbonyls, thus confirming the formulation for the thiolato complex. Furthermore, other observed fragments are $m/e = 112$ (Fe_2), 134 (FeCFSMe), 144 (Fe_2S), 163 ($\text{CF}_3\text{C}_2\text{HCF}_3$), and 178 ($\text{MeCF}_3\text{C}_2\text{HCF}_3$). The infrared spectra in the $\nu(\text{CO})$ region in hexane show the pattern of the expected six carbonyl bands, in contrast with the results of Ros et al.⁷ for similar complexes of the type

$[(\text{CO})_3\text{Fe}(\mu\text{-PhC}=\text{CPhH})(\mu\text{-SR})\text{Fe}(\text{CO})_3]$ ($\text{R} = \text{Et}, \text{Pr}, \text{Ph}, \text{CH}_2\text{Ph}$); this suggests that the symmetry of **4** is lower than that of Ros's compounds. The ^1H NMR spectra show the presence of the vinylic and thiolato protons in a 1:3 ratio. Only one signal for the vinylic proton is observed, which suggests the formation of one isomeric form. This is confirmed by ^{19}F NMR spectra, which show a quartet ($J_{\text{F-F}} = 13.5$ Hz) and a doublet of quartets ($J_{\text{F-F}} = 13.5$ Hz, $J_{\text{F-H}} = 9$ Hz) in accordance with a cis configuration of the CF_3 groups and the presence in the molecule of the $=\text{CHCF}_3$ moiety. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum is rather simple, with two singlets for the methyl and CO carbon atoms, two quartets for the two CF_3 groups, and one quartet of quartets for the tertiary carbon atoms. At room temperature carbonyl scrambling between iron atoms is rapid on the NMR time scale. The mechanism by which this product forms is not fully elucidated. Nevertheless, it is clear that it proceeds according to exchange processes between different iron sites of alkyne and SMe ligands. The vinylic proton arises, in all probability, from the solvent.

As a byproduct of the reaction, the new complex **5** was obtained in yields of up to 5%. The nature of **5** was established by a single-crystal X-ray diffraction study (see Table II and Figure 2). Although **5** is a trinuclear complex, it contains only one Fe-Fe bond which links the eclipsed $\text{Fe}(\text{CO})_3$ units of Fe(2) and Fe(3). The most novel feature of **5** is the new $\text{F}_3\text{CC}=\text{C}=\text{CFe}(\text{CO})_2\text{Cp}$ ligand which

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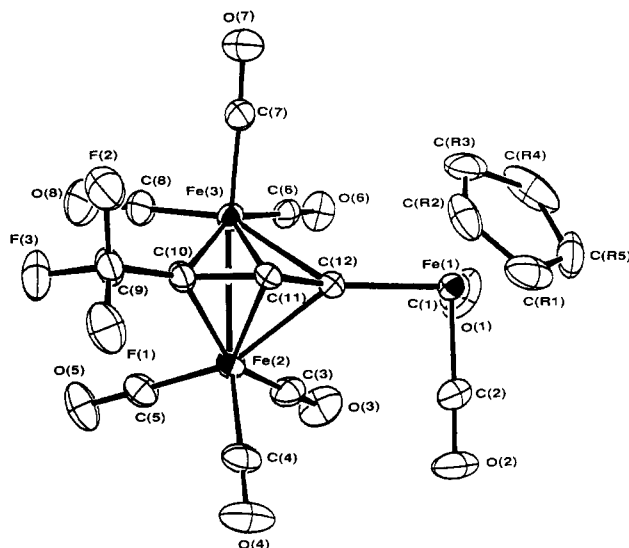


Figure 2. Perspective view of a molecule of $[\text{Fe}(\text{CO})_3]_2(\mu\text{-(CF}_3\text{)CCC[Fe}(\eta^5\text{-C}_5\text{H}_5\text{)(CO)}_2\text{)])$ (**5**). Here and in Figure 3 hydrogen atoms are omitted for clarity.

bridges the Fe(2)–Fe(3) bond. The geometry of this ligand suggests that it should be viewed as quasi-allylic, with a four-electron π -system delocalized across C(10)–C(11)–C(12) shared between Fe(2) and Fe(3) and with additional σ -orbitals on C(10) and C(12) involved in bridging the metal atoms. Fe(2) and Fe(3) thereby each receive 3 electrons from the bridging ligand to complete an 18-electron configuration. Consistent with this view, the chain C(9)–C(10)–C(11)–C(12)–Fe(1) is nearly planar [torsion angles across C(10)–C(11) and C(11)–C(12) respectively 177.3 (11) and -179.4 (12) $^\circ$]. However, the intrachain bond angles at C(10), C(11), and C(12) [129.0 (6), 138.2 (5), and 145.0 (4) $^\circ$] are substantially greater than 120 $^\circ$, suggesting hybridization intermediate between allylic sp^2 and allene-like sp . The bridging Fe–C distances lengthen as one goes from C(10), through C(11) to C(12) [Fe–C(10), 1.992 (6) and 1.971 (6) Å; Fe–C(11), 2.056 (5) and 2.055 (5) Å; μ -Fe–C(12), 2.204 (5) and 2.243 (5) Å]. This may reflect the differing substituents [CF₃ and Fe(CO)₂Cp] on C(10) and C(12) as may the shortening of C(11)–C(12) [1.269 (7) Å] relative to C(10)–C(11) [1.396 (7) Å]. The terminal Fe(1)–C(12) distance of 1.955 (5) Å is shorter than any of the μ -Fe–C bond lengths. The symmetrical disposition of the $\mu\text{-F}_3\text{CC}=\text{C}=\text{CFe}(\text{CO})_2\text{Cp}$ ligand with respect to Fe(2) and Fe(3) is apparent from the μ -Fe–C bond lengths and also from the nearly equivalent displacements of Fe(2) and Fe(3) [1.260 (1) and 1.215 (1) Å] from the plane defined by the C(9)–C(10)–C(11)–C(12)–Fe(1) chain atoms. The normal to this plane makes an angle of 1.7 $^\circ$ with the Fe(2)–Fe(3) vector.

An alternative description of **5** in terms of an Fe(2)–Fe(3)–C(11) triangle μ_3 -bridged on both faces by alkylidene carbons C(10) and C(12) is possible and has the merit of partially rationalizing the unusual coordination of the carbido-like atom C(11). Five of the six valence angles of C(11) are less than 90 $^\circ$ [C(10)–C(11)–C(12) = 138.2 (5) $^\circ$ is the exception], so that C(11) lies at the apex of a square pyramid and is bonded to the four basal atoms C(10), C(12), Fe(2), and Fe(3).

