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Synthesis of Cobaltaferracarboranes: Two Methods

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Summary The addition of $Na^+C_5H_5^-$ and $FeCl_2$ to $(C_5H_5)Co^{III}(C_2B_7H_9)$ previously reduced with sodium naphthalide formed the heterobimetallocarborane, $(C_5H_5)Co^{III}(C_2B_7H_9)Fe^{III}(C_5H_5)$; a larger homologue of this cobaltaferracarborane, $(C_5H_5)Co^{III}(C_2B_9H_{11})Fe^{III}(C_5H_5)$, was prepared by the reaction of $(C_5H_5)Co^{III}(C_2B_{10}H_{12})$ with ethanolic potassium hydroxide in the presence of $FeCl_2$ and C_5H_6.

BIMETALLOCARBORANES containing two cobalt atoms have been prepared in this laboratory by the application of the polyhedral expansion reaction to monometallocarboranes.[1,2] This reaction has recently been extended to give a diamagnetic, monocarbon bimetallocarborane containing cobalt and nickel.[3] We now report two synthetic routes leading to a new class of metallocarboranes formally containing one diamagnetic and one paramagnetic metal centre. In each case, the product is a cobaltaferracarborane having the general formula $(C_5H_5)Co^{III}(C_2B_nH_{n+2})Fe^{III}(C_5H_5)$. One synthesis is a further extension of the polyhedral expansion reaction while the second is derived from the polyhedral contraction reaction.[4,5]

The reduction of 2,1,6-$(C_5H_5)Co^{III}(C_2B_7H_9)$[6] with sodium (3 equiv.) in the presence of naphthalene in tetrahydrofuran followed by the addition of an excess of $Na^+C_5H_5^-$ and $FeCl_2$ formed compound (I), a reddish-brown species isolated by column chromatography in 40% yield. The cutoff in the mass spectrum was observed at *m/e* 355 corresponding to the $^{59}Co^{56}Fe^{12}C_{12}{}^{11}B_7{}^1H_{19}^+$ ion and the isotopic distribution in the parent envelope agreed within 5% with that calculated for (I) as has been observed for cobaltacarboranes.[4] Elemental analysis was consistent with the formulation of $(C_5H_5)Co(C_2B_7H_9)Fe(C_5H_5)$ for (I).

Reduction of (I) in acetonitrile with sodium borohydride formed a reddish diamagnetic species which exhibited an 80·5 MHz ^{11}B n.m.r. spectrum containing an unsymmetrical doublet of intensity 3 at −8·1 p.p.m. and two overlapping doublets each of intensity 2 at + 8·5 and +113 p.p.m. [chemical shifts, p.p.m. relative to $BF_3{\cdot}O(C_2H_5)_2$, J_{B-H} 140 ± 20 Hz]. The octadecahedral structure, shown in Figure 1, is proposed for (I). Consistent with this structure

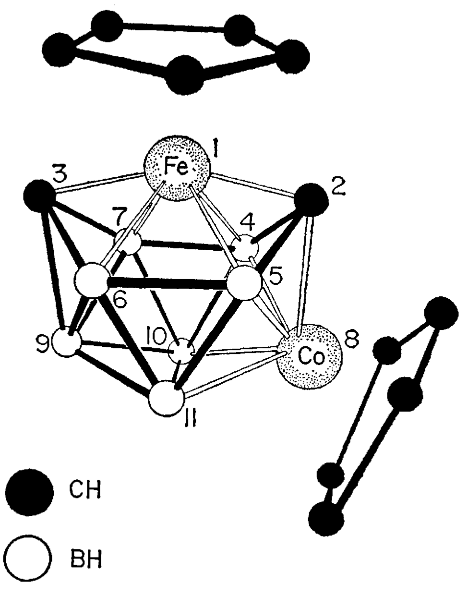

FIGURE 1. The suggested structure of $(C_5H_5)Co^{III}(C_2B_7H_9)Fe^{III}(C_5H_5)$.

