Metal Atom Synthesis of Metalloborane Clusters

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Summary The reaction of cobalt atoms with pentaborane-(9) and cyclopentadiene has been studied and found to give a variety of new metalloborane clusters, of which two examples, $B_5H_5Co_3(\eta\text{-}C_5H_5)_3$ and cyclopentyl-$B_5H_4Co_3(\eta\text{-}C_5H_5)_3$, are presented.

The use of the metal atom technique[1] for the synthesis of organometallic complexes has allowed the synthesis of a wide variety of compounds which have either been previously unknown or difficult to obtain by using more conventional methods. Recent studies in this laboratory have met with similar success when this technique was applied to the synthesis of metalloborane clusters, and we now report studies of the reaction of cobalt atoms with pentaborane(9) and cyclopentadiene. Miller and Grimes had previously studied[2,3] the reaction of NaC_5H_5, NaB_5H_8, and $CoCl_2$ and obtained a number of cobaltaborane clusters containing predominantly 3- and 4-boron units. In contrast to these results, we find that, using the metal atom technique, we obtain not only the previously discovered clusters, but we also produce a series of new complexes, many of which contain 5-boron fragments.

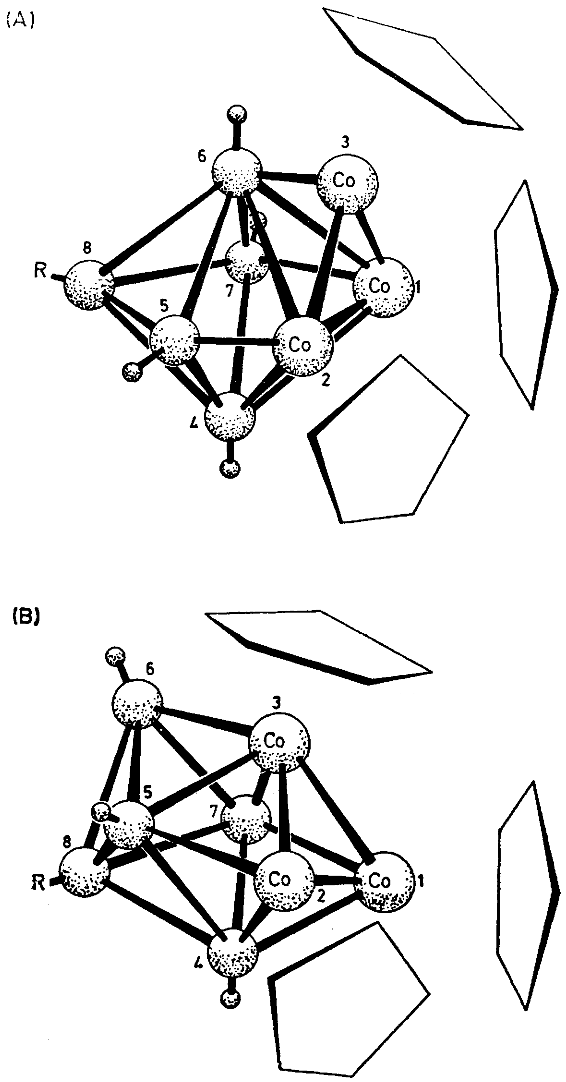

Figure. Possible capped (A) and dodecahedral (B) structures for compound (I) (R = H) and compound (II) (R = cyclopentyl).

Cobalt atoms (0·6 g) were condensed with pentaborane(9) and cyclopentadiene at −196 °C in an approximate 1 : 50 : 50 mole ratio using a standard high temperature reactor.[1] After the condensation was completed, the reactor was allowed to warm to room temperature, the volatile products were removed *in vacuo*, and the residue was extracted with tetrahydrofuran. Separation of the residue by preparative t.l.c. resulted in the isolation of several new five-boron cobaltaborane clusters; we present examples of two of these: $B_5H_5Co_3(\eta\text{-}C_5H_5)_3$ (I) and cyclopentyl-$B_5H_4Co_3(\eta\text{-}C_5H_5)_3$ (II).

Compound (I) is a dark green, air-stable cluster, which from its mass spectrum and elemental analysis has the formula $B_5C_{15}Co_3H_{20}$. The 32·1 MHz ^{11}B n.m.r. spectrum of (I) in CD_2Cl_2 consists of four doublets in the intensity ratio of 1 : 1 : 2 : 1 at −136·8 (*J* 147), −124·4 (*J* 141), −104·0 (*J* 154), and +12·8 p.p.m. (*J* 134 Hz) relative to external BF_3–OEt_2. The 100 MHz ^1H n.m.r. spectrum shows two singlets at δ 4·61 and 4·54 in a 1 : 2 intensity ratio, which may be assigned to non-equivalent cyclopentadienyl groups.

Compound (I) is an example of a 2*n*-electron system (8 framework atoms and 16 electrons) and according to electron counting rules[4] would be predicted to adopt a capped pentagonal bipyramid structure. One possible capped structure which is consistent with the spectroscopic data is shown in the Figure (A); however, an alternate *closo* dodecahedral structure as shown in the Figure (B) cannot be ruled out by any of the data. Grimes and Miller[3] had previously favoured such a dodecahedral structure for another 2*n*-electron, 8-vertex molecule, $B_4H_4Co_4(\eta\text{-}C_5H_5)_4$. We are currently undertaking a crystallographic investigation of compound (I) to confirm its structure.

The spectroscopic data for the yellow-green compound (II) are consistent with its formulation as a cyclopentyl-substituted derivative of (I). The mass spectrum shows a cut-off at *m/e* 500 corresponding to the formula $^{11}B_5{}^{12}C_{20}$-$Co_3{}^1H_{28}$ and the ^{11}B n.m.r. spectrum in CD_2Cl_2 shows three doublets of intensity ratio 1 : 1 : 2 at −137·4 (*J* 138), −123·4 (*J* 137), and −101·2 p.p.m. (*J* 132 Hz), and a singlet with an intensity of 1 at −3·3 p.p.m. Although an unequivocal assignment of the ^{11}B resonance in compounds (I) and (II) is not possible, it seems reasonable to assign the upfield resonance in both compounds to B-8, since this is the only boron not attached to a cobalt. The ^1H n.m.r. spectrum of (II) shows the expected cyclopentadienyl resonances at δ 4·66 and 4·55 of intensity 5 and 10, as well as a multiplet with the most intense peak at δ 1·21 of intensity 9 corresponding to the cyclopentyl group.

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