Carbidocarbonyl Clusters of Iron [and Discussion]

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Carbidocarbonyl clusters of iron

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Under reducing conditions, at elevated temperatures, coordinated carbon monoxide in transition metal carbonyls may disproportionate to CO_2 and a carbon atom. The carbon atom is trapped in a cage of metal atoms, shielded from further reaction in the core of the resulting carbidocarbonyl clusters. This class of compounds, which has been known for some time, bears some structural resemblance to the binary carbides and may therefore be relevant to Fischer–Tropsch catalysis, in which carbide phases and surface carbon atoms are implicated.

The chemical, structural and physical properties of the iron carbidocarbonyls have been investigated. Reactions are described that lead to C–H and C–C bond formation at the carbide carbon, and these are discussed with regard to the nature of this carbon atom. ^{13}C n.m.r. spectroscopy reveals large downfield chemical shifts for the carbide carbon, which may be interpreted as either a reflexion of low electron density at the carbon or the influence of paramagnetic contributions to the shift. Reactions of $[Fe_4(CO)_{12}C{\cdot}CO_2CH_3]^-$, $[Fe_4(CO)_{12}C{\cdot}C(O)CH_3]^-$ and $[Fe_4(CO)_{12}C{\cdot}CHO]^-$ with trimethyloxonium fluoborate yield the corresponding vinylidene clusters $Fe_4(CO)_{12}$-$C{=}C(OCH_3)R$ ($R = OCH_3, CH_3, H$).

1. Introduction

In 1962 Dahl and coworkers reported the synthesis and structure of an iron carbonyl cluster with a unique structural feature (Braye *et al.* 1962). $[Fe_5C(CO)_{15}]$, the new molecule contained, in addition to its carbonyl ligands, a single carbon atom bound only to the five iron atoms in the molecule. This first example of a carbidocarbonyl cluster remained the only example of its type for several years, until the isolation by Lewis and coworkers of $[Ru_6C(CO)_{17}]$ and its derivatives (Johnson *et al.* 1967, 1968). In the mid 1970s, the late Paolo Chini and his coworkers began reporting their successes in the synthesis and structural characterization of a number of cobalt and rhodium carbidocarbonyl clusters, and a similar acceleration occurred in the rate of growth of the analogous chemistry of iron, ruthenium and osmium. As the array of carbidocarbonyl clusters has grown, so their significance as a class has become more obvious. What were once regarded as structural oddities have assumed a more central role in cluster chemistry, at a time when the ostensible similarities between metal cluster compounds and metallic crystallites were being explored in terms of both structure and reactivity (Ugo 1975; Muetterties 1977).

An additional significance for carbidocarbonyl clusters has appeared in the past 3 years, with the discovery of the fascinating reactivity of carbon atoms in low nuclearity iron clusters when they are exposed to reactive molecules. These observations followed on the heels of the recognition of the crucial role played by surface-bound carbon atoms in metal-catalysed carbon monoxide hydrogenation (Ponec 1978), and so a new area of overlap between cluster chemistry and surface chemistry has arisen. Moreover, in this case the comparisons between organometallic and surface chemistry may lie not only in structural similarities but also in chemical reactivity. In this paper, I shall describe some recent developments in the chemistry of the carbidocarbonyl clusters of iron, with emphasis on the reactivity of the cluster-bound carbon atom.

2. Tetranuclear carbidocarbonyl clusters of iron

As mentioned above, the first carbidocarbonyl transition metal cluster to be recognized was $[Fe_5C(CO)_{15}]$, **1**, isolated in very low yield from the reaction of triiron dodecacarbonyl with methylphenylacetylene and characterized by X-ray diffraction by Dahl and coworkers (Braye *et al.* 1962). The molecule comprises a square pyramidal Fe_5 core with the carbide carbon situated 0.08 Å† below the centre of the square face. The hexanuclear analogue to **1** is known, as a dianion. $[Fe_6C(CO)_{16}]^{2-}$, **2**, originally synthesized by the reaction of $Fe(CO)_5$ with a variety of metal carbonyl anions at elevated temperatures, contains an octahedral Fe_6C core, with the carbon atom situated at its centre (Churchill *et al.* 1971).

The defining characteristic of this class of compounds is the lone carbon atom, bound only to metal atoms. Although the metal-centred chemistry of these clusters is undoubtedly affected by the carbon atom, these effects (for example in ligand exchange at the metal) are secondary when compared with the potential for unique chemistry at this carbon, caused by its surrounding metal atoms. However, in neither **1** nor **2** has any reactivity been observed at the carbon atom. This is hardly surprising for the fully encapsulated carbon in **2**, but less expected for **1**, in which the carbon atom is at least partly exposed (Tachikawa & Muetterties 1981).

