toluene-d_8 solution of Cp*$_2$Ti(CH$_3$)$_2$ (2) (32 mg, 87 μmol) and FeCp$_2$ (140 μmol). The color changed immediately to an opaque red-orange. The tube was sealed under N$_2$. Red-orange crystals were noted after 1 h at room temperature. The ^{1}H NMR spectrum showed only resonances that could be assigned to the Cp*, Cp, and methyl hydrogens. The latter appeared at δ 0.22, midway between the methyl resonances of Cp*$_2$Ti(CH$_3$)$_2$ (2) (δ 0.69) and AlMe$_2$Cl (δ 0.38). Subsequent thermolysis of this tube in the JEOL FX90Q at 127.2 °C resulted in uninterpretable ^{1}H NMR spectra. Methane (δ 0.18) was produced, but other resonances were not clearly resolved.

The second experiment involved adding an excess of AlMe$_2$Cl to a turquoise toluene-d_8 solution of Cp*(C$_5$Me$_4$CH$_2$)Ti(CH$_3$) (3) and FeCp$_2$ ($\sim$1:1). The color changed immediately to a green-brown solution which contained dark solid material. The tube was sealed under N$_2$. No ^{1}H NMR spectrum could be observed

for this reaction mixture, however, suggesting the presence of paramagnetic products.

Mechanism of the Reaction of [Fe₆C(CO)₁₆]²⁻ with Tropylium Bromide To Give [Fe₄(CO)₁₂CCO₂CH₃]⁻ and the Molecular Structure of (Et₄N)₂[Fe₅C(CO)₁₂Br₂], a Proposed Intermediate in This Reaction[†]

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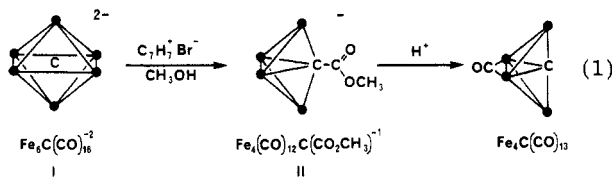
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The reaction of [Fe$_6$C(CO)$_{16}$]$^{2-}$ with tropylium bromide in methanol, which yields [Fe$_4$(CO)$_{12}$CCO$_2$CH$_3$]$^-$, has been shown to comprise the sequential formation of [Fe$_5$C(CO)$_{15}$], [Fe$_5$C(CO)$_{12}$Br$_2$]$^{2-}$, [Fe$_4$C(CO)$_{12}$]$^{2-}$, [Fe$_4$C(CO)$_{13}$], and [Fe$_4$(CO)$_{12}$CCO$_2$CH$_3$]$^-$. The structure of the hitherto unreported (Et$_4$N)$_2$[Fe$_5$C(CO)$_{12}$Br$_2$] has been determined by X-ray diffraction. The cluster crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.361$ (2) Å, $b = 14.958$ (3) Å, $c = 23.472$ (6) Å, $\beta = 95.08$ (2)°, $V = 3973$ Å^3, and $Z = 4$. The geometry of the dianion may be regarded as based on the square-pyramidal [Fe$_5$C(CO)$_{15}$] with two bromide ions replacing three carbonyls from one of the basal Fe(CO)$_3$ groups. Each of the proposed intermediates in the conversion of [Fe$_6$C(CO)$_{16}$]$^{2-}$ to [Fe$_4$C(CO)$_{12}$CCO$_2$CH$_3$]$^-$ has been isolated and their interconversion demonstrated.

Introduction

We recently reported[1] the synthesis of a novel iron carbidocarbonyl cluster Fe$_4$C(CO)$_{13}$ by a sequence of reactions involving the oxidative fragmentation of the hexanuclear octahedral cluster [Fe$_6$C(CO)$_{16}$]$^{2-}$ in methanol, followed by protonation (eq 1). [Fe$_4$C(CO)$_{13}$] is of considerable interest as it is the neutral parent molecule of the Fe$_4$C series, a class of carbidocarbonyl clusters so far unique in that its members contain a carbon atom exposed

$$\text{Fe}_6\text{C(CO)}_{16}^{-2} \xrightarrow[\text{CH}_3\text{OH}]{\text{C}_7\text{H}_7^+ \text{ Br}^-} \text{Fe}_4\text{(CO)}_{12}\text{C(CO}_2\text{CH}_3\text{)}^{-1} \xrightarrow{\text{H}^+} \text{Fe}_4\text{C(CO)}_{13} \quad (1)$$

to a degree sufficient to undergo chemical reactions.[2,3] All higher nuclearity carbidocarbonyl clusters have carbon atoms partially or totally shielded from potential chemical reactivity by encapsulating metal atoms. As a class of compounds, first discovered two decades ago, carbidocarbonyl clusters remained until recently principally of structural interest.[4]

Our observation of the formation of an organic functionality incorporating the exposed carbon atom—the CCO$_2$CH$_3$ group in II—has demonstrated the potential for CO-based chemistry at the CO-derived carbon atom in molecular clusters.[2] This focus of interest has a counterpart in heterogeneously catalyzed CO chemistry, where the intermediacy of surface-bound carbon atoms has recently

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(1) Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* 1981, *103*, 4968.

(2) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* 1979, *101*, 7417.

(3) Bradley, J. S. *Philos. Trans. R. Soc. London* 1982, in press.

