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A novel synthesis of $Fe_5C(CO)_{15}$ from the $[Fe_6C(CO)_{16}]^{2-}$ anion

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In 1962 Braye and co-workers[1] reported the synthesis and X-ray structural characterization of the first transition metal carbonyl carbide $Fe_5C(CO)_{15}$, isolated in very low yield (~0.5%) from the reaction of $Fe_3(CO)_{12}$ and 1-pentyne under rather exacting conditions. Since then several neutral ruthenium carbonyl carbide complexes have been described in the literature[2-5]. More recently an iron carbonyl carbide anion, $[Fe_6C(CO)_{16}]^{2-}$, has been prepared (and fully characterized by X-ray diffraction) from $Fe(CO)_5$ and $Na^+[Mn(CO)_5]^-$ in refluxing diglyme[6]. We have independently synthesized the $[Fe_6C(CO)_{16}]^{2-}$ anion and have found that acidification of this anion affords a more convenient route to $Fe_5C(CO)_{15}$; while the yield is still low (~20%) this method is relatively far superior to the original synthesis[1].

A solution of $[Na(diglyme)_2]^+[V(CO)_6]^-$ (5.73g, 11.2 mmoles) and $Fe(CO)_5$ (30 ml, 223 mmoles) in dry diglyme (150 ml) was heated at 150–160° for 5 h. After cooling to room temperature, the dark red-purple solution was extracted with several portions of n-pentane, leaving a dark, viscous oil to which excess aqueous Et_4NCl was added with stirring. The solid material was collected on filtration and was extracted under nitrogen with refluxing methanol for 20 h in a Soxhlet extractor. After filtration, ethanol was added and the dark red-purple solution was concentrated slowly *in vacuo* (water aspirator) at room temperature to give a black crystalline product (6.72 g, 6.36 mmoles). (*Anal.*: Found: C, 37.27; H, 3.83; Fe, 31.46; N, 2.81; O, 24.74%; $C_{33}H_{40}Fe_6NO_{16}$ calcd.: C, 37.54; H, 3.82; Fe, 31.74; N, 2.65; O, 24.25%.) The infrared spectrum shows carbonyl stretching bands at 2028 vw, 1961 vs, 1931 w(sh), 1772 w(br) (THF solution) or 2028 vw, 1964 vs, 1930 w(sh) cm^{-1} (acetone solution). The Me_4N^+, $(n\text{-}Bu)_4N^+$, and Ph_4As^+ salts were prepared similarly. Further confirmation of the identity of the anion was obtained from a comparison of the lattice parameters of the Me_4N^+ salt with those reported by Churchill *et al.*[6] for $(Me_4N)_2Fe_6C(CO)_{16}$.

A typical synthesis of $Fe_5C(CO)_{15}$ follows. To a stirred slurry of $[(n\text{-}Bu)_4N]_2Fe_6C(CO)_{16}$ (3.63 g, 2.84 mmoles) in n-pentane (100 ml) was added 96% H_2SO_4 (30 ml). The dark brown pentane layer was decanted and additional solvent was added in several portions until the pentane layer became colorless. The pentane extracts were combined and evaporated to dryness to give a dark brown solid residue which was dissolved in ether–heptane (1/1) and chromatographed on Florisil. The grey-purple band was collected, concentrated, and cooled (–78°), affording black crystalline $Fe_5C(CO)_{15}$ (347 mg, 0.49 mmoles). The compound was characterized by its infrared spectrum, mass spectrum★, and lattice parameters.

The infrared spectrum (cyclohexane solution) of $Fe_5C(CO)_{15}$ in the carbonyl stretching region is reported[1] as one very weak band (2101 cm^{-1}) and four strong bands (2049, 2033, 2012, 1992 cm^{-1}). Although our spectrum of $Fe_5C(CO)_{15}$ is in agreement (±3 cm^{-1}) with these band positions (*i.e.*, 2098 vw, 2050 s, 2031 s, 2012 m, 1991 m cm^{-1}) the reported[1] intensities of the two lowest energy bands are clearly in error (see Fig. 1). Based on infrared spectral data it is therefore highly probable that the neutral carbido carbonyl (prepared by acidification of $[Fe_6C(CO)_{16}]^{2-}$) briefly mentioned by Churchill *et al.*[6] is in fact $Fe_5C(CO)_{15}$.