Iron is so far unique in that it alone forms carbidocarbonyl clusters containing only four metal atoms, and the discovery of this class of compounds and of the reactivity of its members has provided one of the more intriguing developments in cluster chemistry over the last few years. We reported in 1979 that the cluster-bound carbon atom, which was apparently inert in Fe_5C and Fe_6C clusters, could display novel chemistry if exposed by the removal of some of its surrounding metal atoms, reducing the coordination number of the carbon atom to four in an open, butterfly geometry (Bradley *et al.* 1979). This, the first observation of the reactivity of a cluster-bound carbon atom, resulted from the partial fragmentation of the octahedral carbide cluster $[Fe_6C(CO)_{16}]^{2-}$, **2**. When treated with tropylium bromide, a mild one-electron oxidizing agent, in methanol, **2** loses two iron vertices (as ferrous ion), exposing the central carbon atom, which reacts with CO and methanol yielding the μ^4-carbomethoxymethylidyne cluster, **3**:

$$\underset{\mathbf{2}}{[Fe_6C(CO)_{16}]^{2-}} \xrightarrow[CH_3OH,\ 25\ ^{\circ}C]{C_7H_7^+Br} \underset{\mathbf{3}}{[Fe_4(CO)_{12}C\cdot CO_2CH_3]^-} + 2Fe^{2+} + 3CO. \qquad (1)$$

The structure of **3** (figure 1), comprises an open, butterfly arrangement of four iron atoms, each bearing three terminal carbonyls. The hitherto encapsulated carbon atom is equidistant (2.00 ± 0.02 Å) from the metal atoms and is now bonded to the carbomethoxy group. The nature of this reaction will be discussed below in the context of other carbon–carbon bond-forming reactions.

The reactivity of the carbon atom when bound to an open Fe_4 cluster has an obvious relevance to the chemistry of surface-bound carbon atoms in heterogeneous catalysis, and is of great interest. Several members of the Fe_4C family have been synthesized and structurally characterized, and the chemistry of these clusters is under investigation in several laboratories.

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† 1 Å = 10^{-10} m = 0.1 nm.

The parent neutral carbido-cluster of this class, $[\mathrm{Fe_4C(CO)_{13}}]$, **4**, is most readily synthesized by protonation of **3** (Bradley *et al.* 1981):

$$\underset{\mathbf{3}}{[\mathrm{Fe_4(CO)_{12}C{\cdot}CO_2CH_3}]^-} \xrightarrow[\text{methylcyclohexane}]{\mathrm{CF_3SO_3H}} \underset{\mathbf{4}}{[\mathrm{Fe_4C(CO)_{13}}]}. \qquad (2)$$

The molecule (figure 2) comprises an open, butterfly-shaped $\mathrm{Fe_4C}$ core, with three terminal carbonyls bound to each ion atom. The thirteenth carbonyl bridges the two iron atoms, which make up the central bond (Fe(1)–Fe(4)) of the butterfly. Further aspects of the structure are described below in comparison with other members of this family.

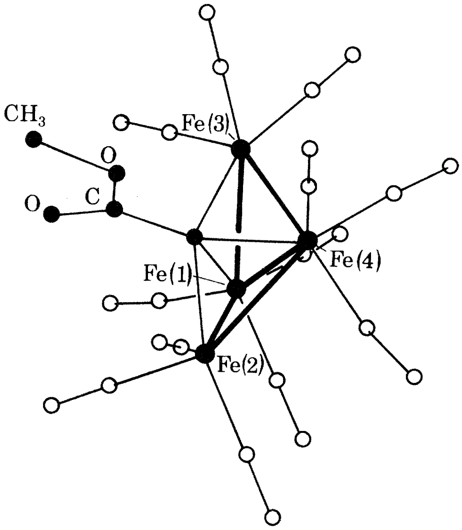

FIGURE 1

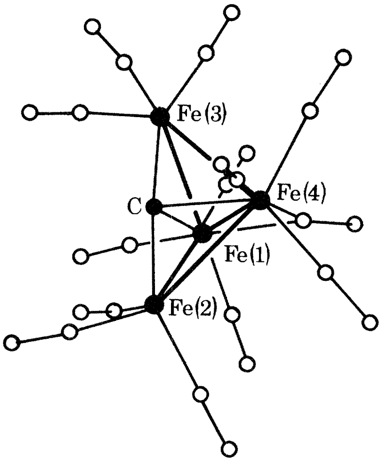

FIGURE 2

FIGURE 1. $\mathrm{Fe_4(CO)_{12}C{\cdot}CO_2CH_3^-}$, **3**, as in its $\mathrm{(C_2H_5)_4N^+}$ salt. A butterfly core of four iron atoms bears twelve terminal carbonyls, three on each iron. Fe(1)–Fe(4) (2.590(1) Å) is significantly longer than the other Fe–Fe bonds (2.503(9) Å mean). The methylidyne carbon is a 2.027(9) Å from Fe(2), 2.012(9) Å from Fe(3), 1.957(9) Å from Fe(1) and 1.952(9) Å from Fe(4). Fe(1), Fe(4) and the carbomethoxy group are coplanar. The dihedral between Fe(1)(3)(4) and Fe(1)(2)(4) is 130°. Angle Fe(2)CFe(3) = 148°.