The Fe(2)–Fe(3) distance [2.477 (2) Å] appears somewhat short for a bond of single order [cf. 2.533 (1) in **2**⁵ and 2.53–2.60 in a selection of trinuclear complexes^{8–10}].

Table II. Selected Interatomic Distances (angstroms) and Angles (degrees) in $[\text{Fe}(\text{CO})_3]_2(\mu_3\text{-(CF}_3\text{)CCCFeCp}(\text{CO})_2)$ (**5**)

Bond Lengths			
Fe(1)–C(1)	1.754 (7)	Fe(2)–Fe(3)	2.477 (2)
Fe(1)–C(12)	1.955 (5)	Fe(2)–C(4)	1.832 (7)
Fe(1)–C(2)	1.755 (7)	Fe(2)–C(10)	1.992 (6)
Fe(1)–C(R) ^a	1.710	Fe(2)–C(12)	2.204 (5)
Fe(2)–C(3)	1.797 (8)	Fe(3)–C(7)	1.794 (7)
Fe(2)–C(5)	1.745 (7)	Fe(3)–C(10)	1.971 (6)
Fe(2)–C(11)	2.056 (5)	Fe(3)–C(12)	2.243 (5)
Fe(3)–C(6)	1.801 (7)	C(9)–C(10)	1.477 (8)
Fe(3)–C(8)	1.753 (7)	C(11)–C(12)	1.269 (7)
Fe(3)–C(11)	2.055 (5)	C–O	1.121 (7)–1.179 (8)
C(10)–C(11)	1.396 (7)		

Bond Angles			
C(1)–Fe(1)–C(2)	95.1 (4)	C(1)–Fe(1)–C(12)	97.8 (3)
C(1)–Fe(1)–C(R)	123.3	C(2)–Fe(1)–C(12)	91.8 (3)
C(2)–Fe(1)–C(R)	121.4	C(12)–Fe(1)–C(R)	120.3
Fe(3)–Fe(2)–C(3)	100.1 (3)	Fe(3)–Fe(2)–C(4)	150.5 (2)
Fe(3)–Fe(2)–C(5)	101.7 (3)	Fe(3)–Fe(2)–C(10)	50.9 (2)
Fe(3)–Fe(2)–C(11)	52.9 (2)	Fe(3)–Fe(2)–C(12)	56.9 (2)
C(3)–Fe(2)–C(10)	150.8 (3)	C(3)–Fe(2)–C(11)	123.2 (3)
C(3)–Fe(2)–C(12)	89.0 (3)	C(4)–Fe(2)–C(11)	98.0 (3)
C(4)–Fe(2)–C(10)	105.1 (3)	C(5)–Fe(2)–C(10)	94.3 (3)
C(4)–Fe(2)–C(12)	103.1 (3)	C(5)–Fe(2)–C(12)	158.6 (3)
C(5)–Fe(2)–C(11)	134.5 (3)	C(10)–Fe(2)–C(12)	72.6 (2)
C(10)–Fe(2)–C(11)	40.3 (2)	Fe(2)–Fe(3)–C(6)	101.4 (2)
C(11)–Fe(2)–C(12)	34.4 (2)	Fe(2)–Fe(3)–C(8)	100.1 (3)
Fe(2)–Fe(3)–C(7)	152.4 (2)	Fe(2)–Fe(3)–C(11)	53.0 (2)
Fe(2)–Fe(3)–C(10)	51.7 (2)	C(6)–Fe(3)–C(10)	152.9 (3)
Fe(2)–Fe(3)–C(12)	55.4 (2)	C(6)–Fe(3)–C(12)	90.3 (3)
C(6)–Fe(3)–C(11)	124.2 (3)	C(7)–Fe(3)–C(10)	106.2 (3)
C(7)–Fe(3)–C(11)	99.8 (3)	C(7)–Fe(3)–C(12)	105.6 (3)
C(8)–Fe(3)–C(10)	92.8 (3)	C(8)–Fe(3)–C(11)	133.1 (3)
C(8)–Fe(3)–C(12)	155.5 (3)	C(10)–Fe(3)–C(11)	40.5 (2)
C(10)–Fe(3)–C(12)	72.1 (3)	C(11)–Fe(3)–C(12)	34.0 (2)
Fe(2)–C(10)–Fe(3)	77.4 (2)	Fe(2)–C(10)–C(9)	137.7 (5)
Fe(2)–C(10)–C(11)	72.3 (3)	Fe(3)–C(10)–C(9)	139.2 (5)
Fe(2)–C(10)–C(11)	73.0 (3)	C(9)–C(10)–C(11)	129.0 (6)
Fe(2)–C(11)–Fe(3)	74.1 (2)	Fe(2)–C(11)–C(10)	67.4 (3)
Fe(2)–C(11)–C(12)	79.2 (4)	Fe(3)–C(11)–C(10)	66.5 (3)
Fe(3)–C(11)–C(12)	81.1 (4)	C(10)–C(11)–C(12)	138.2 (5)
Fe(1)–C(12)–Fe(2)	138.3 (3)	Fe(1)–C(12)–Fe(3)	139.2 (3)
Fe(1)–C(12)–C(11)	145.0 (4)	Fe(2)–C(12)–Fe(3)	67.7 (2)
Fe(2)–C(12)–C(11)	66.4 (3)	Fe(3)–C(12)–C(11)	64.9 (3)

Torsion Angles

C(10)–Fe(2)–Fe(3)–C(11)	51.8 (3)
C(10)–Fe(2)–Fe(3)–C(12)	94.0 (3)
C(11)–Fe(2)–Fe(3)–C(12)	42.1 (3)
C(9)–C(10)–C(11)–C(12)	177.3 (11)
C(10)–C(11)–C(12)–Fe(1)	-179.4 (12)

^a C(R) is the centroid of the cyclopentadienyl ring.

This prompts the suggestion that the Fe₂C₃ core could be regarded as an electron reservoir. The high-field shielding of the μ -carbene atoms, C(11) and C(12), in the ¹³C NMR spectrum (see Table I and below) is consistent with this view.

