

A Cyclopropenylidene Approach to Tricarbide Complexes: Synthesis and Structure of $[\{\text{Fe}(\text{CO})_2(\text{Cp})\}_3(\mu_3\text{-C}_3)][\text{SbF}_6]$

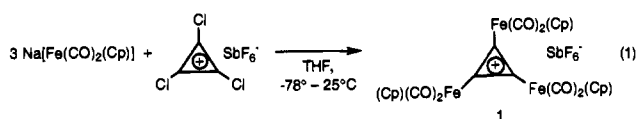
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Received February 27, 1995

Carbon fragments have long been studied in the gas phase and as astrophysical objects.¹ Gaseous carbon fragments such as C_2 and C_3 are generated by subjecting hydrocarbons or graphite to high temperatures or irradiation.² In order to study these fragments in condensed phases, they must be trapped by an organic reaction or by attachment to an inorganic framework. There are several examples of complexes with C_1 or C_2 ligands bridging two or more metals.^{3,4} More recently, complexes with linear C_3 ,^{5,6} and C_4 chains connecting two metals have been reported.^{3,4} Other complexes of pure carbon ligands include a tricobalt complex of *cyclo*- C_{18} ⁷ and several metal complexes of the fullerenes (C_{60} , C_{70} , etc.) prepared by Fagan,⁸ Balch,⁹ and others.⁴ We are interested in preparing metal complexes of other small C_x ligands. We report here the first trimetallic complex of *cyclo*- C_3 .

The reaction of 3 equiv of cyclopentadienyldicarbonyliron anion with $[\text{C}_3\text{Cl}_3][\text{SbF}_6]$, generated from C_3Cl_4 and AgSbF_6 ,^{10,11} produces trimetallic $[\{\text{Fe}(\text{CO})_2(\text{Cp})\}_3(\mu_3\text{-C}_3)]\text{SbF}_6$ (**1**, eq 1) in about 65% yield.¹² An X-ray crystal structure determination¹³



shows that **1** has a nearly equilateral C_3 ring with an iron center bonded to each vertex (Figure 1). The average $\text{Fe}-\text{C}_{\text{ring}}$ bond length in **1**, 1.92 Å, falls near the middle of the range of $\text{Fe}-\text{C}$ bonds with multiple-bond character. Compared to neutral $[\text{Fe}(\text{R})(\text{CO})_2(\text{Cp})]$ compounds, the $\text{Fe}-\text{C}$ bonds in **1** are shorter

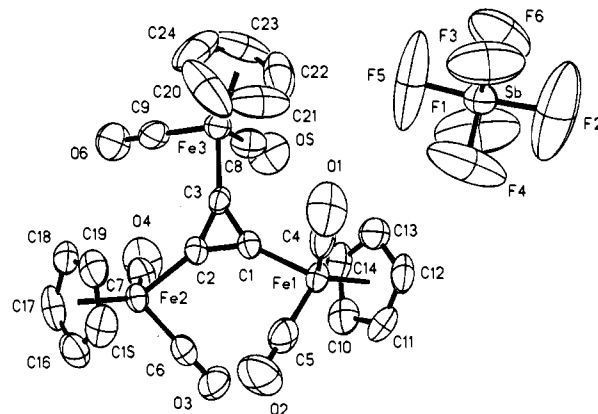
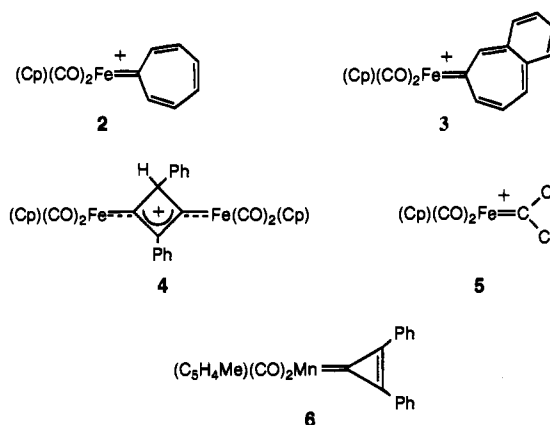


Figure 1. ORTEP plot of the cation of $[\{\text{Fe}(\text{CO})_2(\text{Cp})\}_3(\mu_3\text{-C}_3)][\text{SbF}_6]$ (**1**). Selected distances (Å): $\text{Fe1}-\text{C1}$, 1.913(6); $\text{Fe2}-\text{C2}$, 1.917(6); $\text{Fe3}-\text{C3}$, 1.919(7); $\text{C1}-\text{C2}$, 1.388(9); $\text{C1}-\text{C3}$, 1.394(9); $\text{C2}-\text{C3}$, 1.375(9). Selected angles (deg): $\text{Fe1}-\text{C1}-\text{C2}$, 149.6(5); $\text{Fe1}-\text{C2}-\text{C3}$, 150.6(5); $\text{C2}-\text{C1}-\text{C3}$, 59.2(5); $\text{Fe2}-\text{C2}-\text{C1}$, 148.0(5); $\text{Fe2}-\text{C2}-\text{C3}$, 151.4(5); $\text{C1}-\text{C2}-\text{C3}$, 60.6(4); $\text{Fe3}-\text{C3}-\text{C1}$, 148.3(5); $\text{Fe3}-\text{C3}-\text{C2}$, 151.5(5); $\text{C1}-\text{C3}-\text{C2}$, 60.2(4).

