The Direct Synthesis of a Bimetallic Carborane Complex by Polyhedral Expansion of a Monometallocarborane

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Summary Addition of $Na^+C_5H_5^-$ and $CoCl_2$ to $B_8C_2H_{10}$-CoC_5H_5 previously reduced with $Na^+C_{10}H_8^-$ forms a new bimetallic carborane complex through a new extension of the polyhedral expansion reaction.

We have reported[1-3] the synthesis of several metallocarboranes from *closo*-carboranes by the reaction sequence (1).

$$B_nC_2H_{n+2} \xrightarrow[C_4H_8O]{2Na^+C_{10}H_8^-} \xrightarrow[CoCl_2]{Na^+C_5H_5^-} B_nC_2H_{n+2}CoC_5H_5 \quad (1)$$

$n = 6, 8$, and 10

The transition metal atom and carborane moiety in the product complete a polyhedral structure one atom larger than the polyhedron of the starting carborane. We now report that this 'polyhedral expansion'[2] is not restricted to *closo*-carboranes, and can be applied to *closo*-metallocarboranes as well. For example the reaction can be used to expand an 11-vertex polyhedral monometallocarborane,[2] $B_8C_2H_{10}CoC_5H_5$, to a new bimetallic species $C_5H_5CoB_8C_2$-$H_{10}CoC_5H_5$, (I), in which the cobalt and carborane atoms probably comprise a 12-atom polyhedron.

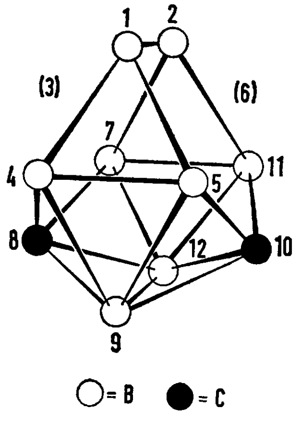

Figure 1. *The skeletal structure of the* (3,6)-8,10-*dicarbacanastide ion.*

Treatment of $B_8C_2H_{10}CoC_5H_5$[2] in tetrahydrofuran at 50° with three equiv. of sodium naphthalide followed by the addition of a four-fold excess of $Na^+C_5H_5^-$ and excess $CoCl_2$ afforded a mixture of products. The compound (I) was isolated by successive column and preparative t.l.c. and recrystallized from CH_2Cl_2 in 26% yield (based on $B_8C_2H_{10}$-CoC_5H_5 consumed), m.p. 275—277. Elemental analysis was in agreement with the formula $B_8C_2H_{10}(CoC_5H_5)_2$; *m/e* 370 corresponded to the $^{59}Co_2{}^{12}C_{12}{}^{11}B_8{}^1H_{20}{}^+$ ion. The isotopic distribution around the most intense peak, observed at *m/e* 369, was consistent with that expected for (I). The electronic spectrum measured in acetonitrile, comprised [λ_{max} 233 (ϵ 21,200), 265 (ϵ 11,500), 308 (ϵ 17,300), 415 (sh) (920), 610 nm (890)]. The 80·5 MHz ^{11}B n.m.r. spectrum, obtained in $(CD_3)_2CO$ using Fourier transform techniques, due to the limited solubility of (I), contained doublets of relative area 1:2:1 at −4·7 (110), +4·3 (150) and +13·3 (130) [chemical shift, p.p.m. relative to $BF_3{\cdot}(OC_2H_5)_2$ (coupling constant, Hz)]. The 251 MHz ^1H n.m.r. spectrum consisted of a sharp singlet at τ 4·08 which was assigned to the cyclopentadienyl protons. The limited solubility of the sample precluded the observation of a carborane C–H resonance.