(4) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* 1981, *28*, 203.

been established in the metal-catalyzed Fischer-Tropsch reaction, converting carbon monoxide and hydrogen into a range of hydrocarbons and oxygenates.[5] The discovery of synthetic routes to Fe_4C clusters has provided a prototype molecular analogue to the surface-bound carbon atom and an example of a useful bridge between surface chemistry and cluster chemistry. Because of this we have continued our effort aimed at expanding the chemistry of the carbon atom in the Fe_4C unit and in other carbido-carbonyl clusters. This report describes more detailed studies of the mechanism of the oxidative fragmentation reaction of $[Fe_6C(CO)_{16}]^{2-}$, which have been carried out with the aim of gaining the knowledge necessary to extend cluster-bound carbon chemistry to other metal cluster units.

The very nature of this reaction has been difficult to understand. Why should mild oxidation cause cluster fragmentation? Our observations in this area have led us to a rational and well-founded mechanism for the transformation of $[Fe_6C(CO)_{16}]^{2-}$ to Fe_4C products. Intermediates in the reaction have been isolated and characterized spectroscopically and crystallographically and their interconversion demonstrated. The insights gained from our study of this reaction may facilitate the extension of this chemistry to other metal carbide clusters.

Experimental Section

All manipulations were carried out either in a nitrogen drybox or on a double manifold Schlenk vacuum line, using solvents dried and distilled in the usual fashion. $(Et_4N)_2[Fe_6C(CO)_{16}]$ was prepared from $Fe(CO)_5$ by the method of Churchill et al.[6] Tropylium tetrafluoroborate was used as purchased from Aldrich.

Infrared spectra were recorded on a Beckmann 4250 spectrophotometer. X-ray fluorescence analysis of the single crystal of $(Et_4N)_2[Fe_5C(CO)_{12}Br_2]$ was performed by E. Prestridge. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Oxidation of $(Et_4N)_2[Fe_6C(CO)_{16}]$ with Tropylium Tetrafluoroborate. $(Et_4N)_2[Fe_6C(CO)_{16}]$ (1.0 g, 0.95 mmol) was dissolved in methanol (100 mL) at 25 °C. Excess tropylium tetrafluoroborate (0.84 g, 4.7 mmol) was added and the suspension stirred for 30 min. During this time a black crystalline solid separated from the reaction mixture. This was isolated by filtration, recrystallized from hexane, and identified as $Fe_5C(CO)_{15}$ by infrared spectroscopy (ν_{CO} (hexane) 2073 (vw), 2055 (s), 2035 (s), 2015 (w), 1992 (m) cm⁻¹). The yield of $Fe_5C(CO)_{15}$ was essentially quantitative (0.68 g, 0.96 mmol).

Reaction of $Et_4N^+Br^-$ with $Fe_5C(CO)_{15}$. $Fe_5C(CO)_{15}$ (prepared as in ref 9; 200 mg) was dissolved in acetone and an excess of tetraethylammonium bromide added. The resulting solution was stirred at room temperature for 2 days, after which time all starting material had been consumed (as shown by infrared spectroscopy) and a deep red solution was obtained. The solvent was evaporated, and the residual solid was washed with water to remove excess $Et_4N^+Br^-$. Extraction into methylene chloride and cooling to -40 °C yielded a black crystalline material: IR (CH_2Cl_2) 2005 (w), 1970 (s), 1945 (s), 1917 (m) cm⁻¹. Anal. Calcd for $(Et_4N)_2Fe_4C(CO)_{12}$: Fe, 26.85; N, 3.36 (Fe:N = 1.95). Found: Fe, 24.99; N, 3.22.

Oxidation of $Fe_4C(CO)_{12}^{2-}$ with Tropylium Tetrafluoroborate. $[(PPh_3)_2N]_2Fe_4C(CO)_{12}$ (1.0 g, 0.61 mmol) was dissolved in CH_2Cl_2 (100 mL). Tropylium tetrafluoroborate (0.31 g, 1.2 mmol) was added, and the initially deep red solution turned brown. Evaporation of the solvent and recrystallization of the residue from hexane yielded $Fe_4C(CO)_{13}$ (0.28 g, 0.48 mmol), identified by comparison of its infrared spectrum with that of an authentic sample.

(5) See, for example: Ponec, V. *Catal. Rev.-Sci. Eng.* **1978**, *18*, 151. Biloen, p.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1981**, *58*, 95. Nijs, H. H.; Jacobs, P. A. *Ibid.* **1980**, *66*, 401.

(6) Churchill, M. R.; Wormald, J.; Knight, J.; Mays, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 3073.

Table I

A. Crystal Data

formula	$Fe_5C_{29}H_{40}N_2O_{12}Br_2$
fw	1047.7
space group	$P2_1/n$
lattice constants	
a, Å	11.361 (2)
b, Å	14.958 (3)
c, Å	23.472 (6)
β, deg	95.08 (2)
V, Å³	3973
Z	4
ρ calcd, g cm⁻³	1.751

B. Data Collection

diffractometer	Enraf-Nonius CAD 4
radiation	Mo Kα, 0.7107 Å
monochromator	graphite
scan range	$0° < 2\theta < 45°$
scan speed	4–20° min⁻¹
reflections examined	8070
reflections observed	3001[a]
criterion	$I > 2\sigma(I)$
absorption correctn	
μ, cm⁻¹	38.31 cm⁻¹
type	psi scans
max/min, deg	0.74–1.00
stability	no intensity decay in 3 check reflections

[a] The low number of observed reflections is a consequence of fluorescence by the bromine-containing crystal in Mo Kα radiation.