With the molecular structure of **5** established by X-ray diffraction, the spectroscopic data are readily interpretable. The infrared spectrum confirms the absence of bridging carbonyl groups. The ¹³C{¹H} NMR spectrum indicates that at room temperature site exchange of carbonyl ligands of the two Fe(CO)₃ groups occurs. The two CO atoms of the CpFe(CO)₂ group give rise to only one resonance at 211.56 ppm. Resonances due to quaternary carbon atoms are observed at 106.88 (s), 96.12 (q, ²J_{F–C} = 48.1 Hz), and 47.52 ppm (q, ³J_{F–C} = 8.5 Hz) and are respectively attributed to C(12), C(10), and C(11); moreover, a quartet

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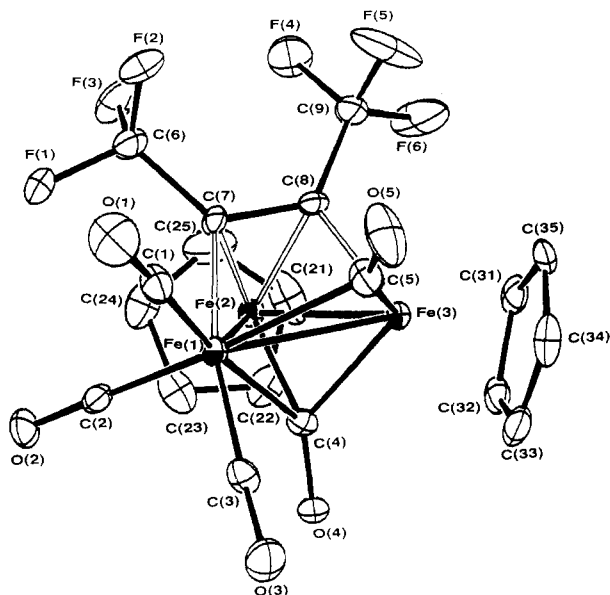


Figure 3. Perspective view of a molecule of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_3\text{-}(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_3(\mu_3\text{-}\eta^2\text{-||-CF}_3\text{C}_2\text{CF}_3)]$ (**6a**).

at 127.8 ppm is assigned to the CF_3 atom. The ^{19}F NMR analysis confirms the presence of only one CF_3 group in the molecule. Unexpectedly, attempts to corroborate the noteworthy nucleophilic character of C(11), shown by its upfield resonance in the ^{13}C NMR spectrum, by reacting **5** with methyl iodide were unsuccessful. The mass spectrum of **5** shows the parent ion and fragment ions corresponding to loss of the eight carbonyl ligands and to the subsequent loss of iron fluorides, FeF_2 , FeF_2Cp , and Fe_2F_3 .

The formation of **5** was of interest because it must involve C–F bond-cleavage reactions. In metal cluster chemistry C–C bond cleavage is known¹¹ and C–H bond cleavage is quite common.¹² Although much rarer, C–F bond cleavage has been seen previously in reaction of nucleophiles with hexafluorobut-2-yne^{13,14} and in the reaction of the trihydride of niobium [Cp_2NbH_3] with $\text{CF}_3\text{C}\equiv\text{CCF}_3$;¹⁵ these reactions involve the elimination of a fluoride ion, and in the case of the niobium reagent the Cp_2Nb moiety acts as a fluorine-abstracting agent to give $\text{Cp}_2\text{NbF}_x\text{Li}$ adducts ($x = 1, 2$). The mechanism by which compound **5** was formed is evidently complex, and the different pathways are not evident at the present time. However, it can be suggested that $\text{CpFe}(\text{CO})_2^-$, generated in situ, reacts with the carbocation, CF_3C^+ , which results from successive C–F bond cleavages, to give the $\text{CpFe}(\text{CO})_2\text{C}=\text{C}=\text{C}(\text{CF}_3)$ ligand, which then coordinates to $\text{Fe}_2(\text{CO})_6$ fragments. A possible precursor of the carbocation CF_3C_3^+ would be the cation $\text{CF}_3\text{C}_2\text{F}_2^+$, which would give rise to complex **3**.

The formulation of complex **6** was established by a combination of X-ray diffraction and spectroscopic studies. Although chromatographic experiments and mass spectral data for this compound are consistent with it being a single cluster, infrared and NMR data show clearly that it is a mixture of inseparable isomers. However, suitable single

crystals of the major (88%) product **6a** were obtained, and the results of the X-ray diffraction have been reported in a preliminary communication.⁵ Formulation of the minor (12%) complex **6b** is firmly based on spectroscopic data.

The complex **6a** is a trimetal species, the core of the molecule consisting of a triangle of iron atoms bridged by the alkyne in $\mu_3\text{-}\eta^2\text{||}$ fashion (Figure 3). The iron triangle, which is nearly isosceles, is capped by a $\mu_3\text{-CO}$ carbonyl. The basal group C(7)–C(8)–Fe(1)–Fe(3) unit is planar to within ± 0.03 Å, and Fe(2) is displaced from this plane by 1.718 (1) Å. The cluster **6a** is formally a 48-electron species, an electron count for which the observed nido square-pyramidal arrangement of the three metals and the two carbon atoms is normally found. The $\mu_3\text{-}\eta^2\text{||}$ coordination mode of an alkyne to a triangular cluster has been already observed in homometallic derivatives $[\text{Os}_3(\text{CO})_{10}(\text{RC}_2\text{R})]^{16}$ and $[\text{M}_3\text{H}_2(\text{CO})_9(\text{RC}_2\text{R})]$ ($\text{M} = \text{Ru}, \text{Os}$)¹⁷ and in several heterometallic clusters.^{2b-d,18} The orientation of the alkyne in M_3C_2 trimetallic alkyne clusters has been reviewed recently,¹⁹ and it was concluded that the nido structure, which is the more common, is also the more stable. Saillard et al.¹⁹ have shown by calculation that in these nido species the alkyne bonds most strongly to basal atoms which usually carry the more electron withdrawing substituents (see below). The X-ray data obtained for **6a** do not confirm these conclusions, since the less electron attracting group, $\text{Fe}(\text{CO})_3$, is here located in the basal position. Moreover, the $\text{Fe}_{\text{basal}}\text{-C}$ distances [1.960 (7) and 1.980 (7) Å] are on average very slightly longer than the $\text{Fe}_{\text{apical}}\text{-C}$ distances [1.932 (7) and 1.960 (7) Å]. This may be explained by the presence of one carbonyl group that semibrings the Fe(1)–Fe(3) bond and of the triply bridging CO group; the role of these ligands is to bring the number of skeletal electron pairs to seven.¹⁹

The spectroscopic data for the major product **6** (Table I and Experimental Section) are in agreement with the results of the X-ray diffraction study. In particular, NMR spectra are in accordance with the asymmetric structure shown in Figure 3. In the infrared spectrum there are three bands in the CO stretching region, and those at 1868 and 1725 cm^{-1} may be assigned to the semibringing ligand C(5)–O(5) and to the $\mu_3\text{-C}(4)\text{-O}(4)$ carbonyl, respectively. Correspondingly, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum there are two CO resonances at 279.5 and 225.4 ppm, which are ascribed to $\mu_3\text{-CO}$ and semibringing carbonyl, respectively; the signals at 209.6, 206.7, and 204.4 ppm are assigned to $\text{Fe}(\text{CO})_3$ groups. The ^{19}F NMR spectra of **6a** exhibit two quartets; the F–F coupling ($J = 12$ Hz) confirms that CF_3 groups have a cis configuration.