Chart 1



than typical $\text{Fe}-\text{C}_{\text{sp}^3}$ or $\text{Fe}-\text{C}_{\text{sp}^2}$ single bonds (2.0–2.1 Å)¹⁴ but about the same length as $\text{Fe}-\text{C}_{\text{sp}}$ bonds (1.9 Å).^{15,16} Compared to similar cationic alkylidene complexes (Chart 1), the $\text{Fe}-\text{C}$ bonds in **1** are shorter than those in the cycloheptatrienyldene complexes **2** and **3** (1.98 and 2.00 Å),^{17,18} similar to those in cyclobutenylidene complex **4** (1.91 Å),¹⁹ but longer than the $\text{Fe}-\text{C}$ bond to the strong π -acceptor CCl_2 in **5** (1.81 Å).²⁰ The $\text{C}-\text{C}$ bond lengths in the ring are about equal, averaging 1.39–(1) Å, nearly equal to the mean $\text{C}-\text{C}$ distance in localized cyclopropenylidene complexes such as **6** (1.349(6) and 1.424–(6) Å).^{21,22} In an 18-electron $[\text{M}(\text{CR}_2)(\text{CO})_2(\text{Cp})]$ complex with significant $\text{M}-\text{C}$ π -donation, such as **5**, the carbene ligand lies in the $[\text{M}(\text{CO})_2(\text{Cp})]$ symmetry plane, with $\text{Cp}(\text{centroid})-\text{M}-\text{C}-\text{R}$ torsion angles of 0° and 180° . In compound **1**, two of

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the cyclopentadienyl rings are above and the other is below the C_3 plane, with scattered Cp(centroid)–Fe– C_α – C_β torsion angles (about Fe1–C1, 99.7°, –65.5°; Fe2–C2, 105.5°, –78.0°; Fe3–C3, 132.0°, –52.2°). This evidence suggests that Fe to cyclopropenyl π -donation is of minor importance in the structure of **1**.²³

Spectroscopic properties of **1** are in accord with the solid-state structure.²⁴ ¹H and ¹³C NMR spectra show a single [Fe(CO)₂(Cp)] environment in **1** from room temperature to –80 °C, consistent with free rotation about the Fe–C bonds in solution. The cyclopropenyl carbon atoms display a single ¹³C NMR resonance at 256.6 ppm, downfield of most organic cyclopropenium ions (118–175 ppm).²⁵ A solution infrared spectrum (CH₂Cl₂) displays three carbonyl stretching absorptions, fewer than the maximum of six absorptions for C_1 or C_3 symmetry. The simple solution spectrum may be attributed to the generation of effective C_3 symmetry by free rotation about Fe–C bonds (unlikely on the infrared time scale), or to the overlap of carbonyl absorptions from several rotamers. A solid-state infrared spectrum (KBr) displays four carbonyl stretching absorptions and two weak shoulders, consistent with C_1 symmetry in the crystal.

While fully metal substituted cyclopropenium salts are unprecedented, several cyclopropenium salts with one metal substituent^{11,26–29} as well as neutral cyclopropenylidene com-

plexes (e.g., **6**)^{21,22,26–28,30–34} are known. Analogous C_3 complexes with [Ru(CO)₂(Cp)], [Re(CO)₅], [Mo(CO)₃(Cp)], and [W(CO)₃(Cp)] substituents can be prepared from [C₃Cl₃][SbF₆]. Further investigations of the chemical properties of **1** and these additional compounds are underway.

Acknowledgment. We are grateful to the U.S. Department of Energy (DE-FG05-85ER13432) and the Kentucky EPSCoR program (NSF EHR-91-08764 and DOE DE-FG02-91ER75657) for financial support, to the NSF (CHE-9113581) for equipment, and to John Layton for NMR assistance.

Supplementary Material Available: Experimental details of the preparation of **1** and tables of crystallographic data, positional and thermal parameters, bond distances and angles, and planes and conformation angles for **1** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950660H

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(24) ¹H NMR (200 MHz, CD₂Cl₂): δ_H 5.18 (s, Cp). ¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ_C 86.7 (s, Cp), 212.6 (s, CO), 256.6 (s, C₃), unchanged to –80 °C. IR (ν (CO), CH₂Cl₂) 2052 (m), 2040 (m), 1997 (m).

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