Reaction of $Fe_4(CO)_{13}C$ in MeOH and Et_3N with Methanol. A 300-mg (0.5-mmol) sample of $Fe_4(CO)_{13}C$ was dissolved in methanol (50 mL). An infrared spectrum of this solution was identical with that of $[Fe_4(CO)_{12}CCO_2CH_3]^-$ in methanol. The methanol was removed under reduced pressure and the residue extracted with CH_2Cl_2. The infrared spectrum was identical with that of $Fe_4(CO)_{13}C$ in CH_2Cl_2. The solvent was removed and the product again extracted into MeOH. Triethylamine was added to the solution, which was then evaporated under reduced pressure. The residue was crystallized from CH_2Cl_2-hexane, yielding a black crystalline solid with the characteristic infrared spectrum of $[Fe_4(CO)_{12}CCO_2CH_3]^-$ (ν_{CO} (CHCl$_2$) 2024 (s), 1998 (s), 1980 (sh), 1970 (sh), 1925 (m), 1650 (w) cm⁻¹).

X-ray Diffraction Study on $(Et_4N)_2[Fe_5C(CO)_{15}Br_2]$, IV. Crystals of IV were isolated as black cubes from a methylene chloride solution at -40 °C. Diffraction data were collected on a crystal 0.25 × 0.25 × 0.25 mm, sealed in a Lindemann capillary. A summary of crystallographic data and the experimental conditions used is given in Table I. All calculations were performed by using the SDP package provided by Enraf-Nonius. The five iron atoms and two bromine atoms were located by a combination of Patterson and direct methods (MULTAN) and the remaining non-hydrogen atoms by difference Fourier techniques. After all non-hydrogen atoms had been located, the positions of the hydrogen atoms in the tetraethylammonium cations were calculated by using program HYDRO from the SDP package. The hydrogen positions were not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters, least-squares refinement converging with residuals of $R_1 = 0.087$ and $R_2 = 0.075$ and an esd of an observation of unit weight of 1.94.

Results and Discussion

The reaction of $[Fe_6C(CO)_{16}]^{2-}$ with tropylium bromide has been analyzed as a series of four steps, each of which will be described separately.

1. Oxidation of $[Fe_6C(CO)_{16}]^{2-}$ to $Fe_5C(CO)_{15}$. It had been reported in 1970 by Graham that treatment of $[Fe_6C(CO)_{16}]^{2-}$ with sulfuric acid resulted in the formation of $Fe_5C(CO)_{15}$ in ca. 20% yield.[7] This was the synthetic method of choice for the synthesis of $Fe_5C(CO)_{15}$ for a

(7) Stewart, R. P.; Anders, U.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C49.

Table II. Atomic Coordinates for $(Et_4N)_2[Fe_5C(CO)_{12}Br_2]$

atom	x	y	z	atom	x	y	z
Br(1)	0.6676 (2)	0.1639 (1)	0.02334 (8)	C(2B)	0.822 (1)	0.2366 (10)	0.2408 (6)
Br(2)	0.9648 (2)	0.1360 (1)	0.11517 (8)	C(2C)	0.610 (1)	0.3108 (9)	0.2486 (6)
Fe(1)	0.8783 (2)	0.4000 (1)	0.08879 (9)	C(3A)	0.642 (1)	0.5272 (10)	0.1109 (6)
Fe(2)	0.7075 (2)	0.2876 (1)	0.19389 (9)	C(3B)	0.520 (1)	0.3894 (10)	0.1432 (6)
Fe(3)	0.6559 (2)	0.4109 (1)	0.11442 (9)	C(3C)	0.599 (1)	0.3894 (11)	0.0397 (7)
Fe(4)	0.8186 (2)	0.4451 (1)	0.19207 (9)	C(4A)	0.863 (1)	0.5531 (10)	0.1750 (6)
Fe(5)	0.7966 (2)	0.2327 (1)	0.09689 (9)	C(4B)	0.721 (1)	0.4830 (9)	0.2425 (6)
O(1A)	1.1227 (9)	0.3760 (8)	0.1318 (5)	C(4C)	0.950 (1)	0.4189 (9)	0.2404 (7)
O(1B)	0.8747 (12)	0.5735 (8)	0.0320 (5)	C(1)	0.702 (1)	0.9081 (11)	0.6509 (7)
O(1C)	0.9057 (9)	0.3045 (7)	-0.0174 (4)	C(2)	0.771 (2)	0.9413 (13)	0.6040 (8)
O(2A)	0.5797 (12)	0.1232 (7)	0.1639 (6)	C(3)	0.680 (1)	0.8316 (12)	0.7393 (7)
O(2B)	0.8897 (9)	0.2068 (8)	0.2728 (5)	C(4)	0.729 (2)	0.7769 (14)	0.7892 (9)
O(2C)	0.5499 (9)	0.3258 (8)	0.2830 (5)	C(5)	0.831 (2)	0.7793 (11)	0.6766 (8)
O(3A)	0.6245 (10)	0.6035 (7)	0.1077 (5)	C(6)	0.753 (2)	0.7105 (12)	0.6451 (9)
O(3B)	0.4260 (9)	0.3812 (8)	0.1570 (5)	C(7)	0.865 (1)	0.9158 (10)	0.7269 (7)
O(3C)	0.5621 (10)	0.3804 (9)	-0.0049 (5)	C(8)	0.823 (1)	0.9973 (11)	0.7560 (7)
O(4A)	0.8964 (10)	0.6254 (7)	0.1667 (5)	C(9)	0.807 (2)	0.3382 (19)	0.4314 (9)
O(4B)	0.6558 (11)	0.5121 (8)	0.2712 (5)	C(10)	0.842 (3)	0.4005 (23)	0.3905 (10)
O(4C)	1.0284 (10)	0.4064 (8)	0.2698 (5)	C(11)	0.718 (2)	0.2823 (13)	0.5139 (9)
N(1)	0.7685 (9)	0.8588 (8)	0.6983 (5)	C(12)	0.810 (2)	0.2232 (13)	0.5384 (10)
N(2)	0.7493 (11)	0.3634 (8)	0.4815 (5)	C(13)	0.641 (2)	0.4199 (14)	0.4671 (10)
C(0)	0.797 (1)	0.3413 (9)	0.1419 (6)	C(14)	0.543 (2)	0.3831 (14)	0.4281 (9)
C(1A)	1.025 (1)	0.3883 (10)	0.1131 (6)	C(15)	0.839 (2)	0.4214 (14)	0.5190 (10)
C(1B)	0.875 (1)	0.5053 (11)	0.0548 (6)	C(16)	0.808 (2)	0.4519 (16)	0.5738 (10)
C(1C)	0.890 (1)	0.3372 (9)	0.0262 (7)				
C(2A)	0.633 (2)	0.1883 (10)	0.1721 (7)				