By subtracting from the NMR and infrared spectra of **6** the peaks belonging to **6a**, we get the spectral patterns of **6b**. These show similarities with those of **6a**. In particular, the infrared and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the two isomers parallel each other well in the carbonyl regions. This coupled with the observation that these two isomers are eluted together by chromatography indicates for **6b** a cluster framework of the type Fe_3C_2 similar to that in **6a**. The infrared and ^{13}C NMR spectra of **6b** suggest that

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(12) Deeming, A. J. In *Transition-Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 391.

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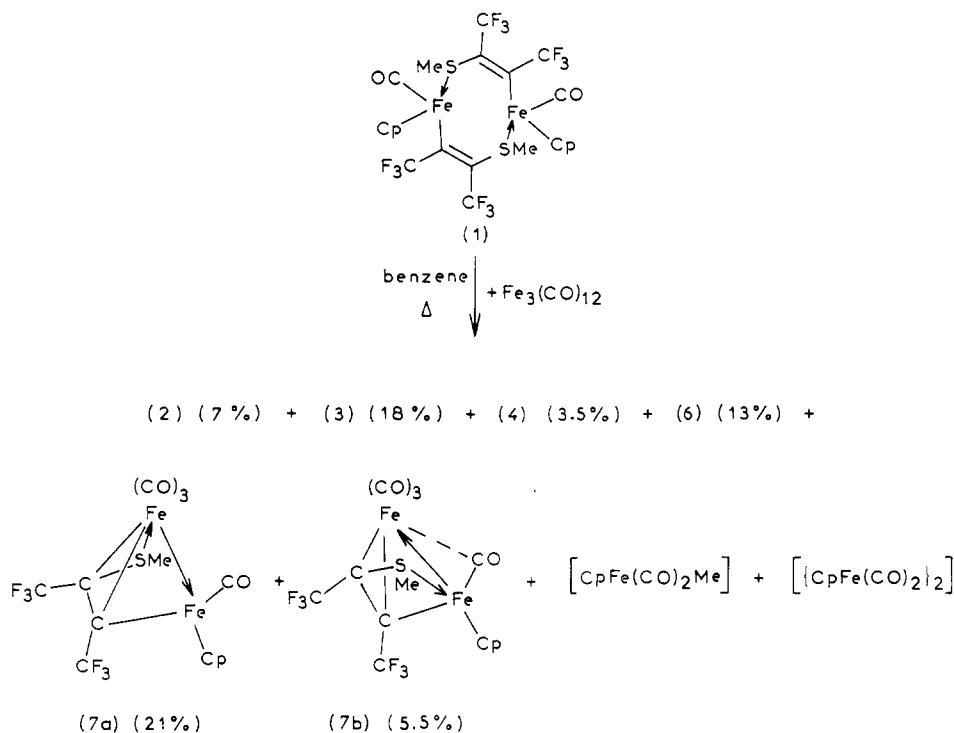
(16) (a) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, 97, 7172. (b) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614. (c) Rosenberg, E.; Bracker-Novak, J.; Gellert, R. W.; Aime, S.; Gobetto, R.; Osella, D. *J. Organomet. Chem.* **1989**, 365, 163.

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(19) (a) Halet, J. F.; Saillard, J. Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, 24, 218. (b) Wade, K. In *Transition-Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 143.

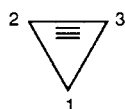
Scheme II



one carbonyl group is attached in an unsymmetrical μ_3 fashion to the Fe_3 triangle, that another bridges an Fe-Fe bond, and that the remaining carbonyls are terminal. Furthermore, the ^1H NMR spectrum shows one singlet at 4.89 ppm, implying equivalent C_5H_5 groups consistent with the symmetrical structure for **6b** shown in Scheme I. The ^{19}F NMR spectrum is also in accordance with such a structure since only one signal is observed.

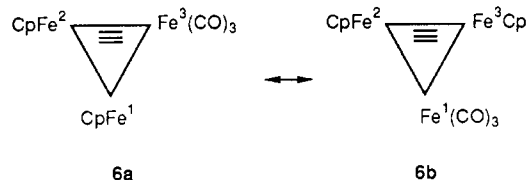
As mentioned above, only a single isomer, **6a**, has been characterized in the solid state, though two isomers, **6a** and **6b**, coexist in solution. The observation that the relative concentrations of the isomers are very different in the two solvents CD_2Cl_2 (**a/b** 7/1) and CD_3CN (**a/b** 13/1) suggests an equilibrium between these two species in solution. This excludes for **6b** a formulation where the number of carbonyl groups is different from that in **6a**. Thus, there is every reason to believe that the structures of **6a** and **6b** are close, and we suggest for **6b** the formulation $\text{Fe}_3(\text{C}_5\text{H}_5)_2(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_3(\mu_3\text{-}\eta^2\text{-||-CF}_3\text{C}_2\text{CF}_3)$ as shown in Scheme I. In **6b** the orientation of the alkyne has changed dramatically compared with that of **6a**. It is now oriented parallel to the CpFe-FeCp edge. Replacement of a carbonyl group on iron by $\text{P}(\text{OMe})_3$ to form a mono-substituted complex confirms these conclusions.²⁰

The orientation of the alkyne in other $\text{nido-M}_3\text{C}_2$ trimetallic clusters has been recently reviewed,^{19a} and the conclusion reached, supported by model calculations, that the orientation may be correlated with electron-accepting properties of the three metal fragments. It appears that in the preferred isomer, the more electron attracting fragments are located in the basal positions 2 or 3 rather than in the apical position 1.^{19a}



According to Saillard et al.^{19a} a CpFe fragment is always

more electron withdrawing than a $\text{Fe}(\text{CO})_3$ fragment. Consequently this should favor the conformation **6b**, whereas here **6a** is the preferred isomer:



This disagreement with the theoretical analyses^{19a} and with most of the experimental data about $\text{nido-M}_3\text{C}_2$ clusters²¹ might be explained by the presence in **6** of additional bridging ligands which alter the electron-attracting nature of the iron fragments. Moreover, we have to point out that in the transformation of complex **6b** to **6a** the energy difference would be small,^{19a} and this could explain the absence of interconversion of the isomers **6** in toluene on the NMR (^{19}F nucleus; 100 MHz) time scale up to 93 °C.

The pathway for the formation of **6** has not yet been determined, and in the absence of experimental evidence supporting possible intermediates will not therefore be discussed further.