FIGURE 2. $\mathrm{Fe_4C(CO)_{13}}$, **4**. The butterfly $\mathrm{Fe_4C}$ core bears twelve terminal carbonyls and a thirteenth bridging Fe(1)–Fe(4). Unbridged Fe–Fe distances average 2.642(4) Å; Fe(1)–Fe(4) = 2.545(1) Å, Fe(1)–C = 1.998(4) Å, Fe(4)–C = 1.987(4) Å, Fe(2)–C = 1.797(4) Å; Fe(3)–C = 1.800(4) Å. Dihedral angle between Fe(1)(3)(4) and Fe(1)(2)(4) = 101°. Angle Fe(2)CFe(3) = 175°.

We have synthesized several phosphine-substituted derivatives of **4** by reaction of trimethylphosphine with **4**. $[\mathrm{Fe_4C(CO)_{13-\mathit{n}}(PMe_3)_\mathit{n}}]$ (n = 3 or 4) have been fully characterized spectroscopically, and the structure of $[\mathrm{Fe_4C(CO)_{10}(PMe_3)_3}]$ is shown in figure 3. The three phosphine ligands are bonded to three of the iron atoms, one wingtip iron at Fe(3) remaining unsubstituted. A triply bridging carbonyl resides on the wing of the $\mathrm{Fe_4C}$ butterfly that contains Fe(3). The tetrakis(trimethylphosphine) derivative $[\mathrm{Fe_4C(CO)_9(PMe_3)_4}]$ has been characterized by ^{1}H, ^{31}P and ^{13}C n.m.r. spectroscopy, and on the basis of the presence of two equally populated phosphine sites is assigned the symmetric structure, each iron atom bearing one phosphine ligand and two carbonyls.

Reduction of **4** by sodium amalgam yields $[\mathrm{Fe_4C(CO)_{12}}]^{2-}$, **5**, in high yield:

$$\underset{\mathbf{4}}{[\mathrm{Fe_4C(CO)_{13}}]} \xrightarrow[25\,^\circ\mathrm{C}]{\text{Na–Hg, THF}} \underset{\mathbf{5}}{[\mathrm{Fe_4C(CO)_{12}}]^{2-}}. \qquad (3)$$

Compound **5** was previously synthesized by Tachikawa and Muetterties (Tachikawa *et al.* 1980), and structurally characterized as its $Zn(NH_3)_4^{2+}$ salt. We have determined independently the structure of the tetraethylammonium salt of **5** (in which the anion is essentially of the same structure as in the zinc salt), and this is shown in figure 4. The anion is similar in geometry to its neutral analogue **4** but lacking the bridging carbonyl found in the latter.