decade and as such attracted our attention when we began our work in the iron carbide cluster area. Indeed our initial attempts to oxidize $[Fe_6C(CO)_{16}]^{2-}$ (I) were in part an attempt to determine whether Graham's synthesis was primarily an oxidation reaction or a protonation or both. The oxidation of I by tropylium bromide in methanol was an attempt to answer this question, and, as we reported previously,[2] this reaction yielded $[Fe_4(CO)_{12}CCO_2CH_3]^-$, II, an intriguing but unexpected result.

Evidence that the first stage in the formation of II from I was the loss a single iron atom was provided by an attempt to use the commercially available tropylium tetrafluoroborate in place of tropylium bromide. The addition of $C_7H_7^+BF_4^-$ to a solution of I in methanol caused the precipitation of a black crystalline solid, which after recrystallization from hexane at -40 °C was identified as $Fe_5C(CO)_{15}$, III, by infrared spectroscopy, elemental analysis, and mass spectrometry.

Based on these observations, it is reasonable to conclude that in the tropylium bromide oxidation of I, the first step in the conversion of the Fe_6C cluster to the Fe_4C cluster is an oxidative loss of one iron vertex from the octahedral I giving the square-pyramidal III, the displaced iron being oxidized to Fe^{2+} (eq 2). The same result has been reported
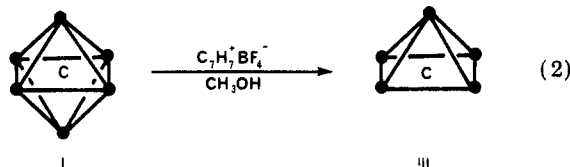
by Tachikawa, who used ferric ion in aqueous solution to oxidize several $MFe_5C(CO)_x^{y-}$ clusters to give the corresponding MFe_4C (M = Cr, Mo, Rh, Fe) products with loss of Fe^{2+}.[8]

2. Reaction of $Fe_5C(CO)_{15}$ with Bromide. The selection of tropylium bromide as the oxidizing agent in our initial experiments[2] was made only on grounds of its ready availability to us at that time. It now transpires that the
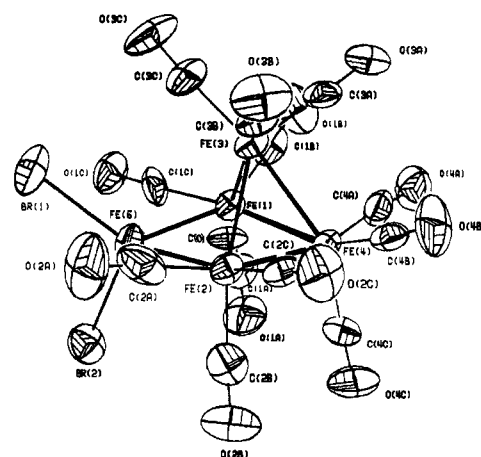
(8) Tachikawa, M.; Sievert, A. C.; Muetterties, E. L.; Thompson, M. R.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1725.

Figure 1. ORTEP drawing of $[Fe_5C(CO)_{12}Br_2]^{2-}$ with the numbering scheme used.

presence of bromide in the oxidation reaction between I and tropylium cation may be crucial to the isolation of the final product II, since it is by a reaction between the primary oxidation product $Fe_5C(CO)_{15}$ (III) and Br^- that access is gained to the Fe_4C cluster series.

The evidence for the necessity of bromide ion in the overall reaction was found (quite serendipitously) in the isolation of minute amounts of the anionic cluster $[Fe_5C-(CO)_{12}Br_2]^{2-}$, IV, which was obtained its tetraethylammonium salt during a series of recrystallizations of an unrelated material derived from II. The dibromide IV had apparently been present as an impurity in II, formed during the synthesis of II from I. A consideration of the reaction history of the sample made it clear that the source of the halogen in the molecule must have been the tropylium bromide used in the synthesis of II.

