Crystal Structure of $[Me_3NCH_2Ph][Fe_4(CO)_{13}H]$. A 'Butterfly' Metal Cluster with an Unusually Bonded Carbonyl Group

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Summary A single-crystal *X*-ray analysis has shown the $[Fe_4(CO)_{13}H]^-$ anion to contain a butterfly arrangement of metal atoms; twelve carbonyl groups are terminally bonded, three to each iron atom, whereas the thirteenth carbonyl group interacts with all the four iron atoms and behaves as a four-electron ligand.

DURING a re-investigation of the chemistry of the polynuclear carbonylferrates,[1] we discovered that $[Fe_4(CO)_{13}H]^-$ undergoes reversible proton dissociation in organic basic solvents and, furthermore, shows two roughly temperature-independent ^1H n.m.r. signals $\{\tau[(CD_3)_2CO; + 40\ ^\circ C]$ 27·2 and 34·6$\}$ in the ratio *ca.* 2:3. Neither of these observations was in agreement with the previously proposed[2] presence of the hydrogen atom in a tetrahedral metal cage, and this prompted the *X*-ray structure determination which we now report.

Crystals of $[Me_3NCH_2Ph]$ $[Fe_4(CO)_{13}H]$ were prepared from [pyH] $[Fe_4(CO)_{13}H]^3$ (py = pyridine) by metathesis with benzyltrimethylammonium chloride in methanol and recrystallized from CH_2Cl_2–heptane. The crystalline phase was homogeneously composed of black, air-sensitive, orthorhombic crystals, space group $P2_12_12_1$; $a = 24{\cdot}62(2)$, $b = 9{\cdot}20(1)$, $c = 12{\cdot}57(1)$ Å, $D_c = 1{\cdot}72$, $D_m = 1{\cdot}69$ g cm^{-3}, $Z = 4$. Intensities were collected on a Pailred diffractometer with Mo-K_α radiation up to $2\theta = 45°$. The structure was refined to $R = 0{\cdot}057$ by block-matrix least-squares, on the basis of 1350 independent observed reflections.

The structure of the $[Fe_4(CO)_{13}H]^-$ anion (Figure) consists of a 'butterfly' arrangement of metal atoms with a dihedral angle of 117°, in which all the five Fe–Fe bond distances are equivalent within experimental error (mean 2·627 Å). 12 of the 13 carbonyl groups are terminally bonded, three to each iron atom (mean interactions being

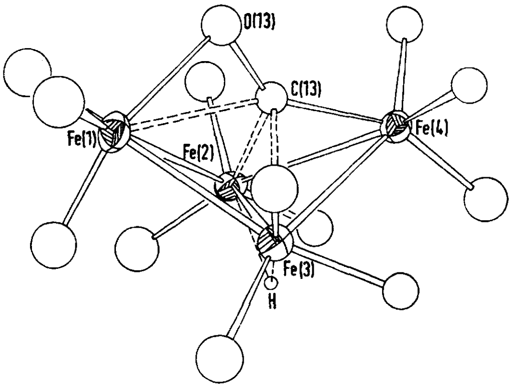

FIGURE. Perspective view of $[Fe_4(CO)_{13}H]^-$. The hydride atom is located on the basis of indirect evidence (see text). Terminal oxygen atoms are omitted. Principal bond lengths are: C(13)–O(13) 1·26, C(13)–Fe(4) 1·81, C(13)–Fe(3) 2·10, C(13)–Fe(2) 2·10, C(13)–Fe(1) 2·17, O(13)–Fe(1) 2·00 Å. Typical e.s.d.s are Fe–Fe 0·005, Fe–C 0·02, C–O 0·03 Å.

Fe–C 1·74 and C–O 1·18 Å), whereas the remaining carbonyl group is trapped among the two 'butterfly wings' in an unusual[4] bonding situation, which is the most salient feature of the structure. Thus, while the C–O separation is rather long, C(13) is at a bonding distance from all the four iron atoms and, furthermore, O(13) is tilted toward Fe(1) to give rise to a short bonding interaction. This carbonyl group therefore behaves as a four-electron donor, allowing the cluster to achieve 62 valence electrons and to conform to the noble gas formalism, as does the parent 60 valence electron tetrahedral $[Fe_4(CO)_{13}]^{2-}$ dianion.[5]

Although there is not yet conclusive direct evidence for the location of the hydrido-hydrogen atom, its position could be inferred from the stereochemistry of Fe(2) and Fe(3) and from the calculated intramolecular non-bonding contacts, which show a co-ordination 'hole', at *ca.* 1·65 Å from the metal atoms and 2·25 Å from the nearest carbon atoms (Figure).

Finally, the polyhedron described by the carbon atoms of the 12 terminal carbonyl groups may be depicted as a distorted tetracapped cube. This arrangement provides two further co-ordination sites (as required by the 13th carbonyl group and the hydrido-hydrogen atom), to be compared with the single co-ordination position allowed by the icosahedral arrangement in the $[Fe_4(CO)_{13}]^{2-}$ dianion. It seems likely therefore that the structural changes occurring on protonation of the dianion, as shown by the crystal structures of $[Fe_4(CO)_{13}]^{2-}$ and $[Fe_4(CO)_{13}H]^{-}$, are essentially due to steric requirements.

As these results do not unambiguously account for the presence in solution of two ^1H n.m.r. signals, the ^{13}C n.m.r. spectrum of the compound is presently under investigation.[1]

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