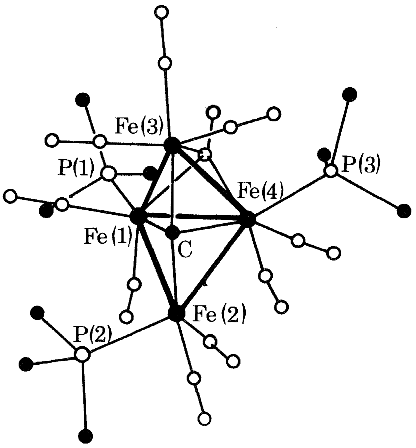

FIGURE 3

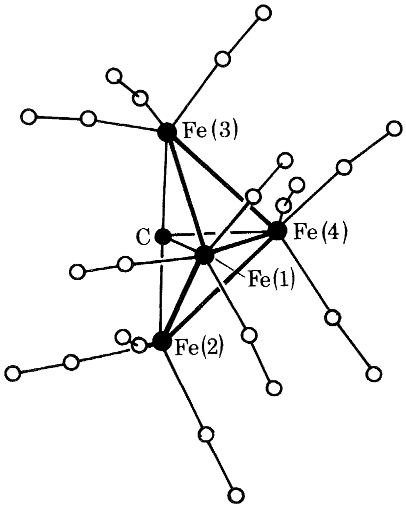

FIGURE 4

FIGURE 3. $Fe_4C(CO)_{10}(P(CH_3)_3)_3$. The three trimethylphosphine ligands are coordinated to Fe(1), Fe(2) and Fe(4). Of the ten carbonyl ligands nine are terminal, and one is triply bridging on the Fe(1)(3)(4) face. Fe(1)–Fe(4) = 2.528(1) Å, the shortest of the metal–metal bonds. The other Fe–Fe distances average 2.644(19) Å. Fe(1)–C = 1.979(4) Å, Fe(4)–C = 2.014(4) Å, Fe(2)–C = 1.785(4) Å, Fe(3)–C = 1.838(4) Å. The dihedral angle between Fe(1)(2)(4) and Fe(1)(3)(4) = 102.4°. Angle Fe(2)CFe(3) = 174°.

FIGURE 4. $Fe_4C(CO)_{12}^{2-}$, **5**, as in its $(C_2H_5)_4N^+$ salt. Fe(1)–Fe(2) = Fe(1)–Fe(3) = 2.640(2) Å. Fe(2)–Fe(4) = Fe(3)–Fe(4) = 2.641(3) Å. Fe(1)–Fe(4) = 2.521(2) Å. Fe(1)–C = 1.936(12) Å, Fe(2)–C = 1.772(11) Å, Fe(3)–C = 1.803(12) Å, Fe(4)–C = 1.969(12) Å. Dihedral at Fe(1)–Fe(4) = 101°. Angle Fe(2)Fe(3) = 178°.

Oxidation of **5** by ferrocenium cation in methylene chloride under carbon monoxide regenerates **4**.

Reduction of $[Fe_4(CO)_{12}CCO_2CH_3]^-$, **3**, with $BH_3 \cdot THF$ in THF proceeds smoothly at 25 °C to give $[HFe_4C(CO)_{12}]^-$, **6**, isolated in high yield as the tetraethylammonium salt. This compound has been reported independently by Davis *et al.* (1981), and by Holt *et al.* (1981), who also determined the structure of the bis(triphenylphosphineiminium) salt, locating the hydride on the central Fe–Fe bond of the Fe_4C butterfly.

3. STRUCTURAL FEATURES OF Fe_4C CLUSTERS

The three isoelectronic clusters $[Fe_4C(CO)_{13}]$, **4**, $[Fe_4C(CO)_{12}]^{2-}$, **5**, and $[HFe_4C(CO)_{12}]^-$, **6**, provide the central characters in the Fe_4C family. Their structures have been determined by X-ray diffraction, and in all three cases there is a basic $[Fe_4C(CO)_{12}]$ core of relatively invariant geometry, with the open, butterfly arrangement characteristic of Fe_4C clusters. Consistent with the predictions of Wade's rules (Wade 1972), these 62-electron clusters, possessing seven skeletal electron pairs and four vertices, adopt an *arachno* structure based on the octahedron. The carbonyls in the $Fe_4C(CO)_{12}$ unit are all terminal in groups of three on each iron atom, and the carbido carbon atom is situated centrally above the midpoint of the central Fe–Fe bond, midway between the two 'wingtips'. The dihedral angle between the two triangular wings of the butterfly averages 102 ± 2 Å over the three clusters (table 1), the angle subtended at the carbide carbon atom by the wingtip iron atoms averages 176 ± 2°, and the Fe–C_{carbide} distances *a* and *b* are almost constant (see figure 5).

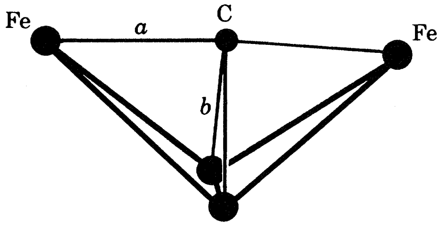

FIGURE 5

TABLE 1

	dihedral δ / deg	angle FeCFe / deg	a / Å	b / Å	references
$[Fe_4C(CO)_{13}]$, **4**	101	175	1.80	1.94	Bradley *et al.* (1981)
$[Fe_4C(CO)_{12}]^{2-}$, **5**	101	178	1.79	1.97	this work and Tachikawa *et al.* (1980)
$[Fe_4C(CO)_{12}H]^{-}$, **6**	104	174	1.79	1.99	Holt *et al.* (1981)

The dihedral angle δ is rather less than the 109° provided by a regular octahedral cavity (from which the butterfly is derived), and this compression is reflected in the disparity between the two sets of Fe–C_{carbide} distances *a* and *b* (see figure 5).