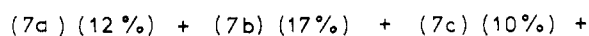
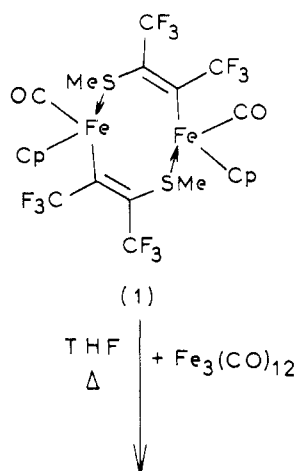
Reaction of $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})_2\text{Fe}(\text{CO})\text{Cp}]$ (1) with $[\text{Fe}_3(\text{CO})_{12}]$ in Benzene and in Tetrahydrofuran. When the reaction of **1** with an excess of $[\text{Fe}_3(\text{CO})_{12}]$ was undertaken in refluxing benzene, most of the products of Scheme I were again formed but with

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Scheme III

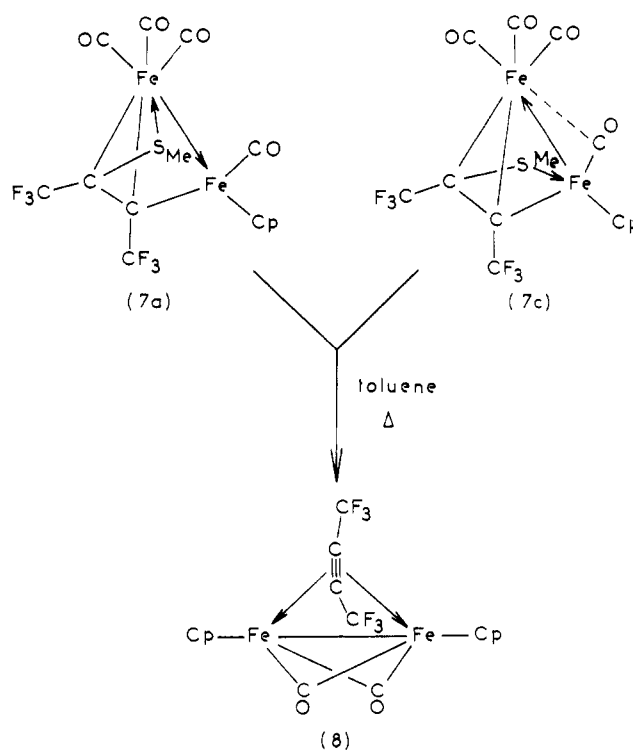


different yields, together with two additional isomeric adducts, **7a** and **7b** (Scheme II).

On the other hand, none of the alkyne complexes that were isolated in Scheme I were obtained when the reaction was performed in refluxing tetrahydrofuran. Instead, only three isomeric compounds **7a**, **7b**, and **7c** were isolated (Scheme III).

The isomeric complexes **7** have been characterized by their infrared, NMR, and mass spectra and by elemental analysis, all of which are consistent with the formulations given. In the mass spectra peaks higher than m/e 498 were not observed, and the stepwise loss of four carbonyls occurs: the complexes are then formulated as $\text{Fe}_2(\text{C}_5\text{H}_5)\text{C}-\text{O}_4(\text{CF}_3)_2$. The three adducts show very similar mass patterns, apart from some additional peaks in the spectrum of **7a**. The electrochemical behavior of **7b** and **7c** is virtually identical but different from that of **7a**,²³ implying the structures of **7b** and **7c** are similar. The presence of the $\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe}$ ligand in each of the isomers is supported by the observation of a quartet in the range expected for a Me group in the ^1H NMR spectra, implying a hydrogen-fluorine coupling between the methyl moiety and a CF_3 group. In the infrared spectra no bands assignable to bridging carbonyls are observed for **7a**, whereas **7b** and **7c** both show a semibridging carbonyl near 1860 cm^{-1} . The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7b** and **7c** show resonances assignable to a semibridging CO carbon atom, confirming the infrared assignment. The dinuclear nature of these derivatives suggested by the mass spectra is then confirmed by these infrared and NMR data. The observation of a terminal carbonyl stretching band at 1925 cm^{-1} , a frequency too low to be due to the terminal carbonyl of a $\text{Fe}(\text{CO})_3$ or $\text{Fe}(\text{CO})_4$ moiety, is indicative of the presence of a $\text{CpFe}(\text{CO})$ unit in **7a**. Therefore, on the basis of these spectral data we suggest for the complexes **7** structures in which the $\text{Cp}(\text{CO})\text{Fe}-\text{Fe}(\text{CO})_3$ unit satisfies its electronic requirement by coordination with the $\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe}$ ligand via one σ - and one π -Fe-C bond and one σ -Fe-S bond (Scheme II). The major structural differences between **7a** and **7b** or **7c** arise from (i) the presence of a

Scheme IV



semibridging carbonyl in **7b** and **7c** and (ii) the identity of the iron atom that coordinates the sulfur atom: in **7a**, the SMe group is bound to a $\text{Fe}(\text{CO})_3$ unit, whereas it is bound to a $\text{Cp}(\text{CO})\text{Fe}$ moiety in **7b** and **7c**. The isolation of isomers of both types (**7a** and **7b** or **7c**) appears to originate from the ability of the sulfur atom to coordinate alternatively two different iron centers. This might be allowed if the SMe group is equidistant from the two iron atoms, as is the sulfur atom in the corresponding complex **2**. The observed behavior suggests that, in its main features, the reaction that gives rise to isomers **7** follows a pathway analogous to that for **2**, except for the cleavage of the S-CH₃ bond. We now consider the nature of the structural differences between **7b** and **7c**. The ^1H NMR spectra of **7b** and **7c** exhibit resonances for methyl groups in different environments; the chemical shifts are respectively 1.65 and 2.25 ppm. Correspondingly in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7b** and **7c** the chemical shifts due to the Me groups are at 22.5 and 29.0 ppm, respectively. This is conclusive evidence that the positions of the Me groups and the sulfur lone pairs relative to the Fe-Fe axes in the isomers **7b** and **7c** are different. On the other hand, in their ^1H and ^{13}C NMR spectra, **7a** and **7c** have similar patterns in the methyl region, which suggests similar sulfur environments.

To our knowledge, isomeric complexes **7** are new. However, corresponding compounds of the type $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})(\mu\text{-CR}=\text{CH}(\text{R}')\text{Fe}(\text{CO})_3)]$ ($\text{R} = \text{H}$, $\text{R}' = \text{CO}_2\text{Me}$;²⁴ $\text{R} = \text{OCH}_3$, $\text{R}' = \text{Me}$)²⁵ have been previously reported.