The 1:2:1 pattern of doublets observed in the ^{11}B n.m.r, spectrum of (I) is consistent with the geometry of the previously established (3,6)-dicarbacanastide structure[4] (Figure 1) in which the carbon atoms could be located at positions 1, 2; 8, 10 or 9, 12. Examination of the ^{11}B n.m.r. spectra of $B_9C_2H_{11}CoB_8C_2H_{10}CoB_9C_2H_{11}{}^{2-}$ (II)[4] and B_9C_2-$H_{11}CoB_8C_2H_{10}CoB_8C_2H_{10}CoB_9C_2H_{11}{}^{3-}$ (III),[5] compounds in which *X*-ray structure determinations[5,6] have confirmed a 1,2-dicarbacanastide structure for the $B_8C_2H_{10}{}^{4-}$ ligand. and the ^{11}B n.m.r. spectrum of $C_5H_5CoB_8C_2H_{10}CoB_8C_2H_{10}$-$CoC_5H_5{}^-$ (IV), recently synthesized in a manner similar to that employed for (II) and (III),[7] indicates that (I) does not contain carbon atoms at the 1 and 2 positions. The ^{11}B n.m.r. spectrum of the $B_8C_2H_{10}{}^{4-}$ ion in (IV) consists of a doublet of area 2 at +9·2 p.p.m., overlapping doublets of area 2 at +2·4 p.p.m., and two doublets of area 1 at −16·1 and −21·1 p.p.m. relative to $BF_3{\cdot}O(C_2H_5)_2$. The low field doublets of area 1 can be assigned to the 8, 10 boron atoms which are rendered nonequivalent by the C_5H_5Co group on one face and the $CoB_8C_2H_{10}CoC_5H_5$ group on the other face of the $B_8C_2H_{10}{}^{-4}$ ligand. Similar low field resonances can be assigned to the 8, 10 boron atoms in (II) and (III). A doublet of area 2 occurs at −20·8 p.p.m. in the ^{11}B n.m.r. spectrum of (II) which contains equivalent 8, 10 boron atoms

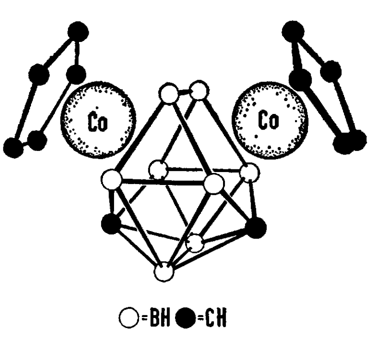

Figure 2. *A possible structure for* $C_5H_5CoB_8C_2H_{10}CoC_5H_5$.

in the $B_8C_2H_{10}^{4-}$ ion. In the spectrum of (III), the non-equivalent 8, 10 boron atoms appear as doublets of area 1 at −20·0 and −17·6 p.p.m. Since the spectrum of (I) contains no doublets within 11 p.p.m. of these low field resonances, the presence of the 1,2-dicarbacanastide structure is unlikely. Also unlikely is the structure in which the carbon atoms are at the 9, 12 positions, as this would require the carbon atoms of the starting material to move together as nearest neighbours in the product. This type of movement is not to be expected in view of the rearrangement studies reported with $B_9C_2H_{11}CoC_5H_5$.[8] Therefore, of the possible (3,6)-dicarbacanastide structures we consider the 8, 10 isomer the most probable (Figure 2). An alternate structure containing a nearest neighbour cobalt–cobalt interaction is also consistent with these data and cannot be disregarded at this time. Using the numbering system in Figure 1, such a structure for (I) could accommodate cobalt atoms at the 1, 2 positions and carbon atoms at the (3), (6) positions. This structure would be the first example of a metallocarborane containing a polyhedral metal–metal interaction.

The results of the extension of the polyhedral expansion reaction to other *closo*-carboranes and metallocarboranes will be reported in a forthcoming paper. We presently are examining the thermal rearrangements of (I) which should lead to other icosahedral structures containing cobalt atoms at the (3), (6) or 1, 2 positions as well as icosahedra with cobalt atoms at the (3), 10 positions.

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