A Mixed-metal Trimetallic Metallocarborane, $[\{(CO)_3Fe\}_2(\eta^5\text{-}C_5H_5)CoMe_2C_2B_4H_4]$

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Summary The reaction of $[1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoMe_2C_2B_4H_4]$ with $[Fe(CO)_5]$ produced $[\{(CO)_3Fe\}_2(\eta^5\text{-}C_5H_5)CoMe_2C_2B_4H_4]$, which is a nine-vertex polyhedral cage system containing the highest ratio of metal to nonmetal cage atoms among known metallocarboranes and the first example of a mixed-metal trimetallocarborane.

The preparation of metallocarboranes by the direct insertion of metal atoms into closed polyhedral systems without a prior cage-opening step is a highly versatile method, successfully applied to 7-,[1] 8-,[2] 9-[3] 10-,[1] and 11-[3,4] vertex carboranes by Stone and his co-workers, and to 5-, 6-, 7-, and 12-vertex carboranes by our group.[5,6] Products containing 1, 2, or 3 cage metal atoms have been obtained. We report here the application of this technique to the synthesis of a novel compound, $[\{(CO)_3Fe\}_2(\eta^5\text{-}C_5H_5)CoMe_2C_2B_4H_4]$ (I), which is the first example of a mixed-metal trimetallocarborane and contains the highest proportion of metal atoms of any known metallocarborane cage system. Compound (I), which incorporates the *C,C*-dimethyl derivative of the unknown $C_2B_4H_6{}^{6-}$ ligand (isoelectronic with $C_6H_6{}^{2-}$), is formally derived from the known *closo*-$Me_2C_2B_7H_7$ system by replacement of three BH units with electronically equivalent[7] $(\eta^5\text{-}C_5H_5)Co$ and $(CO)_3Fe$ groups.

The reaction of $[1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoMe_2C_2B_4H_4]$[8] with excess of $[Fe(CO)_5]$ in n-nonane at 125 °C *in vacuo* for 12·5 h produced (I) in 5% yield, isolated by column and thick layer chromatography. The only other product detected was $[Fe_3(CO)_{12}]$. The 32·1 MHz ^{11}B n.m.r. spectrum of (I) in $CDCl_3$ exhibited four doublets of equal area at $-107{\cdot}2(170)$, $-51{\cdot}2(156)$, $-19{\cdot}5(166)$, and $+1{\cdot}3(142)$ [chemical shifts, p.p.m. relative to $BF_3{\cdot}OEt_2$ (coupling constant, Hz)]. The 100 MHz ^1H n.m.r. spectrum contained singlet methyl resonances at τ 8·39 and 7·60 and a cyclopentadienyl peak at τ 5·19, with relative areas 3:3:5. On selective decoupling of the individual ^{11}B nuclei, the ^{1}H signals arising from B–H groups were observed as singlets of area 1 at τ $-1·91$, 2·92, 6·31, and 7·80. The mass spectrum contained a parent peak at *m/e* 506 and a pattern of relative intensities corresponding to the expected isotopic distribution; the successive loss of six carbonyl groups was also observed. The composition was confirmed by a high-resolution chemical ionization mass spectrum which exhibited an $M + 1$ peak at 506·9331 (calc. for $^{56}Fe_2{}^{59}Co^{12}C_{15}{}^{11}B_4{}^{16}O_6{}^{1}H_{16}{}^{+}$, 506·9349).

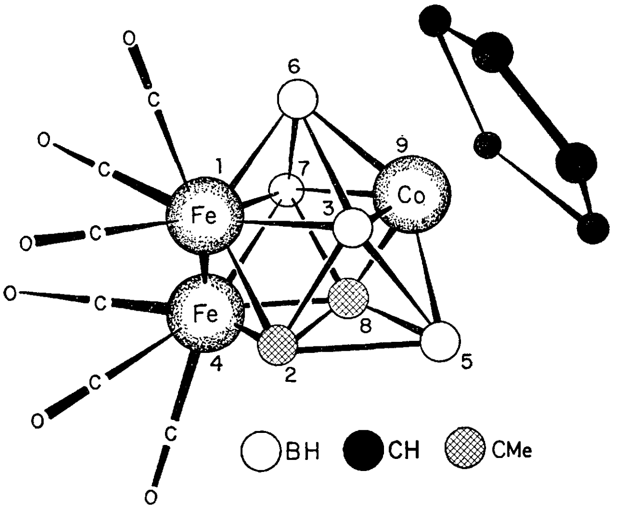

FIGURE. Proposed structure of $[\{(CO)_3Fe\}_2(\eta^5\text{-}C_5H_5)CoMe_2\text{-}C_2B_4H_4]$.

Compound (I) is cage-isoelectronic with numerous other 9-vertex carboranes and metallocarboranes containing 20 skeletal valence electrons, *e.g.*, $[(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7]$,[6,9] and is assumed to adopt a similar gross tricapped trigonal prismatic geometry. A possible structure, depicted in the Figure, is based on the assumptions that (i) the cage carbon atoms remain adjacent as in the precursor species (the reaction temperature is considered insufficient to effect carbon migration); (ii) the extremely low-field ^{11}B n.m.r. peak at -107 p.p.m. arises from a 4-co-ordinate BH group 'between' two metal atoms as in $[1,8,5,6\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7]$[9]† (confirmed in an *X*-ray study[10]) and $[2,4,10\text{-}(\eta^5\text{-}C_5H_5)_2NiCoCB_7H_8]$,[11] whose analogous BH groups in each case exhibit ^{11}B resonances at -116 p.p.m.; and (iii) the ^{11}B n.m.r. peak at -51 p.p.m. arises from a 4-co-ordinate BH group adjacent to one metal atom.[9,12] If (ii) and (iii) are correct, the third metal atom must occupy a 4-co-ordinate vertex; precedence for iron in a low-co-ordinate site in a 9-vertex metallocarborane is found in the proposed structure of $[(\eta^5\text{-}C_5H_5)FeC_2B_6H_8]$.[12] The introduction of $Fe(CO)_3$ groups into adjacent four- and five-co-ordinate vertices in a polyhedron was noted previously in the preparation of $[1,2,3,5\text{-}\{(CO)_3Fe\}_2C_2B_3H_5]$ from $[1,2,4\text{-}(CO)_3\text{-}FeC_2B_3H_5]$ and $[Fe(CO)_5]$.[6] However, other possible arrangements for (I) cannot be excluded pending an *X*-ray investigation.

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