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Preliminary communication

A novel pentanuclear carbidocarbonyl anion of iron

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Despite recent interest in polynuclear carbonyl complexes[1,2], very few polymetallic carbidocarbonyl complexes have been synthesised. These include the neutral $Fe_5C(CO)_{15}$ [3], $Ru_6C(CO)_{17}$ [4,5] and $Ru_6C(CO)_{14}(arene)$[5,6], and the anion $Fe_6C(CO)_{16}{}^{2-}$ [7]. During the course of an investigation of polynuclear mixed metal carbonyl complexes[8–10], we find that $C_5H_5(CO)_3Mo^-$ reacts with $Fe(CO)_5$ to give the unique pentanuclear carbidocarbonylferrate anion, $Fe_5C(CO)_{14}{}^{2-}$, which was isolated and characterised as its tetramethylammonium salt.

A solution of $C_5H_5(CO)_3Mo^-$, prepared from $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (1.96 g, 4.0 mmole) by sodium amalgam (1–2%, 10 ml) reduction in 25 ml of dry diglyme, was added to an excess (ca. 3 ml) of $Fe(CO)_5$, and the mixture was gradually heated to reflux. After ½ h, the reddish brown solution was evaporated *in vacuo* to about half its original volume [to remove most of the unreacted $Fe(CO)_5$] and added to 200 ml of water. After filtration, the red-violet solution[★★] was treated with a saturated aqueous solution of Me_4NCl in excess to produce a voluminous precipitate which was then collected by filtration, washed well with water and dried *in vacuo* over phosphoric oxide for 1 h. The red-brown residue was extracted with anhydrous methanol (ca. 125 ml) and the deep red-violet solution was filtered, concentrated under a stream of nitrogen and cooled to −20° to give red-violet to almost black needles of the complex (2.3 g, 68% based on molybdenum). (Found: C, 33.0; H, 2.9; Fe, 32.8; N, 3.3; O, 26.1. $C_{23}H_{24}Fe_5N_2O_4$ calcd.: C, 33.2; H, 2.9; Fe, 33.6; N, 3.4; O, 26.9%.)

The absence of a $\pi\text{-}C_5H_5Mo$ group in this complex is indicated by its NMR spectrum (in acetone-d_6) which shows only a singlet resonance at τ6.57, attributable to the methyl protons.

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[★★] Acidification of this solution gives $Fe_5C(CO)_{15}$ as the major product.

Its IR spectrum (Table 1) exhibits a total of five carbonyl stretching absorptions both in the solid state and in solution. A survey of the stretching frequencies for bridging carbonyl groups in related anionic clusters such as the polynuclear carbonylferrates[11] or carbonylcobaltates[12,13] reveals that triply (or face) bridging carbonyl stretching modes absorb in the 1600–1700 cm^{-1} region while doubly (or edge) bridging carbonyl stretching frequencies occur in the 1700–1800 cm^{-1} region. Thus, the four higher-frequency absorptions may therefore be unequivocally assigned to terminal carbonyl stretching modes. The peak at ca. 1770 cm^{-1} may then be associated with stretching vibrations arising from edge-bridging carbonyl groups.

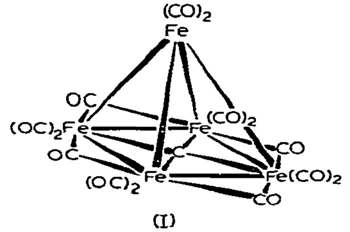
TABLE 1

INFRARED SPECTRA OF $[Me_4N]_2[Fe_5C(CO)_{14}]$ AND RELATED COMPLEXES

Complex	*Phase*	*ν(C–O)* [a]
$[Me_4N]_2[Fe_5C(CO)_{14}]$	nujol	2032 w, 1954 vs, 1938 s(sh), 1892 m(sh), 1766 ms
	THF	2018 mw, 1979 m(sh,br), 1925 vs, 1895 s(sh), 1771 s
	MeCN	2021 vw, 1966 vs, 1930 mw(sh), 1897 w, 1773 mw
$Fe_5C(CO)_{15}$	C_6H_{12} [b]	2098 vw, 2050 s, 2031 s, 2012 m, 1991 m
$[Me_4N]_2[Fe_6C(CO)_{16}]$	nujol [c]	1956 (sh), 1944 s, 1925 (sh), 1750 w(br)
	THF [c]	1964 s, 1957 (sh), 1930 (sh), 1775 w(br)

[a] In cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad.
[b] From ref. 3 and 19.
[c] From ref. 7.

From its empirical formulae, it is apparent that the anion is very closely related to the only other known pentanuclear carbidocarbonyl complex, $Fe_5C(CO)_{15}$[3], in having the same metal-atom framework. The most plausible structure which conforms to the "noble gas formalism" is therefore (I). For this symmetry (C_{2v}), group theory predicts nine terminal and three bridging carbonyl stretching modes which are infrared active.



(I)

The reaction of $Fe(CO)_5$ with $C_5H_5(CO)_3Mo^-$ in tetrahydrofuran either at room temperature or under reflux, leads only to the formation of $Fe(CO)_4{}^{2-}$ ★ and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. It has previously been shown that the products obtainable

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★ Along with oxidation/decomposition products therefrom.

from the reaction of $Fe(CO)_5$ with $Mn(CO)_5$ are critically dependent on the reaction conditions. Thus, ultraviolet irradiation of this mixture in tetrahydrofuran gives the anion $MnFe(CO)_9^-$ [14], mere heating in the same solvent yields $Fe(CO)_4^{2-}$ ★ and $Mn_2(CO)_{10}$ [15], while in refluxing diglyme, the trinuclear $MnFe_2(CO)_{12}^-$ is formed after five minutes[16] and $Fe_6C(CO)_{16}^{2-}$ after an hour[7]. Further investigation on this latter system indicates that at least one other anionic species is present in the reaction mixture and that this anion is, in fact, $Fe_5C(CO)_{14}^{2-}$ on the basis of infrared evidence[17]

The thermal stability of the anion, $Fe_5C(CO)_{14}^{2-}$, is rather remarkable despite it being air-sensitive both in the solid state and in solution. The high thermal stability of this as well as other related known carbidocarbonyl complexes such as $Fe_6C(CO)_{16}^{2-}$ [7] and $Ru_6C(CO)_{17}$ [4,5] must reflect a much greater stabilising effect achieved by the carbido carbon atom in these molecules. Such thermal stability also implies the probable existence of other members in the series, $Fe_5C(CO)_{15}$, $Fe_5C(CO)_{14}^{2-}$, $Fe_5C(CO)_{13}^{4-}$ and $Fe_6C(CO)_{17}$, $Fe_6C(CO)_{16}^{2-}$, $Fe_6C(CO)_{15}^{4-}$, in parallel with the well known series, $Co_6(CO)_{16}$ [18], $Co_6(CO)_{15}^{2-}$ [12] and $Co_6(CO)_{14}^{4-}$ [13].

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★See footnote previous page.