As pointed out above, the geometries of the three isomers **7** are similar, and we therefore thought that these complexes would readily interconvert upon thermolysis. However, on heating **7a** and **7c** in toluene, interconversion was not observed. Instead, the complexes decomposed to give compound **8** (Scheme IV). This is consistent with

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an analysis of the ^1H and ^{19}F NMR spectra at variable temperature, which indicated that interconversion did not occur up to 80°C .

The formulation proposed for complex **8** is based on microanalysis and spectroscopic data. The mass spectrum of the compound shows the parent ion, fragment ions corresponding to loss of the two carbonyl ligands, and a mass peak attributable to the $[\text{Fe}_2(\text{C}_5\text{H}_5)_2\text{F}]^+$ ion. The carbonyl-region infrared spectrum of **8** reveals one characteristic intense band at 1803 cm^{-1} assignable to a bridging C–O stretch. There are no terminal carbonyls in **8**, as shown by the infrared spectrum as well as by ^{13}C NMR analysis. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits the expected resonance for two equivalent bridging carbonyl groups. According to the ^{19}F NMR data, the two CF_3 groups are chemically equivalent. The high symmetry in **8** is confirmed by the presence in the ^1H NMR spectrum of only one resonance assignable to the C_5H_5 moieties. Surprisingly, in view of its simple and symmetrical structure, **8** does not appear to have been previously reported.

$[\text{Fe}_3(\text{C}_5\text{H}_5)_2(\mu_3\text{-CO})(\mu\text{-CO})(\text{CO})_3(\text{CF}_3\text{C}_2\text{CF}_3)]$ (**6**)
Catalyzed Isomerization of 1-Hexene. Complex **6** readily catalyzes the isomerization of 1-hexene to give a mixture of *cis*- and *trans*-2-hexene in 40 and 30% yields, respectively, and *cis*- and *trans*-3-hexene in 12 and 18% yields, respectively. When the reaction was carried out in neat 1-hexene (3.2×10^{-3} mol) with 3.3×10^{-6} mol of cluster **6** at 132°C , approximately 32% of the 1-hexene was isomerized to *cis*- and *trans*-2- or -3-hexene after 1.5 h, giving a turnover for the catalysis of approximately 210 mol of hexene/mol of iron cluster per hour. Spectral (IR and NMR) analyses of the solid obtained following evaporation of the olefin mixture showed that the bulk of the cluster **6** remained unchanged in several runs. No evident fragmentation of the cluster occurs, which suggests strongly that **6** acts as an isomerization catalyst in the reactions described above.

Experimental Section

The reactions were performed under a nitrogen atmosphere using standard Schlenk techniques and solvents deoxygenated and dried by standard methods. Infrared spectra were obtained with a Pye-Unicam SP 2000 spectrophotometer in hexane or dichloromethane solutions in the $\nu(\text{CO})$ and $\nu(\text{C}=\text{C})$ region. The mass spectra were measured on a VARIAN MAT 311 in the Mesures Physiques laboratory, University of Rennes. NMR spectra (^1H , ^{13}C , ^{19}F), in CDCl_3 or CD_2Cl_2 solution, were recorded on a JEOL FX 100 or a Bruker AC 300 and were referenced to Me_4Si or CFCl_3 . Chemical analyses were performed by the Centre de Microanalyses du CNRS de Lyon.

The compound $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})_2\text{Fe}(\text{CO})\text{Cp}]$ (**1**) was prepared by literature methods.²⁶ All other reagents were commercial grade and used as obtained.

Reaction between $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})_2\text{Fe}(\text{CO})\text{Cp}]$ (1**) and $[\text{Fe}_3(\text{CO})_{12}]$.** (a) **In Toluene.** In a typical procedure ca. 1 g of $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})_2\text{Fe}(\text{CO})\text{Cp}]$ (**1**, 1.4×10^{-3} mol) was dissolved in toluene (60 cm^3), and toluene solution containing $[\text{Fe}_3(\text{CO})_{12}]$ (5.6 g , 11.2×10^{-3} mol) was added under nitrogen. The reaction mixture was refluxed for 5 h. The mixture was evaporated to dryness under high vacuum and then extracted with CH_2Cl_2 . Chromatography of the dichloromethane solution on a silica gel column eluting with pentane afforded a yellow band, from which a mixture of $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3)]$ and **2** was isolated. Further elution with pentane yielded a yellow–orange fraction, from which a mixture of **3** and **4** was obtained. Elution with CH_2Cl_2 /pentane (1:10) served to remove the red band, which was evaporated to yield product **5**, purified by crystallization from pentane/ CH_2Cl_2 solution (0.075

g, 5%). Elution with CH_2Cl_2 /pentane (2.5:10) gave a red–brown fraction, which yielded complex **6** (0.12 g, 14%). Finally elution with CH_2Cl_2 /pentane (5:10) afforded a dark-red fraction of $[\text{CpFe}(\text{CO})_2]_2$ (0.30 g).

Complex **2** (ca. 0.30 g, 23%) was separated from $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3)]$ (0.08 g) by crystallization in cold pentane (-70°C). In a similar way, compound **3** (0.28 g, 21%) was separated from **4** (0.1 g, 7%) by crystallization in pentane (-30°C). **2–4** are yellow, orange–yellow, and orange compounds, respectively, which are soluble in common organic solvents.

2: Anal. Calcd for $\text{C}_{10}\text{F}_6\text{Fe}_2\text{O}_6\text{S}$: C, 25.3; Fe, 23.5. Found: C, 25.3; Fe, 23.0. IR $\nu_{\text{max}}(\text{CO})$ 2098 m, 2065 s, 2033 s, 2025 s cm^{-1} (hexane); mass spectrum, m/e 474 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-6$), $\text{M}^+ - [x(\text{CO}) + y(\text{F})]$ ($x = 0-6$, $y = 1$).

3: Anal. Calcd for $\text{C}_{11}\text{H}_5\text{F}_6\text{Fe}_2\text{O}_6\text{S}$: C, 28.2; H, 0.64; F, 20.2; Fe, 23.9; S, 6.8. Found: C, 28.3; H, 0.66; F, 19.7; Fe, 24.0; S, 6.4. IR $\nu_{\text{max}}(\text{CO})$ 2088 s, 2064 m, 2051 s, 2037 w, 2018 s, 1997 s cm^{-1} (hexane); ^1H NMR δ 2.56 (q, $J_{\text{F-H}} = 1\text{ Hz}$) (CDCl_3); ^{13}C NMR δ 209.8, 207.6, 203.2 (s, CO), 159.1–120.2 (m), 69.6 (m), 32.5 (s, SCH_3) (CDCl_3); ^{19}F NMR δ -58.9 (m), -81.0 (m) (CDCl_3); mass spectrum, m/e 470 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-6$), $\text{M}^+ - [x(\text{CO}) + y(\text{F})]$ ($x = 0-6$, $y = 1$), 307 [$\text{M}^+ - 4\text{CO} - \text{F} - \text{S}$].

