Isomeric *Hypho* Borane Structures $B_5H_9.L$ [L = $(Ph_2P)_2CH_2$, $(Ph_2PCH_2)_2$, or $(Me_2NCH_2)_2$]; *X*-Ray Crystal and Molecular Structures

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Summary The *X*-ray crystal structures of the 1 : 1 complexes, containing *hypho* boron polyhedra, derived from pentaborane(9) and the ligands bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), and tetramethylethylenediamine (tmed) are reported; the dppm and dppe structures both show the phosphorus atoms bridging the apical and basal atoms of a flattened pyramidal B_5 framework (with rearrangement of the hydrogen atoms), the tmed complex differing markedly, with the ligand chelating one of the originally basal boron atoms, which becomes singly bonded to the apical boron atom and is separated from the remaining basal atoms by typical non-bonded contact distances.

The boranes and carbaboranes form *closo-*, *nido-*, *arachno-*, and *hypho*-derivatives,[1] and a knowledge of all these classes is required before their co-operative role in rearrangement reactions of polyhedral frameworks, or as reaction intermediates can be fully rationalised.[2] Unfortunately, very few examples of the *hypho*-class are known. Such systems should possess ($n + 4$) skeletal electron pairs with the framework atoms occupying n vertices of an ($n + 3$) vertex polyhedron, and some support for this proposal has come from the crystal structures of the adducts $B_5H_9 \cdot 2L$ and $B_6H_{10} \cdot 2L$ (L = PMe_3).[3,4] We now report the properties and crystal structures of three further derivatives which are isoelectronic with the hypothetical *hypho*-$B_5H_{11}^{2-}$ ion, *viz.* $B_5H_9 \cdot L$ [L = dppm, (I); dppe, (II); and tmed, (III)†] and which show significant differences, illustrating the diversity possible within such a related series.

The colourless adducts (I) (m.p. 185—187 °C), and (II) (m.p. 159—160 °C) were prepared by stirring equimolar quantities of B_5H_9 and the ligand in tetrahydrofuran

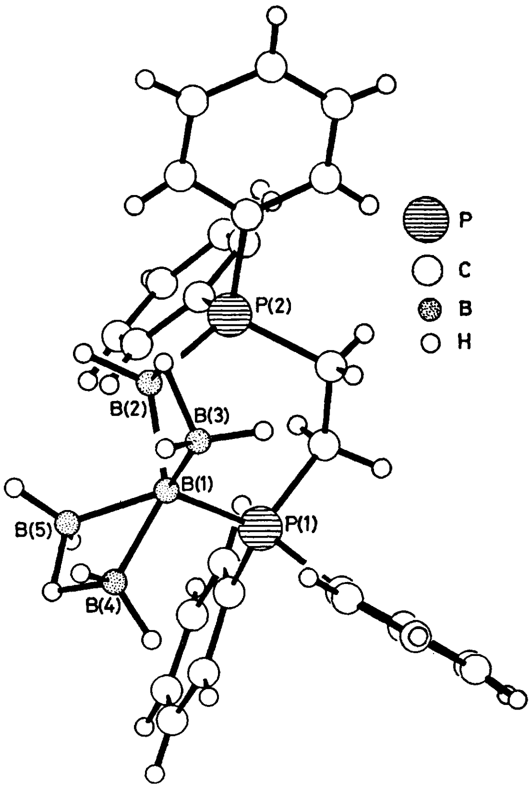

Figure 1. General view of molecule of (II). Distances P(1)–B(1) and P(2)–B(2) are 1·953(4) and 1·939(4) Å, respectively.

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† dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, tmed = tetramethylethylenediamine.

(THF) at 25 °C for 72 h; variations in the conditions led to high-melting polymeric products. Both adducts are stable in air, and only slowly hydrolysed by hot water or acid, which is remarkable for B_5H_9 derivatives. However, the anions, $B_5H_8{\cdot}L^-$ (L = dppm or dppe), are similar to $B_5H_8^-$ itself, and are readily hydrolysed. The adduct (III), obtained by condensing an excess of B_5H_9 on the ligand, was air-sensitive and could only be stored or recrystallised without decomposition if an excess of ligand was present.

Crystal data: (I), $C_{25}H_{31}B_5P_2{\cdot}\frac{1}{2}C_4H_4O$, M 481·5, orthorhombic, $a = 7{\cdot}931(4)$, $b = 16{\cdot}816(5)$, $c = 23{\cdot}271(8)$ Å, $U = 3105(2)$ Å^3, $D_c = 1{\cdot}03$ g cm^{-3}, $Z = 4$, space group $P2_12_12_1$. (II), $C_{26}H_{33}B_5P_2$, M 461·6, orthorhombic, $a = 14{\cdot}297(4)$, $b = 16{\cdot}492(6)$, $c = 22{\cdot}280(9)$ Å, $U = 5243(3)$ Å^3, $D_c = 1{\cdot}17$ g cm^{-3}, $Z = 8$, space group $Pbca$. (III), $C_6H_{25}B_5N_2$, M 179·3, orthorhombic, $a = 12{\cdot}940(2)$, $b = 12{\cdot}911(3)$, $c = 15{\cdot}046(2)$ Å, $U = 2513{\cdot}9(8)$ Å^3, $D_c = 0{\cdot}95$ g cm^{-3}, $Z = 8$ (2 independent molecules), space group $P2_12_12_1$.