It is also interesting in this respect to compare the geometry of the Fe_4C family with that of the hexanuclear and pentanuclear homologues $[Fe_6C(CO)_{16}]^{2-}$, and $[Fe_5C(CO)_{15}]$. If it were true that the octahedral cavity in the dianion was too small for the adequate accommodation of the carbon atom, it would be expected that in the more open Fe_5C and Fe_4C clusters some relaxation would occur, allowing the carbon atom to adopt a less crowded position. In fact the effective radius of the carbon atom in $[Fe_5C(CO)_{15}]$ is 0.57 Å (Braye *et al.* 1962), an increase of only 0.02 Å from that in $[Fe_6C(CO)_{16}]^{2-}$ (Churchill *et al.* 1971), and in the even more open structures of **4**, **5** and **6** the average value is still only 0.58 Å. (These last values are derived by using a mean of the five Fe–Fe distances for each molecule.)

4. CHEMICAL REACTIVITY OF THE CARBON ATOM IN Fe_4C CLUSTERS

This aspect of the chemistry of carbidocarbonyl clusters is a relatively recently observed phenomenon. Carbon atom chemistry is found so far exclusively in the Fe_4C group of clusters, although increased activity in this area will undoubtedly uncover analogous reactions with other metals.

A number of reactions of Fe_4C clusters have been observed in which either C–C or C–H bonds to the carbide carbon are formed.

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(*a*) C–C *bond formation*

(i) *Reaction of* $Fe_4C(CO)_{13}$ *with alcohols*

$$Fe_4C(CO)_{13} + ROH \longrightarrow Fe_4(CO)_{13}CCO_2R^- + H^+ \; (R = CH_3, C_2H_5, \text{iso-}C_3H_7). \tag{4}$$

The reaction, either in undiluted alcohol or in an inert polar solvent, is reversible on evacuation to remove solvent (Bradley *et al.* 1981). Addition of base is required to allow the isolation of the crystalline product, which has been fully characterized crystallographically for $R = CH_3$ (Bradley *et al.* 1979) as its tetraethyl ammonium salt (see figure 1). The *C*-carboalkoxy group is bound to the hitherto exposed carbon atom of the Fe_4C core, which has distorted from its original butterfly shape (101° dihedral, angle FeCFe = 175°) to a bipyramidal form with the μ^4-methylidyne carbon atom at an equatorial vertex, consistent with the 60 valence electrons in the cluster (Wade 1972).

(ii) *Reaction of* $Fe_4C(CO)_{13}$ *with secondary amines*

$$\underset{\mathbf{4}}{Fe_4C(CO)_{13}} + 2R_2NH \longrightarrow (R_2NH_2)^+[Fe_4(CO)_{12}C\cdot C(O)NR_2]^-. \tag{5}$$

The addition of two equivalents of the amine to a methylene chloride solution of **4** at 25 °C results in the rapid formation of the *C*-dialkylamide derivatives ($R = C_2H_5$, iso-C_3H_7). Although no X-ray structural data have been obtained on these compounds, their infrared and ^{1}H n.m.r. spectra are consistent with their formulation, and presumably they have structures similar to the carboalkoxy analogues with which they are isoelectronic.

(iii) *Reaction of* $Fe_4C(CO)_{13}$ *with hydride*

$$\underset{\mathbf{4}}{[Fe_4C(CO)_{13}]} + LiEt_3BH \longrightarrow Li^+\underset{\mathbf{7}}{[Fe_4(CO)_{12}C\cdot CHO]^-}. \tag{6}$$

The addition of one equivalent of lithium triethylborohydride in diethyl ether to an ether solution of **4** results in the formation of the lithium salt of the *C*-formyl derivative, **7**, which is apparently stable only as its ion-paired lithium salt ($\nu_{CO(formyl)} = 1560\,cm^{-1}$). Attempts to isolate salts with other cations result in decomposition to $[HFe_4C(CO)_{12}]^-$, but the reactivity of **7** with alkylating agents to give a neutral vinylidene cluster (see § 5*d*) supports the formulation of **7** as $Li^+[Fe_4(CO)_{12}C\cdot CHO]^-$.

(iv) *Reaction of* $Fe_4C(CO)_{12}^{2-}$ *with alkylating agents*

$$\underset{\mathbf{5}}{[Fe_4C(CO)_{12}]^{2-}} + RI \longrightarrow [Fe_4(CO)_{12}CC(O)R]^- + I^-. \tag{7}$$

Reaction of the dianion **5** with alkyl iodides in methylene chloride yields the *C*-acyl derivatives (reported previously for $R = CH_3$) (Davis *et al.* 1981), in a process that requires one mol of carbon monoxide. The reaction proceeds in only moderate yield, which suggests that the additional CO is provided by sacrificial reaction of some of the reagent molecules. No structural data are yet available.