The crucial position of $[Fe_5C(CO)_{12}Br_2]^{2-}$ in the overall fragmentation reaction sequence became clear when the structure of IV was elucidated by X-ray diffraction. Atomic cordinates for the anion are listed in Table II and interatomic distances and selected bond angles in Table III. The anion (Figure 1) comprises five iron atoms in an array most instructively seen as a distorted square pyra-

Table III

a. Interatomic Distances,ᵃ Å

Iron–Iron

Fe(1)-Fe(3)	2.654 (2)	Fe(2)-Fe(3)	2.651 (2)	Fe(3)-Fe(4)	2.531 (2)
Fe(1)-Fe(4)	2.661 (2)	Fe(2)-Fe(4)	2.674 (2)	Fe(3)···Fe(5)	3.153 (2)
Fe(1)-Fe(5)	2.681 (2)	Fe(2)-Fe(5)	2.700 (2)		

Iron–Carbide Carbon

Fe(1)-C(0)	1.839 (10)	Fe(3)-C(0)	1.974 (9)	Fe(5)-C(0)	1.938 (11)
Fe(2)-C(0)	1.841 (10)	Fe(4)-C(0)	1.951 (11)		

Iron–Bromide

Fe(5)-Br(1)	2.396 (2)	Fe(5)-Br(2)	2.405 (2)

Iron–Carbon

Fe(1)-C(1A)	1.724 (13)	Fe(2)-C(2B)	1.797 (16)	Fe(3)-C(3C)	1.842 (14)
Fe(1)-C(1B)	1.764 (15)	Fe(2)-C(2C)	1.799 (13)	Fe(4)-C(4A)	1.748 (15)
Fe(1)-C(1C)	1.760 (14)	Fe(3)-C(3A)	1.749 (14)	Fe(4)-C(4B)	1.787 (14)
Fe(2)-C(2A)	1.765 (17)	Fe(3)-C(3B)	1.764 (13)	Fe(4)-C(4C)	1.832 (14)

Carbon–Oxygen

C(1A)-O(1A)	1.170 (13)	C(2B)-O(2B)	1.120 (15)	C(3C)-O(3C)	1.103 (13)
C(1B)-O(1B)	1.153 (14)	C(2C)-O(2C)	1.129 (12)	C(4A)-O(4A)	1.170 (14)
C(1C)-O(1C)	1.161 (13)	C(3A)-O(3A)	1.159 (13)	C(4B)-O(4B)	1.129 (13)
C(2A)-O(2A)	1.152 (15)	C(3B)-O(3B)	1.155 (12)	C(4C)-O(4C)	1.097 (13)

b. Selected Bond Angles,ᵃ Deg

Fe Core
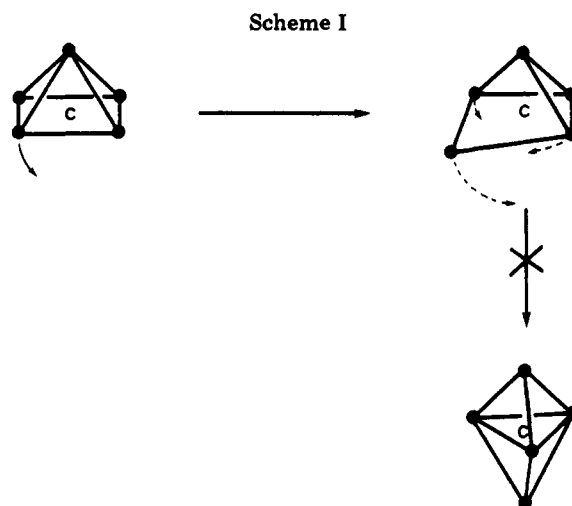
Fe(3)-Fe(1)-Fe(4)	56.88 (6)	Fe(4)-Fe(2)-Fe(5)	92.40 (7)	Fe(1)-Fe(4)-Fe(2)	87.12 (7)
Fe(3)-Fe(1)-Fe(5)	72.47 (6)	Fe(1)-Fe(3)-Fe(2)	87.76 (7)	Fe(1)-Fe(4)-Fe(3)	61.41 (6)
Fe(4)-Fe(1)-Fe(5)	93.13 (7)	Fe(1)-Fe(3)-Fe(4)	61.71 (6)	Fe(2)-Fe(4)-Fe(3)	61.15 (6)
Fe(3)-Fe(2)-Fe(4)	56.76 (6)	Fe(2)-Fe(3)-Fe(4)	62.09 (6)	Fe(1)-Fe(5)-Fe(2)	86.20 (7)
Fe(3)-Fe(2)-Fe(5)	72.21 (6)				

Angles at Carbide

Fe(1)-C(0)-Fe(2)	176.12 (59)	Fe(2)-C(0)-Fe(3)	87.99 (37)	Fe(3)-C(0)-Fe(5)	107.46 (49)
Fe(1)-C(0)-Fe(3)	88.17 (42)	Fe(3)-C(0)-Fe(4)	80.32 (40)	Fe(4)-C(0)-Fe(5)	172.19 (54)

Br–Fe–Br

Br(1)-Fe(5)-Br(2)	107.18 (8)

Fe–C–O

Fe(1)-C(1A)-O(1A)	175.7 (12)	Fe(2)-C(2B)-O(2B)	175.8 (13)	Fe(3)-C(3C)-O(3C)	176.5 (13)
Fe(1)-C(1B)-O(1B)	178.9 (11)	Fe(2)-C(2C)-O(2C)	179.6 (6)	Fe(4)-C(4A)-O(4A)	175.8 (12)
Fe(1)-C(1C)-O(1C)	171.7 (11)	Fe(3)-C(3A)-O(3A)	175.5 (11)	Fe(4)-C(4B)-O(4B)	174.2 (12)
Fe(2)-C(2A)-O(2A)	172.4 (13)	Fe(3)-C(3B)-O(3B)	172.3 (10)	Fe(4)-C(4C)-O(4C)	177.5 (12)

ᵃ Estimated standard deviations are in parentheses.