is the paramagnetic ^{11}B n.m.r. spectrum comprised of a broad area 4 resonance ($w_{1/2}$ = 5000 Hz) and an area 3 resonance ($w_{1/2}$ = 650 Hz)[7,8] and μ_{eff} = 1·82 B.M., similar to that of 1,2,3-$(C_5H_5)Fe(C_2B_8H_{10})$ (1·60 B.M.)[8] rather than that of 1,2,3-$(C_5H_5)Fe(C_2B_9H_{11})$ (2·30 B.M.).[9]

Treatment of $(C_5H_5)Co^{III}(6,7\text{-}C_2B_{10}H_{12})$[10] with ethanolic potassium hydroxide in the presence of excess $FeCl_2$ and C_5H_6 gave compound (II), a brownish-purple species formulated as $(C_5H_5)Co^{III}(C_2B_9H_{11})Fe^{III}(C_5H_5)$. The mass spectrum of (II) showed a cutoff at *m/e* 379 corresponding to the $^{59}Co^{56}Fe^{12}C_{12}{}^{11}B_9{}^{1}H_{21}{}^{+}$ ion, and the elemental analysis was consistent with this formulation. The magnetic moment, μ_{eff} = 1·88 B.M.

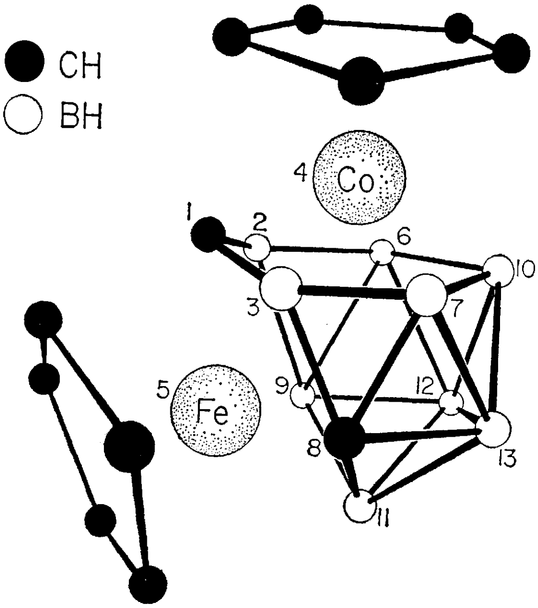

FIGURE 2. The proposed structure of $(C_5H_5)Co^{III}(C_2B_9H_{11})Fe^{III}\text{-}(C_5H_5)$.

Reduction of (II) with sodium borohydride gave the green diamagnetic complex $[(C_5H_5)Co^{III}(C_2B_9H_{11})Fe^{II}(C_5H_5)]^{-1}$; ^1H n.m.r. τ (CD_3CN) 5·35 and 5·99, sharp singlets assigned to the two sets of cyclopentadienyl protons. The broad singlets due to the carborane C–H units were not observed. The 80.5 MHz ^{11}B n.m.r. spectrum of the reduced species, also in CD_3CN, contained doublets of area ratios 1:1:2:1:1:1:1:1 at −11·8(128), −6·7(128), −3·5(118), −2·5 (131), +4·5(122), +4·8(125), +11·2(131), and +14.2(144).

The structure proposed for (II) is shown in Figure 2. The gross geometry is identical to that established for a 13-vertex metallocarborane.[10,11] The removal of a formal BH^{2+} unit from the high co-ordinate position adjacent to both carbon atoms in $(C_5H_5)Co^{III}(6,7\text{-}C_2B_{10}H_{12})$ *via* the polyhedral contraction mechanism followed by the insertion of a formal $(C_5H_5)Fe^{2+}$ unit generates the 13-vertex, polyhedral structure proposed for (II). Since the molecule is asymmetric, the doublet of area 2 in the ^{11}B n.m.r. spectrum must necessarily be due to the coincidental overlap of two resonances of area 1 to be consistent with a static structure.

These results constitute an interesting extension of the field of heterobimetallocarboranes. The magnetic, spectral, and electrical consequences of having both a diamagnetic and a paramagnetic metal centre within a metallocarborane environment are currently under investigation in this laboratory. Furthermore, the modified polyhedral contraction reaction, which we will henceforth refer to as the "polyhedral subrogation" reaction, potentially represents a new general synthesis of polymetallocarboranes which will complement the existing polyhedral expansion reaction. We now have at our disposal two different approaches by which we may synthesize bimetallocarboranes.

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