Observation of the ions $[Fe_5C(CO)_x]^+$ (x = 0–15) and the doubly-charged ions $[Fe_5C(CO)_y]^{2+}$ (y = 0–13) in the mass spectrum of $Fe_5C(CO)_{15}$ together with the high relative abundance (100%) of the $[Fe_5C]^+$ ion★★ is similar to the behavior of $Ru_6C(CO)_{17}$ under electron impact[2] and suggests an inherent stability of the $[Fe_5C]^+$ unit. However, unlike $Ru_6C(CO)_{17}$ where $[Ru_5C]^+$ is the only ion observed from the fragmentation of the $[Ru_6C]^+$ cluster,[2] the $[Fe_5C]^+$ cluster undergoes further fragmentation to $[Fe_nC]^+$ (n = 1–4) and other ions. This may perhaps be associated with a lower stability of the $[Fe_5C]^+$ cluster relative to $[Ru_6C]^+$ but it is difficult to draw meaningful conclusions from mass spectral results obtained under different conditions.

The original investigation of the $[MnFe_2(CO)_{12}]^-$ ion in this laboratory[7] indicated the formation of a dark red-purple anionic species at long reaction times, although a suitable formulation for this species was not then possible[8]. The trinuclear species has now been shown[6] to be an intermediate in the formation of $[Fe_6C(CO)_{16}]^{2-}$. In the reaction of $[M(CO)_n]^-$ (M = V, n = 6; M = Mn, n = 5) with $Fe(CO)_5$ at 150–160° the metal carbonyl

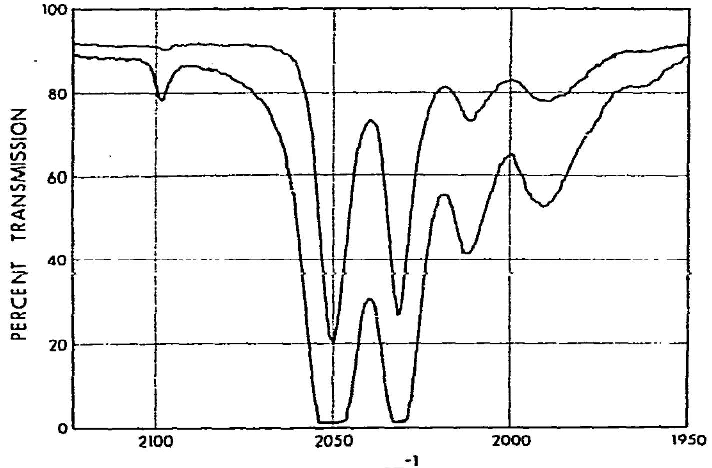

Fig.1. Infrared spectrum of $Fe_5C(CO)_{15}$ (cyclohexane solution).

★Parent ion: measured mass, 711.5998; computed for $[Fe_5C(CO)_{15}]^+$, 711.5985.
★★Measured mass, 291.6738; computed for $[Fe_5C]^+$, 291.6746.

anion apparently acts as a reducing agent, although for vanadium no intermediate analogous to $[MnFe_2(CO)_{12}]^-$ has been detected. The observation[8] that $[Fe_6C(CO)_{16}]^{2-}$ also results when only $Fe(CO)_5$ and diglyme are heated at 150–160° indicates that such an intermediate is not necessary. It is significant that $[Co(CO)_4]^-$ reacts similarly with $Fe(CO)_5$ [8,9]. Bis-(biphenyl)chromium[10] and cobaltocene,[11] on the other hand, reduce $Fe(CO)_5$ at 80–100° to the corresponding $(Ph{-}Ph)_2Cr^+$ and Cp_2Co^+ salts of the $Fe_4(CO)_{13}{}^{2-}$ anion.

Thus far attempts to prepare a *neutral* hexanuclear iron carbide cluster by either protonation (96% H_2SO_4, 85% H_3PO_4, 6 *N* HCl) or oxidation ($Ph_3C^+PF_6^-$, $AgBF_4$) of $[Fe_6C(CO)_{16}]^{2-}$ salts have failed, giving instead $Fe_5C(CO)_{15}$.

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