mid, with a carbon atom C(0) near the center of the base at the intersection of the Fe(2)-Fe(4) and Fe(3)-Fe(5) vectors. Four of the iron atoms Fe(1-4), each bear three terminal carbonyls, and the two bromine atoms are bound to Fe(5).[9]

A pronounced distortion of the Fe₅C core from the C_{4v} symmetry found for Fe₅C(CO)₁₅[10] is observed. The base of the pyramid is elongated along the Fe(4)-Fe(5) direction, resulting in Fe-Fe-Fe angles at Fe(1) and Fe(2) of 93.1 and 92.4° and at Fe(4) and Fe(5) of 87.1 and 86.2°. Fe(3) no longer is situated immediately over the carbide carbon C(0), as shown by the reduction of the Fe(3)-C-(0)-Fe(4) angle to 80.3°. The Fe(3)-Fe(4) bond of 2.531 (2) Å is correspondingly shorter than the Fe(3)-Fe(1) and Fe(3)-Fe(2) separations of 2.655 and 2.652 Å, respectively.

The most interesting and significant aspect of the structure is the long Fe(3)-Fe(5) distance, 3.153 Å, which is ca. 0.5 Å longer than the other Fe-Fe bonds, and, as

Scheme I

(9) The identity of the two bromine atoms was not obvious initially. Until the final stages of the structure refinement they remained as unidentified heavy atoms and were first revealed as bromine atoms by consideration of the reaction history of the sample and subsequent successful refinement using scattering factors for bromine. Confirmation was obtained from an X-ray fluorescence analysis of the actual crystal which had been used for diffraction data collection, which showed the presence of bromine in the crystal.

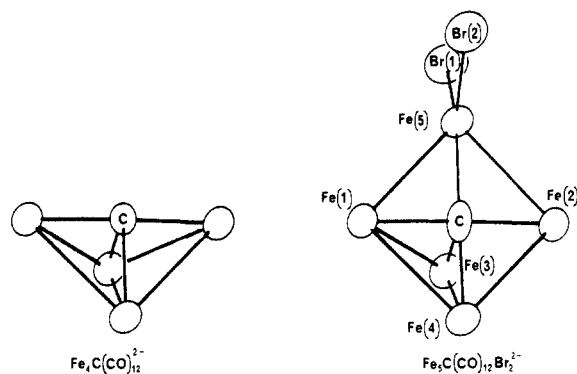(10) Braye, E. H.; Dahl, L. F.; Hubel, W.; Wampler, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 4663.

such, is not to be considered a bonding contact.

The features of predominant interest to an understanding of the cluster fragmentation process in which IV is a probable intermediate are all contained in the [Br₂-Fe₅C] unit, when compared to the Fe₅C(CO)₁₅ structure. Fe₅C(CO)₁₅, III, is a five-vertex cluster containing 74 valence electrons. Application of Wades electron-counting rules[11] results in seven electron pairs being considered as

Figure 2. The Fe_5Br_2C core of IV in comparison with the Fe_4C core in $[Fe_4C(CO)_{12}]^{2-}$.

available for skeletal bonding in the cluster. For a five-vertex cluster these 14 electrons are accommodated in a nido structure based on the octahedron, i.e., a square pyramid, and this is indeed the structure of $Fe_5C(CO)_{15}$ as determined by Dahl and co-workers.[10] In $[Fe_5C-(CO)_{12}Br_2]^{2-}$ there are only 72 valence electrons, since three two-electron CO ligands have been replaced by two two-electron Br^- ligands. Thus there are only six skeletal bonding pairs available, and these can be accommodated in a closo five-vertex cluster, i.e., a trigonal bipyramid. The transformation from square pyramid to trigonal bipyramid could be accomplished by the distortion shown in Scheme I, but this motion is interrupted by the steric requirement of the central carbon atom. This arrangement precludes the formation of a closed trigonal bipyramid around it, since the equatorial plane would be a carbon centered equilateral triangle of iron atoms, requiring impossibly short iron–carbon distances of 1.50 Å. (Conversely, a more usual Fe–C distance of 1.90 Å is accommodated by an Fe_3 triangle with sides of 3.3 Å, much longer than a typical Fe–Fe bond.) Thus the structure of III may be seen as resulting from the incomplete transformation of a square pyramidal nido structure to a closo trigonal bipyramid. Whatever the cause of the distortion in the molecule, it is clear that Fe(5) is no longer bound as closely to the remaining Fe_4C unit as it had been in the precursor III.

The distortion of a cluster core when the number of valence electrons in the cluster is altered by the addition of halide ions has been noted in the case of a related osmium carbidocarbonyl cluster. $[Os_5C(CO)_{15}]$ reacts with iodide to yield $[Os_5C(CO)_{15}I]^-$, and in this case the halide adds to the cluster and no carbonyls are lost. The resulting anion has gained two electrons and accordingly adopts an open structure based on a pentagonal bipyramid.[12]

The geometry of the Fe_4C fragment formed by Fe(1–4) and C(0) is remarkably similar to the core geometry in $[Fe_4C(CO)_{12}]^{2-}$[14] as shown in Figure 2. The Fe(3)–Fe(4) distance is 2.531 (1) Å, compared to 2.534 (1) Å for the corresponding distance in $[Fe_4C(CO)_2]^{2-}$; the remaining metal–metal bonds average 2.66 Å (2.65 Å for $[Fe_4C-(CO)_{12}]^{2-}$). The dihedral at Fe(3)–Fe(4) between triangular faces Fe(1,3,4) and Fe(2,3,4) is 103.6° (cf. 101°) and the Fe(1)–C(0)–Fe(2) angle is 177.4° (cf. 178.3 Å). This comparison leads to a view of IV as a probable precursor to $[Fe_4C(CO)_{12}]^{2-}$ and suggests that the latter, formed by loss