(*b*) C–H *bond formation*

(i) *Reaction of* $Fe_4C(CO)_{13}$ *with dihydrogen*

$$\underset{\mathbf{4}}{Fe_4C(CO)_{13}} + H_2 \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\mathbf{8}}{HFe_4(CO)_{12}CH} + CO. \tag{8}$$

The thermal decarbonylation of $Fe_4C(CO)_{13}$ in refluxing toluene generates coordinatively unsaturated $[Fe_4C(CO)_{12}]$, which then reacts with dihydrogen to yield the hydrido methylidyne cluster, **8**. This compound was previously synthesized by Tachikawa & Muetterties (1980) by the reaction of $[Fe_4C(CO)_{12}]^{2-}$ with silver ion under hydrogen (probably via the same intermediate) and was fully characterized by X-ray (Beno *et al.* 1980) and neutron diffraction (Beno *et al.* 1981). The outstanding structural feature of the butterfly shaped molecule is a three-centre FeHC interaction involving a wingtip iron atom and the methylidyne group. The formation of the C–H group by reaction between the cluster bound carbon atom and hydrogen is highly significant in that it provides a molecular analogue for the reaction of surface-bound carbon atoms with hydrogen in heterogeneously catalysed methanation and Fischer–Tropsch catalysis.

It is noteworthy that the methylidyne hydrogen in **8** is quite acidic, and ionization in methanol is quantitative, yielding $[HFe_4C(CO)_{12}]^-$, **6** (Holt *et al.* 1981). The protonation of the dianion **5** to **6** by one equivalent of acid reflects the low basicity of the exposed carbon atom in **5**.

The reactivity of the carbon atom raises questions about its chemical nature: should it be regarded as cationic, neutral (carbenoid perhaps) or anionic, as the name carbidocarbonyl has long implied? No mechanistic data are available for the reactions at the carbon atom, and so any observations we can make on the nature of the carbon in its cluster-bound environment must remain speculative. We have suggested (Bradley *et al.* 1979) that the reaction between alcohols (and amines) with $Fe_4C(CO)_{13}$ may proceed via a ketenylidene intermediate $Fe_4(CO)_{12}\!:C\!:CO$. Although there is no direct evidence for this, the reactions of $H_2Os_3(CO)_{10}CCO$ and $Co_3(CO)_9$-CCO^+ with alcohols to give $H_3Os_3(CO)_{12}C\cdot CO_2R$ (Sievert *et al.* 1982) and $Co_3(CO)_9CCO_2R$ (Seyferth *et al.* 1974) provide support for this route. These reactions may be interpreted in terms of a positively charged carbon atom, by analogy with the similar reactions of carbonium ions with carbon monoxide and alcohols to give esters. Consistent with this proposal, we have observed that increasing the electron density on the cluster by substituting trimethylphosphine for carbon monoxide (see above) prevents the formation of the carbomethoxymethylidyne cluster:

$$\begin{tikzcd}
Fe_4C(CO)_{13} \arrow[r, "MeOH"] \arrow[d, "PMe_3"] & {[Fe_4(CO)_{12}C\cdot CO_2Me]^-} \\
Fe_4C(CO)_9(PMe_3)_4 \arrow[r, "MeOH"] & \text{no reaction.}
\end{tikzcd} \qquad (9)$$

Few spectroscopic data are available that might shed light on the electronic nature of the lone carbon atom in these clusters. In an attempt to gain some insight into this property, we have measured the ^{13}C n.m.r. chemical shifts of the carbide carbon atoms in a series of iron carbidocarbonyl clusters (see table 2). In every case, the carbide resonances are shifted strongly to low field and represent the largest ^{13}C shifts yet reported for diamagnetic organometallic molecules. This might be interpreted in terms of a deshielded positively charged carbon atom, but this is by no means an indisputable correlation. There seems to be no connection between the charge on the molecule and $\delta_{C_{\text{carbide}}}$. In the series $[Fe_4C(CO)_{13}]$, $[HFe_4C(CO)_{12}]^-$ and $[Fe_4C(CO)_{12}]^{2-}$, which are very similar in geometry (see figure 5) the carbide resonances are found at 469.8, 464.2 and 478.0×10^{-6}. The cause of the shifts observed for cluster-bound carbon atoms is not clear and may reflect the predominance of paramagnetic contributions to the chemical shift rather than simply deshielding at a cationic centre. Temperature-dependent solid-state ^{13}C n.m.r. studies are in progress to resolve this question, and more illuminating evidence on the nature of the carbon atom in this unique environment must await further spectroscopic and theoretical investigations, which are so far lacking for these molecules.