4: Anal. Calcd for $\text{C}_{11}\text{H}_4\text{F}_6\text{Fe}_2\text{O}_6\text{S}$: C, 26.9; H, 0.8. Found: C, 26.9; H, 0.9. IR $\nu_{\text{max}}(\text{CO})$ 2088 m, 2061 s, 2050 m, 2037 s, 2017 s, 2007 s cm^{-1} (hexane); mass spectrum, m/e 490 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-6$), $\text{M}^+ - [x(\text{CO}) + \text{F}]$ ($x = 0, 2-5$), $\text{M}^+ - [x(\text{CO}) + \text{S}]$ ($x = 5, 6$), $\text{M}^+ - [x(\text{CO}) + \text{S} + \text{Fe}]$ ($x = 6$).

5: Anal. Calcd for $\text{C}_{17}\text{H}_5\text{F}_3\text{Fe}_3\text{O}_8\text{S}$: C, 36.4; H, 1.0; F, 10.1. Found: C, 36.4; H, 1.3; F, 9.4. IR $\nu_{\text{max}}(\text{CO})$ 2071 s, 2045 s, 2023 s, 2009 m, 1989 s, 1972 s, 1955 sh, $\nu(\text{CC})$ 1675 w cm^{-1} (CH_2Cl_2); mass spectrum, m/e 562 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-8$), $\text{M}^+ - [x(\text{CO}) + \text{F}]$ ($x = 2$), $\text{M}^+ - [x(\text{CO}) + \text{Fe}_y\text{F}_{2+z}]$ ($x = 8$; $y = 1$, $z = 0$; $y = 2$, $z = 1$).

6: Anal. Calcd for $\text{C}_{19}\text{H}_{10}\text{F}_6\text{Fe}_3\text{O}_5$: C, 38.0; H, 1.7. Found: C, 37.6; H, 1.7. IR $\nu_{\text{max}}(\text{CO})_{\text{major}}$ 2074 s, 2029 s, 2005 s, 1868 s, 1725 s, $\nu_{\text{max}}(\text{CO})_{\text{minor}}$ 2061, 1995, 1839, 1749 cm^{-1} (hexane); mass spectrum, m/e 600 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-4$), 432 ($\text{M} - \text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_4$), 413 ($\text{M}^+ - \text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_4\text{F}$), 404 ($\text{M}^+ - \text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_5$), 385 ($\text{M}^+ - \text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_5\text{F}$), 366 ($\text{M} - \text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_5\text{F}_2$).

(b) **In Benzene.** A mixture of **1** (0.86 g , 1.2×10^{-3} mol) and $[\text{Fe}_3(\text{CO})_{12}]$ (4.5 g , 9×10^{-3} mol) was heated in benzene at reflux for 24 h. The solvent was removed in vacuo, the residue was extracted with dichloromethane, and the extracts were chromatographed. Elution with hexane separated two fractions, which were yellow and yellow–orange. Removal of solvent in vacuo from the first fraction yielded a mixture of **2** and $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3)$; **2** (0.08 g , 7%) was separated from $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_3)$ (0.03 g , 7%) by crystallization as described above. The yellow–orange eluate afforded a mixture of **3** (0.20 g , 17%) and **4** (0.04 g , 3.5%), which again were purified as described above. Further elution of the chromatography column with dichloromethane–hexane, increasing the proportion of CH_2Cl_2 to 1:20, to 1:4, to 1:1.85, and finally to 1:1, led, respectively, to the recovery of the maroon, dark-green, red–brown, and dark-red fractions. Removal of solvent in vacuo from the first eluate afforded dark-green microcrystals of $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})\text{Fe}(\text{CO})_3]$ (**7a**, 0.26 g , 21%), from the second eluate dark-green microcrystals of **7b** (0.07 g , 5.5%), from the third eluate red–brown microcrystals of **6** (0.09 g , 12.5%), and from the fourth eluate 0.15 g of $[\text{CpFe}(\text{CO})_2]$.

7a: Anal. Calcd for $\text{C}_{14}\text{H}_3\text{F}_6\text{Fe}_2\text{O}_4\text{S}$: C, 33.8; H, 1.6; S, 6.4. Found: C, 34.0; H, 1.6; S, 6.1. IR $\nu_{\text{max}}(\text{CO})$ 2057 s, 1998 vs, 1986 s, 1925 cm^{-1} (hexane); mass spectrum, m/e 498 (M^+), other peaks, 497 ($\text{M} - \text{H}$), 479 ($\text{M} - \text{F}$), 478 ($\text{M} - \text{HF}$), 470 ($\text{M} - \text{CO}$), 451 ($\text{M} - \text{CO} - \text{F}$), 442 ($\text{M} - 2\text{CO}$), 432 ($\text{M} - \text{CO} - 2\text{F}$), 423 ($\text{M} - 2\text{CO} - \text{F}$), 413 ($\text{M} - \text{CO} - 3\text{F}$), 403 ($\text{M} - 3\text{CO}$), 386 ($\text{M} - 4\text{CO}$).

7b: Anal. Calcd for $\text{C}_{14}\text{H}_3\text{F}_6\text{Fe}_2\text{O}_4\text{S}$: C, 33.8; H, 1.6; S, 6.4. Found: C, 34.2; H, 1.6; S, 6.3. IR $\nu_{\text{max}}(\text{CO})$ 2063 s, 2008 s, 1985 s, 1854 cm^{-1} (hexane); mass spectrum, m/e 498 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-4$), 292 ($\text{M} - 4\text{CO} - \text{FeF}_2$), 198 ($\text{M} - 4\text{CO} - 2\text{FeF}_2$), 152 ($\text{M} - 4\text{CO} - \text{C}_6\text{H}_5 - \text{FeF}_{1.5}$).

(c) **In Tetrahydrofuran.** A mixture of **1** (0.20 g , 2.8×10^{-4} mol) and $[\text{Fe}_3(\text{CO})_{12}]$ (1.1 g , 2.2×10^{-3} mol) was heated in THF at reflux for 44 h. The solvent was then evaporated to dryness, the residue was redissolved in a minimum of dichloromethane, and

(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. 4, pp 99, 119.

the solution chromatographed on silica gel. Elution with dichloromethane-hexane, increasing the proportion of CH_2Cl_2 from 1:20 to 1:4, to 1:2.3, and finally to 1:1, removed in sequence maroon, dark-green, green, and dark-red bands. The first eluate afforded **7a** (0.035 g, 12%), and the dark-green fraction, after removal of solvent, gave **7b** (0.05 g, 17%). The green eluate yielded dark-green microcrystals of **7c** (0.03 g, 10%), and the dark-red eluate gave 0.06 g of $\{\text{CpFe}(\text{CO})_2\}_2$.

