Synthesis of Fourteen Vertex Metallocarboranes by Polyhedral Expansion

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Summary The first fourteen vertex metallocarboranes of formula $(C_5H_5)_2Co_2C_2B_{10}H_{12}$ have been synthesized from 4,1,12- and 4,1,8-$C_5H_5CoC_2B_{10}H_{12}$.

THE reaction involving the reduction of a carborane[1] or metallocarborane[2] followed by the addition of sodium cyclopentadienide and a transition metal has allowed the synthesis of a wide variety of new polyhedral metallocarboranes containing one or two additional metal vertices. One of the aspects of this polyhedral expansion reaction is that the synthesis of increasingly larger polyhedra is possible. Hence, the polyhedral expansion of 1,2-$C_2B_{10}H_{12}$ resulted in the unprecedented thirteen vertex supraicosahedral species $C_5H_5MC_2B_{10}H_{12}$.[3] We report here the synthesis of an even larger type of *closo*-polyhedral heteroborane which contains fourteen vertices.

The reduction of the red-orange[3] isomer of $C_5H_5CoC_2B_{10}H_{12}$ was readily accomplished with 3 equiv. of sodium in the presence of naphthalene in tetrahydrofuran. Addition of NaC_5H_5 and $CoCl_2$ followed by air-oxidation resulted in a mixture of products. The primary bimetallic species separated by liquid chromatography was a purple compound (I). The cutoff in the mass spectrum was observed at *m/e* 394 corresponding to M^+ $^{11}B_{10}{}^{12}C_{12}{}^{1}H_{22}{}^{59}Co_2{}^+$. Elemental analysis was in agreement with the mass spectral data and (I) was formulated as $(C_5H_5)_2Co_2C_2B_{10}H_{12}$. The cyclic voltammogram of (I) was similar to that of other bimetallocarboranes containing a reversible oxidation wave at +1·17 V and a reversible reduction wave at −1·10 V. The 80·5 MHz ^{11}B n.m.r. spectrum in dimethylformamide comprised four resonances of relative intensity 2:4:2:2 at

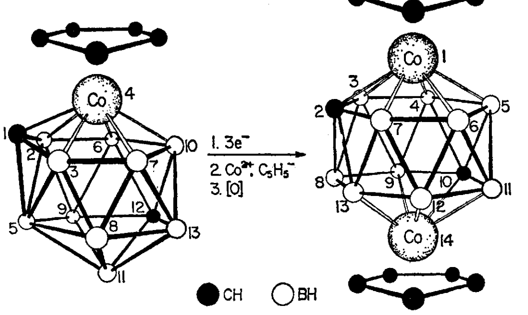

FIGURE. The formation and proposed structure of $(C_5H_5)_2$-$Co_2C_2B_{10}H_{12}$, (I), from the red-orange $X[4,1,12\text{-}C_5H_5CoC_2B_{10}H_{12}]$. An idealized view with planar six-membered rings is shown although distortions from this geometry as in $C_5H_5CoC_2B_{10}H_{12}$ are also possible for (I).

$+5{\cdot}2$, $+12{\cdot}3$, $+15{\cdot}1$, and $+17{\cdot}9$ p.p.m. (chemical shift, relative to $BF_3{\cdot}OEt_2$; d, $J_{B-H} = 140 \pm 20$ Hz). A single cyclopentadienyl signal at τ 5·08 was observed in the 60 MHz ^1H n.m.r. spectrum of (I).

The similarity of the physical properties of (I) to other closo bimetallocarboranes as well as the high molecular symmetry suggested by the n.m.r. data indicated a fourteen vertex *closo*-polyhedral structure for (I). A geometry comprised of four planes containing 1,6,6, and 1 atoms is proposed (Figure). Although other fourteen vertex geometries are possible, the proposed structure incorporates co-ordination numbers for the constituent atoms more consistent with those observed in metallocarboranes and is the obvious bimetallic extension of the thirteen vertex structure of $C_5H_5CoC_2B_{10}H_{12}$ (Figure). Assuming coincidental overlap of two area 2 resonances at $+12{\cdot}3$ p.p.m. in the ^{11}B n.m.r. spectrum, several isomeric structures are possible. A likely structure for (I) is X[1,14,2,10-$(C_5H_5)_2$-$Co_2C_2B_{10}H_{12}$] (Figure), in which the cobalt atoms are in the high co-ordinate positions and the relative carbon atom positions are the same as proposed for the monometallic precursor.[3]

The room temperature polyhedral expansion of the orange isomer of $C_5H_5CoC_2B_{10}H_{12}$, for which the structure X[4,1,8-$C_5H_5CoC_2B_{10}H_{12}$] has been proposed,[3] afforded a second isomer of $(C_5H_5)_2Co_2C_2B_{10}H_{12}$, (II). The formula of the red-brown (II) was confirmed by an exact mass measurement. The 80·5 MHz ^{11}B n.m.r. spectrum in CH_2Cl_2, comprised five resonances of equal intensity, at $-3{\cdot}6$, $+2{\cdot}0$, $+4{\cdot}8$, $+14{\cdot}7$, and $+29{\cdot}8$ p.p.m. relative to $BF_3{\cdot}OEt$, and the ^1H n.m.r. spectrum in $(CD_3)_2CO$, containing a single cyclopentadienyl signal at τ 4·8, suggested the symmetry of (II) was similar to that of (I). The structure X[1,14,2,9-$(C_5H_5)_2Co_2C_2B_{10}H_{12}$] is proposed for (II) using the same reasoning employed to assign the structure of (I). The structures of (I) and (II) differ by one carbon atom position in exactly the same manner as the monometallic precursors. An additional piece of datum concerning the structure of (II) is the observation that the boron resonance at $+2{\cdot}0$ p.p.m. has a somewhat smaller line width, a spectral characteristic generally observed for boron atoms located between two carbon atoms. Two such boron atoms are present in the proposed structure of (II) at the equivalent positions 3 and 8 which is additional evidence supporting the X[1,14,2,9-$(C_5H_5)Co_2C_2B_{10}H_{12}$] structure.

The fact that metallocarboranes undergo polyhedral expansion as readily as carboranes appears to be a chemical consequence of the electronic similarity of $C_5H_5Co^{2+}$ and BH^{2+}.[5] That such large supraicosahedral metallocarborane polyhedra can be synthesized is probably a consequence of a difference between the two units, *viz.* the greater stability of the $C_5H_5Co^{2+}$ vertex in high co-ordinate positions.

We thank Dr. R. J. Wiersema for measuring the ^{11}B n.m.r. spectra. This research was supported by the Army Research Office (Durham).

(*Received*, *24th September* 1973; *Com.* 1333.)

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