Synthesis and *X*-Ray Crystal Structures of Two 14-Vertex Di-iron Tetracarbon Metallocarbaboranes

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Summary The reaction of $Me_4C_4B_8H_8$ with $NaC_{10}H_8$, NaC_5H_5, and $FeCl_2$ produces at least four isomers of $[(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8]$, two of which have been structurally characterized from *X*-ray crystallographic studies and form 14-vertex polyhedra; neither compound has the *closo*-structure predicted from electron-counting rules, containing instead a 5-membered and a 4-membered open face respectively.

Studies in this laboratory[1] have established that the tetracarbaborane $Me_4C_4B_8H_8$ reacts with carbonyls of molybdenum and tungsten to produce $[(CO)_3MMe_4C_4B_8H_8]$ (M = Mo or W), the first metallocarbaboranes containing four skeletal carbon atoms. Subsequent work has generated an extensive series of tetracarbon metallocarbaboranes of iron, cobalt, and nickel whose stereochemistry is complex and is currently under investigation. We describe here the synthesis and structures of two isomers of the di-iron system $[(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8]$ (I) and (II) which proved to be structurally novel and are the first tetracarbon metallocarbaboranes as well as the first 14-vertex polyhedra of any type to be crystallographically characterized.

The reaction of $Me_4C_4B_8H_8$ below 20 °C with sodium naphthalide and sodium cyclopentadienide, followed by addition of $FeCl_2$, produced a mixture of products from which four isomers of $[(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8]$ including (I) and (II) were isolated in low yield by preparative-layer chromatography on silica gel. Single crystal *X*-ray diffraction studies established the structures of the brown (I) and green (II), as shown in Figures 1 and 2 respectively. *Crystal data:* compound (I): monoclinic, space group $P2_1/n$, $a = 10{\cdot}676(2)$, $b = 14{\cdot}009(5)$, $c = 13{\cdot}669(5)$ Å, $\beta =$

93·97(3)°, R = 0·051 for 2796 significant reflections; compound (II): monoclinic, space group $C2/c$, a = 16·338(3), b = 8·210(2), c = 31·547(12) Å, β = 103·74(2)°, R = 0·044 for 2468 significant reflections.

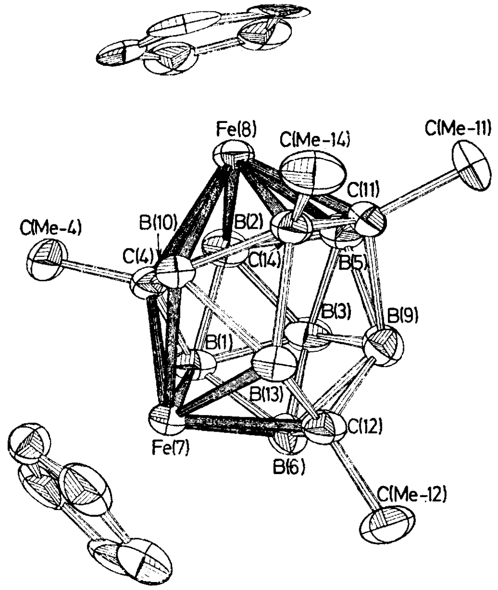

FIGURE 1. Structure of [$(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8$] (I). C(Me-4), C(Me-11), C(Me-12), and C(Me-14) are methyl group carbon atoms.

Each isomer contains 14 cage atoms and 30 valence electrons in the skeletal framework, and thus was expected to have closed polyhedral geometry (all faces triangular);[2] indeed, *closo*-structures (bicapped hexagonal antiprisms) have been postulated for isomers of the 14-vertex [$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_{10}H_{12}$] system.[3] However, the structures of (I) and (II) do not fulfill this expectation. Compound (I) has a pentagonal open face containing three carbon atoms in 4-co-ordinate vertices, the other cage carbon atom occupying a 5-co-ordinate vertex off the open face. The geometry is that of a 15-vertex *closo*-polyhedron with one missing vertex (located above the open face). Distances across the pentagonal ring range from 2·577(4) [B(9)–B(13)] to 2·868(3) Å [C(11)–C(12)] and are clearly nonbonding; all other nearest-neighbour distances in the polyhedron are within normal bonding ranges.

Compound (II) is a highly irregular polyhedron containing a 4-membered open face bounded by Fe(7), C(14), C(11), and B(9). The distances B(9)–C(14) [2·567(5)] and Fe(7)–C(11) [2·765(3) Å] are nonbonding; in addition, the interactions B(10)–B(1) [1·999(6)], B(13)–B(1) [2·095(6)], Fe(7)–B(9) [2·250(4)], and Fe(7)–B(10) [2·311(4) Å] are unusually long although within significant bonding range. All other distances are normal.

The two polyhedra are strikingly different in that (I) contains two 6-co-ordinate vertices, both occupied by iron, while (II) has three 6-co-ordinate vertices of which two are iron and the other is boron [B(1)]. Furthermore, in contrast to the arrangement of carbon atoms in (I), described above, (II) has only two carbon atoms on the open face.

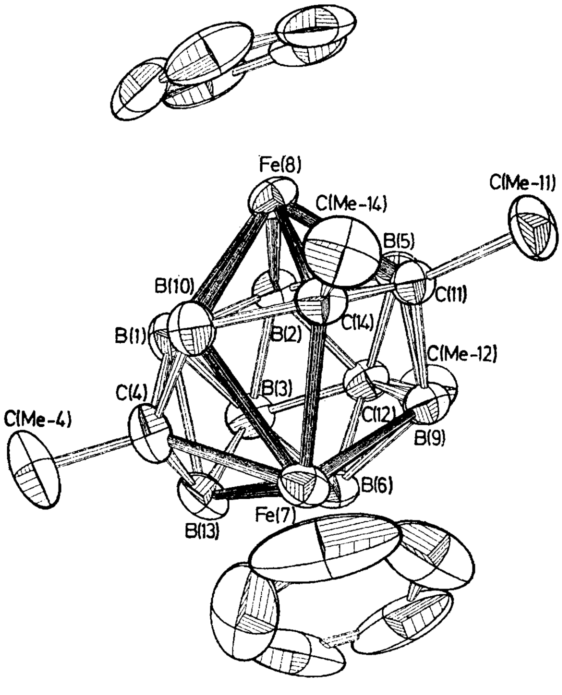

FIGURE 2. Structure of [$\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8$] (II).

The structures of (I) and (II) apparently reflect the mechanistic paths followed in their formation and do not represent the thermodynamically favoured geometry; at elevated temperatures both isomers rearrange to still other isomers whose structures are as yet undetermined. It is noteworthy that (I) and (II) represent a very rare example in metallocarbaborane chemistry of isomers having different gross polyhedral geometry.

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[3] W. J. Evans and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1974, 38.