Synthesis of a Trimetallic Metallocarborane by Polyhedral Expansion

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Summary An icosahedral metallocarborane containing three transition metal vertices has been synthesized from 2,1,6-$C_5H_5CoC_2B_7H_9$ by polyhedral expansion.

THE general reaction involving the reduction of a carborane with subsequent[1] or concomitant[2] complexation with a transition metal to produce a metallocarborane has been established. In our studies to determine the generality of this polyhedral expansion as applied to metallocarboranes[3] [see reaction (1)] we have synthesized the first metallocarborane in which three transition metals occupy vertices in a single icosahedron.

$$C_5H_5MC_2B_nH_{n+2} \xrightarrow[C_{10}H_8]{3Na} \xrightarrow[MCl_2]{NaC_5H_5} (C_5H_5M)_2C_2B_nH_{n+2} \quad (1)$$

Reduction of 2,1,6-$C_5H_5CoC_2B_7H_9$†[4] was effected with 3 equiv. of sodium in the presence of naphthalene in THF. Following the addition of NaC_5H_5 and $CoCl_2$, the product mixture was separated by column chromatography on silica gel. In addition to the expected product, $(C_5H_5)_2Co_2C_2B_7H_9$, (I), m.p. 265–266°, formed in 22% yield, a green compound, (II), m.p. 237–240° (decomp.) was isolated. The mass-spectral cut-off of (II) at *m/e* 482, corresponded to the $^{11}B_7{}^{12}C_{17}{}^{1}H_{24}{}^{59}Co_3{}^{+}$ ion. The isotopic distribution in the parent envelope as well as elemental analysis was consistent with the formulation $(C_5H_5)_3Co_3C_2B_7H_9$. The electronic spectrum measured in acetonitrile was λ_{max} 248 (log ϵ 4·40), 294 (4·55), 414 (3·38), 484 (3·12), and 648 nm (3·36). The 80·5 MHz ^{11}B n.m.r. spectrum of (II) in $CDCl_3$ exhibited doublets of relative area 2:2:2:1 at −12·7, −8·4, +5·8, and +22·3 [chemical shift, relative to $BF_3{\cdot}O(Et_2)$, J_{B-H} 140 ± 20 Hz]. Two sharp singlets assigned to cyclopentadienyl protons were observed at τ 4·5 and 5·1 in a ratio of 2:1 in the 60 MHz ^1H n.m.r. spectrum of (II) in $CDCl_3$.

Although stable as a pure solid, (II) readily decomposed in solution or on silica gel over a period of days to the red brown compound (I). Loss of a cobalt vertex from the icosahedral (II) presumably forms a *nido* species which closes to the octadecahedral (I). Simple closure without extensive atomic rearrangement might be expected under these mild conditions and hence the structures of (I) and (II) may be closely related. We suggest the atomic arrangement shown in the Figure based on the following data for (I).

The 80·5 MHz ^{11}B n.m.r. spectrum of (I) in CH_2Cl_2 comprises doublets of relative area 1:2:2:2 at −21·8, −7·1, +0·4, and +1·2 relative to $BF_3{\cdot}OEt_2$. The 251 MHz ^1H n.m.r. of (I) in CD_3CN consisted of two sharp cyclopentadienyl resonances of equal intensity at τ 4·6 and 4·9 as well as two broader resonances at 3·6 and 1·7 assigned to carborane CH protons. On the assumption that one of the cobalt atoms is in the high-co-ordinate position 1, the absence of any low field resonances in the ^{11}B n.m.r. spectrum suggests that the low-co-ordinate positions 2 and 3 are not occupied by boron atoms.[1] Two structures are consistent with these observations: 1,8,2,3- and 1,2,3,8-$(C_5H_5)_2Co_2C_2B_7H_9$. We favour the former structure shown in the Figure in which carbon rather than cobalt occupies the low-co-ordinate position.

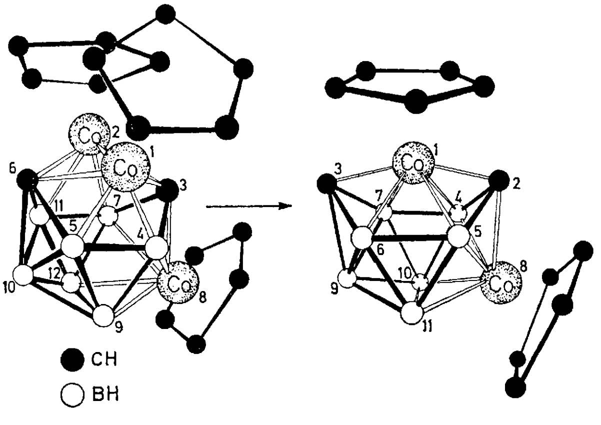

FIGURE. Decomposition of the suggested 1,2,8,3,6-$(C_5H_5)_3Co_3C_2B_7H_9$ to 1,8,2,3-$(C_5H_5)_2CoC_2B_7H_9$.

The synthesis of a trimetallic metallocarborane by polyhedral expansion apparently brings the fields of transition metal cluster chemistry and polyhedral borane chemistry one step closer. Indeed, the similarities of these areas based on electronic considerations have been pointed out.[5] However, the decomposition reactions described above in which icosahedral species decompose to the generally less stable[6] octadecahedral geometry suggest that care

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† Numbers preceding formulae refer in order to the positions of the heteroatoms as written in the formulae.

must be used in extending these ideas to polymetallics. Additional factors affecting stability are evidently extant in borane polyhedra containing several metal atoms especially when metal–metal interactions are involved. While it is perhaps too early to identify these factors, the extension of the polyhedral expansion reaction to other systems should allow the accumulation of more data on polymetallic species such that these requirements can be better defined.

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