TABLE 2. $\delta_{\mathrm{C_{carbide}}}$ FOR CARBIDOCARBONYL CLUSTERS OF IRON

(Recorded at 22.5 MHz on a Jeol FX-900 spectrometer, at probe temperature. All samples were enriched to *ca.* 20 % ^{13}C by ^{13}CO exchange with $Fe(CO)_5$, which was used as the precursor for all the clusters synthesized.)

	$10^6\delta$
$Fe_4C(CO)_{13}$†	468.9
$HFe_4C(CO)_{12}^-$†	464.2
$Fe_4C(CO)_{12}^{2-}$†	478.0
$Fe_4C(CO)_9(PMe_3)_4$†	471.5
$Fe_5C(CO)_{15}$†	486.0
$Fe_6C(CO)_{16}^{2-}$‡	484.6

† CD_2Cl_2 solution; ‡ $(CD_3)_2CO$ solution.

5. THE CHEMISTRY OF CARBIDE-BASED ORGANOMETALLIC Fe_4 CLUSTERS

We have investigated the chemistry of some of the *C*-derivatized Fe_4C clusters described above, and these will be exemplified by the chemistry of the carbomethoxymethylidyne cluster.

(*a*) *Reaction with hydrogen*

$$\underset{\mathbf{3}}{[Fe_4(CO)_{12}C\cdot CO_2CH_3]^-} \xrightarrow[2.8\,\mathrm{MPa},\ 120\ ^\circ\mathrm{C}]{H_2,\ \mathrm{THF}} CH_3CO_2CH_3 + \underset{\mathbf{2}}{[Fe_6C(CO)_{16}]^{2-}}. \qquad (10)$$

On treatment of **3** in THF with hydrogen at 2.8 MPa (400 lbf in^{-2}) and 120 °C, the four Fe–C bonds to the organic group are hydrogenolysed to give methyl acetate, and under the conditions of this reaction the iron species present agglomerate to **2** in a carbide-producing reaction. Because **2** was the starting material for the synthesis of **3**, the potential (as yet unrealized) exists for a catalytic synthesis of methyl acetate. Attempts to produce more than a stoichiometric amount of methyl acetate by treating **3** with carbon monoxide and hydrogen in methanol have proved unsuccessful, with the irreversible formation of **2**.

(*b*) *Reaction with acid*

$$\underset{\mathbf{3}}{[Fe_4(CO)_{12}CCO_2CH_3]^-} + H^+ \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{hexane}} \underset{\mathbf{4}}{[Fe_4C(CO)_{13}]} + CH_3OH. \qquad (11)$$

As described earlier, protonation of the *C*-carbomethoxy derivative cleaves the methoxy group as methanol and produces the parent carbidocarbonyl of the Fe_4 family $[Fe_4C(CO)_{13}]$ in high yield.

(*c*) *Reaction with* $BH_3\cdot$THF

$$\underset{\mathbf{3}}{[Fe_4(CO)_{12}C\cdot CO_2CH_3]^-} \xrightarrow[25\ ^\circ\mathrm{C}]{BH_3\cdot\mathrm{THF}} \underset{\mathbf{6}}{[HFe_4C(CO)_{12}]^-}. \qquad (12)$$

The borane reduction of the carbomethoxy derivative **3** produces the monoanion **6** in high yield. This material was previously prepared by other routes (Davis *et al.* 1981; Holt *et al.* 1981).

(*d*) *Reaction with alkylating agents*

$$\underset{\mathbf{3}}{[Fe_4(CO)_{12}CCO_2CH_3]^-} + (CH_3)_3O^+ \xrightarrow[25\,^{\circ}C]{CH_2Cl_2} \underset{\mathbf{9}}{[Fe_4(CO)_{12}C{=}C(OCH_3)_2]}. \qquad (13)$$

The carbonyl of the *C*-carbomethoxy group **3** is methylated by trimethyloxonium fluoborate to yield the neutral dimethoxyvinylidene cluster, **9**, which has been characterized crystallographically.

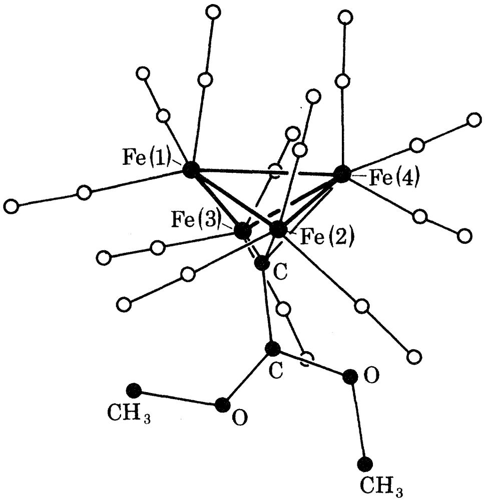


FIGURE 6. $Fe_4(CO)_{12}(C{=}C(OCH_3)_2)$, **9**. Fe(1)–Fe(2) = Fe(1)–Fe(3) = 2.491(3) Å; Fe(2)–Fe(4) = Fe(3)–Fe(4) = 2.555(2) Å; Fe(1)–Fe(4) = 2.532(2) Å. Fe(1)–C = 1.976(9) Å; Fe(2)–C = 2.026(9) Å; Fe(3)–C = 2.028(9) Å; Fe(4)–C = 1.960(9) Å, vinylidene C=C = 1.434(14) Å. Dihedral at Fe(1)–Fe(4) = 127°, Angle Fe(2)CFe(3) = 149°.