7c: IR $\nu_{\text{max}}(\text{CO})$ 2067 s, 2016 s, 1860 s cm^{-1} (hexane); mass spectrum, m/e 498 (M^+), other peaks, $\text{M}^+ - x(\text{CO})$ ($x = 1-4$), 292 ($\text{M} - 4\text{CO} - \text{FeF}_2$), 198 ($\text{M} - 4\text{CO} - 2\text{FeF}_2$).

Thermal Transformation of Complexes $[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SMe})\text{Fe}(\text{CO})_3]$ (7a** and **7c**) to $[(\text{CpFe})_2(\mu\text{-CO})_2(\mu\text{-C}(\text{CF}_3)=\text{C}(\text{CF}_3))]_2$ (**8**).** Approximately 0.15 g of **7a** was heated in toluene at reflux for 3 h, affording a dark-violet solution. The solvent was removed in vacuo, the residue was extracted with dichloromethane, and the extracts were chromatographed on silica gel. Elution with dichloromethane-hexane (1:9) removed a violet band, which was evaporated to yield product **8** (0.05 g, 72%).

Similarly, **7c** heated in toluene at reflux for 24 h gave mostly **8** with traces of **7a** and **7b** (^1H NMR analysis).

8: Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{F}_6\text{Fe}_2\text{O}_2$: C, 41.8; H, 2.2. Found: C, 41.6; H, 2.3. IR $\nu_{\text{max}}(\text{CO})$ 1803 s, $\nu(\text{CC})$ 1600 m cm^{-1} (CH_2Cl_2); mass spectrum, m/e 460 (M^+), other peaks, 432 ($\text{M} - \text{CO}$), 404 ($\text{M} - 2\text{CO}$), 261 ($\text{M} - 2\text{CO} - \text{C}_4\text{F}_6$).

Isomerization Experiments. The reaction was performed in a sealed glass tube (volume 3 cm^3) containing cluster **6** (2 mg, 3.3×10^{-6} mol), along with the 1-hexene (0.4 cm^3 , 3.2×10^{-3} mol) to be isomerized; the tube was filled with nitrogen by standard vacuum techniques. The reaction was conducted at 132 °C for 1.5 h, and at this stage about 32% of 1-hexene had been isomerized. The isomerization solutions were examined by ^1H and ^{13}C NMR spectroscopy to reveal the extent of isomerized hexene. The organic products in solution after isomerization experiments were analyzed by GLC (PPG/Chromosorb-W).

Crystal Structure of $\{\text{Fe}(\text{CO})_3\}_2(\mu\text{-}(\text{CF}_3)_3\text{CCC}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2])_2$ (5**).** The specimen was a red plate $0.84 \times 0.72 \times 0.36$ mm. All measurements were made at 22 °C on an Enraf-Nonius CAD4F diffractometer using $\text{Mo K}\alpha$ X-rays, $\lambda = 0.71069$ Å, monochromated by reflection from a graphite crystal.

Crystal data: $\text{C}_{17}\text{H}_5\text{F}_3\text{Fe}_3\text{O}_8$, $M_r = 561.8$, orthorhombic, space group $Pbca$, $a = 13.533$ (4), $b = 14.748$ (4), $c = 20.067$ (3) Å³, $U = 4005$ (2) Å³, $Z = 8$, $D_{\text{calcd}} = 1.863$ g cm^{-3} , $F(000) = 2208$, $\mu(\text{Mo K}\alpha) = 22.1$ cm^{-1} .

Cell dimensions were determined from the setting angles of 23 reflections with $13 \leq \theta(\text{Mo K}\alpha) \leq 17^\circ$, and the space group from the systematic absences. The intensities of 9694 reflections (h 19 to 19, k 7 to 20, l 9 to 28) with $2 \leq \theta(\text{Mo K}\alpha) \leq 30^\circ$ were determined from $\omega/2\theta$ scans of 0.90° in ω . Correction for Lp and absorption effects (relative transmission factors on F 0.75-1.22) and averaging ($R_{\text{int}} = 0.035$) yielded 5790 unique intensities, of which 2619 with $I \geq 3\sigma(I)$ were subsequently used.

The iron atoms were located from a sharpened Patterson synthesis, and the remaining atoms from difference syntheses. In the final full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F) + 0.0004F^2$ the positions and anisotropic displacement parameters of all non-hydrogen atoms were refined. Hydrogen atoms were constrained to ride on the carbon atoms to which they were attached, with $\text{C-H} = 0.96$ Å and $U(\text{H}) \approx 1.2U(\text{C})$. The refinement converged ($\Delta/\sigma < 0.08$ with $R = 0.041$ and $R_w = 0.055$). Final $[\Delta\rho]$ values did not exceed 0.63 e Å⁻³. Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref 26. Calculations were performed on a Gould 3227 computer with the GX package.²⁷ Final atomic coordinates are listed in Table III (supplementary material).

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Registry No. 1, 104730-97-4; 2, 118773-68-5; 3, 125051-03-8; 4, 118772-53-5; 5, 125051-04-9; 6a, 118772-52-4; 6b, 125076-47-3; 7a, 125076-46-2; 7b, 125051-06-1; 7c, 125134-35-2; 8, 125051-05-0; $\text{Fe}_3(\text{CO})_{12}$, 17685-52-8; Fe, 7439-89-6; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8.

Supplementary Material Available: Tables of fractional atomic coordinates and isotropic and anisotropic displacement parameters and a complete bond length and angle listing for **5** (4 pages); a listing of observed and calculated structure factors for **5** (12 pages). Ordering information is given on any current masthead page.

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Variable-Temperature NMR Investigation into the Fluxional Thermodynamics of Metallocene-Containing Cryptands

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Variable-temperature ^{13}C and ^1H 2D COSY and ^{13}C - ^1H shift correlation spectra have been used to determine the solution structure of 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)ferrocene and its ruthenium homologue together with the thermodynamic parameters for rotation of the amide carbonyl group in both molecules. Consideration of the ^{13}C NMR spectra allows a correlation to be established between the shielding effects and the metallocene-centered molecular orbital structure of these molecules.

Introduction

Metallocene-containing cryptands are attractive as redox-active host molecules for selective recognition and binding of cations.¹⁻⁸ To assess the potential for inter-

active phenomena between two proximally disposed metal centers, it is important to appreciate the dynamics of

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