Scheme II
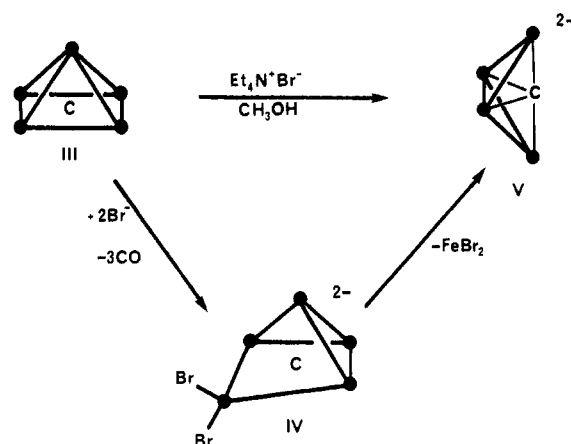
of $FeBr_2$ from IV, is the next intermediate in the fragmentation of I. It was established earlier that the iron vertices lost from I in the synthesis of II (eq 1) were in the form of Fe^{2+} ions. In order to determine whether $Fe_5C-(CO)_{15}$ could be induced to fragment by the displacement of carbonyl ligands by bromide, we reacted the neutral cluster with tetraethylammonium bromide.

Addition of excess $Et_4N^+Br^-$ to a solution of $Fe_5C(CO)_{15}$ in methanol under nitrogen caused the replacement of the infrared absorbances of the starting material by new bands at 2005 (w), 1970 (s), 1945 (s), 1917 (m) cm^{-1}. The product, V, was isolated after the solution was stirred several hours at room temperature as a black crystalline solid. The most available means of comparison between this material and the fortuitously isolated IV was by crystallographic measurement, since IV had been isolated only in miniscule yield and no infrared data had been recorded. Crystals of IV were grown from methylene chloride solution and data collected on an approximately cubic crystal with 0.2-mm sides. Measurement of the lattice parameters of V revealed, however, that III and IV were not identical, and elemental analysis confirmed that IV contained no bromine and suggested that the new compound was not an Fe_5C dianion at all but $(Et_4N)_2[Fe_4C(CO)_{12}]$, V. The collection of a complete X-ray diffraction data set and solution of the structure confirmed the identity of IV as the Fe_4 dianion. (The structure of the Et_4N^+ salt is not significantly different from that reported by Davis et al.[13] for the $Zn(NH_3)_4^{2+}$ salt and will be described separately.)

The direct formation of $[Fe_4C(CO)_{12}]^{2-}$ by reaction of $Fe_5C(CO)_{15}$ cluster with bromide ion was unexpected but nonetheless revealing, since it confirmed the necessity of the halide ion in the fragmentation (Scheme II), as had been suggested by the structure of IV. Although we had expected to be able to isolate IV from the reaction of III with bromide, the ready loss of $FeBr_2$ from IV to yield V is not totally surprising given the structure of IV. It is as yet unclear why we were able to isolate IV originally intact as a byproduct from the reaction of I with tropylium bromide whereas it spontaneously fragmented to V in our directed synthesis. All attempts to repeat the isolation of IV have been unsuccessful.

3. Oxidation of $[Fe_4C(CO)_{12}]^{2-}$ to $[Fe_4C(CO)_{13}]$. The route from the Fe_6C cluster (I) to the Fe_4C cluster (V) via tropylium bromide oxidation thus having been established, it remained to demonstrate the means by which V was converted to the final product II. Since V was originally generated in a system containing an excess of oxidizing agent (tropylium ion), it was reasonable to assume the further electron-transfer reaction between V and tropylium

(11) Wade, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559.

(12) Farrar, D. H.; Jackson, P. G.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1009.

(13) Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668.

(14) Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics*, **1982**, *1*, 214.

ion would occur to generate a reactive, coordinatively unsaturated cluster $[Fe_4C(CO)_{12}]$ as had been observed previously by using silver ion as the oxidant.[13] In the overall reaction (eq 1) free carbon monoxide is present due to the fragmentation of $[Fe_6C(CO)_{16}]^{2-}$, and so to model this step in the reaction, $[Fe_4C(CO)_{12}]^{2-}$ was treated with 2 equiv of tropylium tetrafluoroborate in methylene chloride under an atmosphere of carbon monoxide. The infrared spectrum of the reaction mixture revealed a smooth conversion of the dianion V to $[Fe_4C(CO)_{13}]$, VI (eq 3). This cluster

(3)
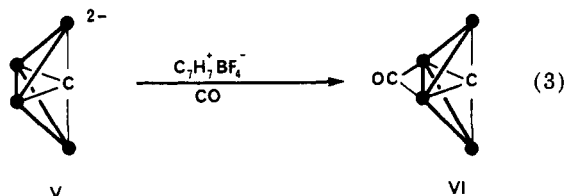
had been isolated previously by the protonation of II and its structure determined by X-ray diffraction.[1] The molecule is similar in geometry to the dianion V, with the familiar butterfly Fe₄C core, but the two electrons removed in the oxidation of V are replaced by a thirteenth carbonyl which bridges the central iron–iron bond of the cluster.