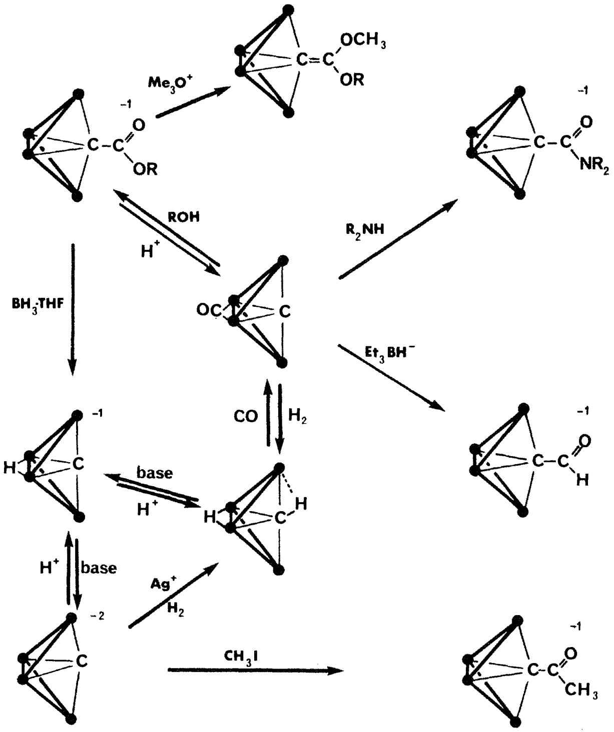
The structure of **9** is shown in figure 6. The open Fe_4 framework remains, with three terminal carbonyls on each metal atom. The geometry of the $[Fe_4(CO)_{12}C]$ core has altered little from that of the anionic precursor **3** (see figure 1). The dihedral angle at Fe(1)–Fe(4) between the two triangular wings of the butterfly is 127° (cf. 130° in **3**) and the methylidyne carbon in **3** has not moved significantly in becoming the vinylidene carbon in **9** (angle Fe(2)CFe(3) = 149°, cf. 148° for the corresponding angle in **3**). The dimethoxy vinylidene group is orientated in a plane that also includes the central iron–iron bond Fe(1)–Fe(4) of the butterfly. Analogous reactions of trimethyloxonium fluoroborate with the *C*-acetyl and *C*-formyl clusters anions yield $Fe_4(CO)_{12}C{=}C(CH_3)OCH_3$ and $Fe_4(CO)_{12}C{=}C(H)OCH_3$, respectively.

6. SUMMARY

The chemistry of the Fe_4C family of clusters is summarized in scheme 1.

The synthesis and chemistry of these molecules is providing a rich and growing area of organometallic cluster chemistry. It remains to be seen whether or not the properties of this intriguing class of clusters will shed light on the reactivity of surface-bound carbon atoms on metallic heterogeneous catalysts. Such interdisciplinary analogies, while often stimulating and instructive, remain secondary to the fascination of the chemistry of the clusters themselves.

The extension of this area to the carbon atom chemistry in clusters of other metals than iron is a challenging goal, and its achievement, together with spectroscopic and theoretical investigations of the nature of the cluster-bound carbon atom, is eagerly awaited.



SCHEME 1. ●, $Fe(CO)_3$.

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Discussion

E. W. Randall (*Chemistry Department, Queen Mary College, London, U.K.*). If one is allowed to use the concept of bond order in clusters, what are the indications concerning the bond orders for the iron–carbido carbon interactions? The chemical shift for ^{13}C is dominated by the second-order paramagnetic effect, as Dr J. Mason would agree, for most carbons and almost certainly therefore for the carbido carbon.

J. S. Bradley. It is clearly not simple to define bond orders for the metal–carbon bonds in these clusters. Molecular orbital calculations are being done by my colleague Dr S. Harris to provide a clearer understanding of the nature of the interactions between the iron atoms and the carbide carbon. Our initial results indicate that the carbide carbon carries a fractional negative charge, which rules out any interpretation of the large downfield ^{13}C chemical shifts in terms of simple deshielding at a cationic centre.