Three-dimentional X-ray data for all three compounds were collected on a Syntex $P2_1$ diffractometer using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). 1850, 2643, and 1200 independent reflections with $I/\sigma(I) > 3{\cdot}0$ were collected for compounds (I), (II), and (III), respectively. All three structures were solved using the direct methods programs NORMAL and MULTAN. Block diagonal least-squares refinement has produced R factors of 0·070 (I), 0·047 (II), and 0·062 (III), using anisotropic temperature factors for all non-hydrogen atoms except for the disordered THF solvent in (I) and for one of the tmed ligands in (III) which exists in two different conformations.‡

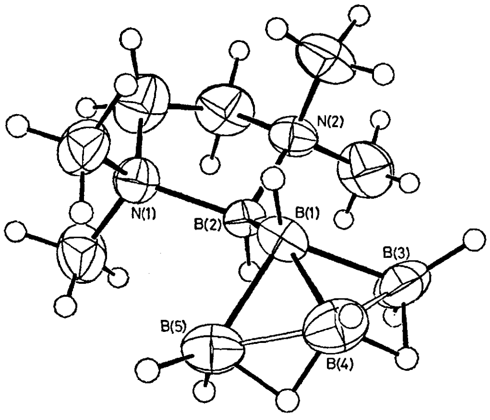
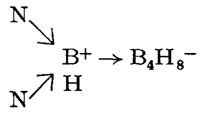


Figure 2. ORTEP view of the ordered molecule of (III). Some distances are: N(1)–B(2), 1·684(9); N(2)–B(2), 1·663(9); B(1)–B(2), 1·718(10); B(1)–B(3), 1·823(12); B(1)–B(4), 1·686(12); and B(1)–B(5), 1·808(12) Å. The non-bonded distances B(2) · · · B(3) and B(2) · · · B(5) are 2·728(12) and 2·718(11) Å, respectively.

In both B_5H_9·dppm (I) and B_5H_9·dppe (II) (Figure 1), the B_5H_9 species has become a shallow pyramid with major rearrangements of the hydrogen atoms; the hydrogen at the apex has moved to the base where three BH_2 groups and two symmetrical B–H–B bridges are found. The phosphorus atoms bridge the apical and basal positions, and the angle between opposite triangular B_3 faces is 130·4° (I) and 126·5° (II) compared with 90—91° in B_5H_9. With 9 electron pairs to accommodate in the *hypho*-B_5 skeleton, the boron atoms should occupy all but three vertices of an 8-vertex polyhedron, the most common example of which is the dodecahedron. However, the present B_5 geometry more closely resembles a hexagonal bipyramid with a centre to apex height of 0·64 Å and with edge lengths of 1·81 (equatorial) and 1·77 Å (apex to base) in (I). The corresponding values in (II) are 0·645, 1·82, and 1·78 Å. Although full structural parameters have not been published, the *hypho*-B_5 group in $B_5H_9{\cdot}2PMe_3$ is apparently similar to those in (I) and (II). The average non-bonded distances of B(2) · · · B(5) and B(3) · · · B(4) in (I) and (II) are 2·76 and 2·74 Å respectively, close to the corresponding distance of 2·97 Å in B_5H_{11}.[5]

In B_5H_9·tmed (III) (Figure 2), both independent molecules contain a B_5 framework which is markedly different from those in (I) and (II). Both nitrogen atoms donate to the same 'basal' boron atom. This atom has become singly bonded to the apical boron atom of the remaining B_4H_8 and is separated from the remaining basal atoms by non-bonded contact distances. Such an arrangement of atoms at the 'basal' boron appears to be unique amongst the boranes and their ions. The overall atomic arrangement is still an example of the *hypho* class, however, although the structure can be interpreted in terms of a zwitterionic canonical form (**A**), since it shows strong



$$\begin{matrix} N \searrow & & \\ & B^+ \rightarrow B_4H_8^- & \\ N \nearrow & H & \end{matrix}$$

(**A**)

similarities to adducts of the type $L{\cdot}B_4H_8$, where the B_4 fragment would be an *arachno* species.[6] The parent polyhedron for (III) can again be seen as a hexagonal bipyramid [∠B(3)–B(4)–B(5) 108·2 and 107·0°] especially as the B(1),B(3),B(4)–B(1),B(4),B(5) dihedral angles (129·4 and 127·4°) are higher than the value of 118·1° in B_4H_{10}.[7] A structure involving the ligand chelating at a single boron position was previously favoured on the basis of i.r. and n.m.r. evidence, although the arrangement of boron and hydrogen atoms was uncertain.[8] A gross movement of one of the basal boron atoms also occurs when B_6H_{10} is converted into $B_6H_{10}{\cdot}2PMe_3$, although in this case the resulting *hypho*-B_6 fragment forms an open framework resembling the equatorial belt of an icosahedron rather than occupying all but three vertices of a 9-vertex polyhedron such as a tricapped trigonal prism.[4]

The differences between the structures of (I) and (II) compared with (III) are surprising. In B_5H_9 there is residual negative charge at the apical boron atom, and the ability of the phosphine ligands to withdraw electron density through π-type interactions might account for their preferential co-ordination at the apical position,[2,9] while the co-ordination of tmed at the basal positions could be predicted since no π-effects are possible. The different

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

framework arrangements in (I) and (II) and (III) could also reflect the need to delocalise the greater electron density placed on the B_5 skeleton by the tmed ligand, and the retention of an integral B_4 unit in (III) is significant in contrast to the two distinct B_3 fragments in (I) and (II). Finally, the presence of a chelate effect is apparent in all the adducts, the monodentate ligand species being much less stable, so that, for example, $B_5H_9\cdot 2PPh_3$ is completely dissociated at 25 °C.[10] We are investigating the influence of related ligands on the skeletal atom arrangement.

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