4. Reaction of [Fe₄C(CO)₁₃], VI, with Methanol. The most interesting feature of VI is, as we noted previously, the exposed carbon atom, and the transformation of VI to $[Fe_4(CO)_{12}CCO_2CH_3]^-$, II, by reaction with methanol is an example of the novel reactivity of cluster bound carbon atoms.[1] On dissolving VI in methanol under nitrogen, a dark green solution is obtained (VI in nonreactive solvents gives dark brown solutions, consistent with the color of the crystalline solid). The infrared spectrum of this solution shows absorbances at 2035 (s), 1992 (s), 1980 (sh), 1932 (mbr), 1640 (w) cm⁻¹. This pattern is recognizable as diagnostic of a cluster of the type $[Fe_4(CO)_{12}C(=O)X]^-$ (by comparison with $[Fe_4(CO)_{12}CCO_2R]^-$, $[Fe_4(CO)_{12}CC(=O)NR_2]^-$, and $[Fe_4(CO)_{12}CC(=O)R]^-$) as is the dark green color. However, on evacuation of the methanolic solution, a brown residue resulted, and the infrared spectrum of a methylene chloride solution of this material revealed it to be $[Fe_4C(CO)_{13}]$, VI. Thus the reaction with methanol is seen to be reversible, and indeed this cycle can be repeated at will.

Assuming the product from the reaction of VI with methanol was closely related to II, we assigned it a tentative formula $H^+[Fe_4(CO)_{12}CCO_2CH_3]$. The synthesis of II was completed by addition of one equivalent of base (eq 4). Either methanolic KOH or triethylamine were used, and the resulting salt of II was identified by infrared spectroscopy.

(4)
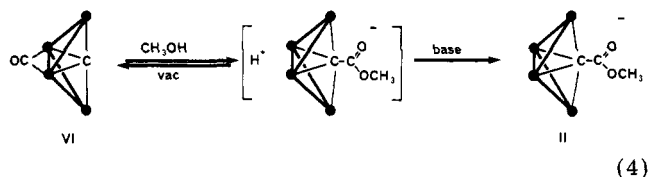
We have suggested previously that the formation of II may proceed via migration of carbon monoxide to the exposed carbon atom to give a ketenylidene cluster $[Fe_4(CO)_{12}(CCO)]$, which then reacts with methanol to give II. Although there is no direct evidence for the existence of the proposed intermediate, the recently reported isolation of $[H_2Os_3(CO)_{10}(CCO)]$ and its reaction with alcohols to

Scheme III
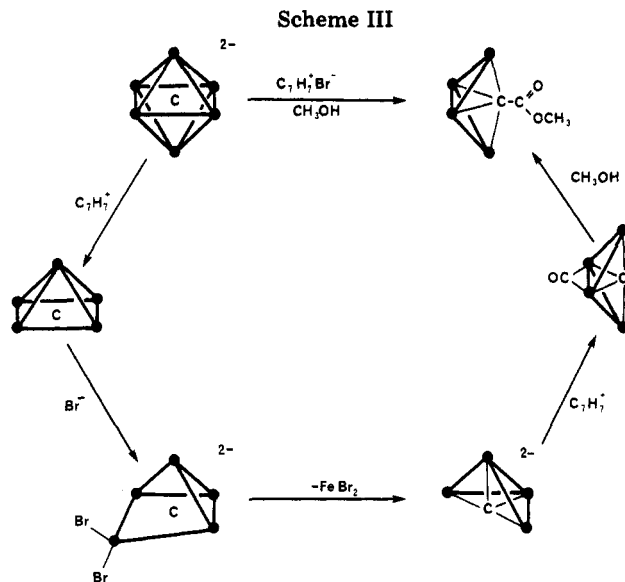
give $[H_3Os_3(CO)_{10}(CCO_2R)]$[14] lends some support to our suggestion. The most likely alternative to this route would be the attack of methoxide at a carbonyl ligand on one of the iron atoms, followed by migration of the resulting carboalkoxy group to the carbide carbon. In order to differentiate between these alternatives, we dissolved VI in dry dimethoxyethane and the mixture was treated with either methanol or sodium methoxide. In the former case the initially brown solution rapidly became dark green, with infrared absorptions characteristic of the formation of II, whereas in the latter, a deep red solution resulted after several hours, in which the principal species was $[Fe_4C(CO)_{12}]^{2-}$. By elimination of methoxide attack at an iron bound carbonyl as a possible route to II from VI further support is added to the ketenylidene alternative.

On the basis of these observations we propose the reaction sequence shown in Scheme III for the oxidative fragmentation of $[Fe_6C(CO)_{16}]^{2-}$ (I) in methanol with tropylium bromide to give $[Fe_4(CO)_{12}CCO_2CH_3]^-$, II. Both I and II and the intermediates III, IV, V, and VI have all been isolated and their structures determined by X-ray crystallography, and the stepwise conversion I → III → IV → V → VI → II demonstrated individually.

The overall reaction of $[Fe_6C(CO)_{16}]^{2-}$, I, with tropylium bromide to yield $[Fe_4(CO)_{12}CCO_2CH_3]^-$, II, is dependent on the presence of bromide ion in the reaction mixture. This was readily demonstrated by the use of tropylium tetrafluoroborate as oxidant in the reaction, where no trace of $[Fe_4(CO)_{12}CCO_2CH_3]^-$ was observed by infrared spectroscopy, and the reaction yielded $[Fe_5C(CO)_{15}]$ and small amounts of as yet uncharacterized products. However, if tetraethylammonium bromide was added to the reaction mixture prior to addition of the tropylium salt, II is formed smoothly and is formed in high yield, and this is now our preferred synthesis for II.