Isomeric *hypho*-Boranes. Properties and Molecular Structures of the Adducts $B_5H_9{\cdot}L$ (L = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or $Me_2NCH_2CH_2NMe_2$) and $B_4H_8{\cdot}L$ (L = $Me_2NCH_2CH_2NMe_2$) †

Nathaniel W. Alcock,* Howard M. Colquhoun, Gerald Haran, Jeffrey F. Sawyer, and Malcolm G. H. Wallbridge *
Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The air-stable adducts $B_5H_9{\cdot}L$ [L = bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and *NNN'N'*-tetramethylethylenediamine (tmen)] and $B_4H_8{\cdot}$tmen are formed by the action of the ligand on the borane at room temperature; no cleavage of the B_5 group to form $BH_3{\cdot}L$ species occurs, even with an excess of ligand. The B_5H_9 complexes, which may be regarded as derivatives of the *hypho*-$B_5H_{11}^{2-}$ ion, have been fully characterised by *X*-ray methods; for $B_4H_8{\cdot}$tmen an approximate structure is 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 tmen complexes differ markedly; each has 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.

Several different types of reactions have now been observed when pentaborane(9) reacts with ligand molecules, the pathway being determined by the type of ligand. Thus nucleophiles such as H^-, R^- (R = alkyl: in LiR, NaR, *etc.*), or OH^- cleave the basal B–H–B bridges yielding hydrogen and the $B_5H_8^-$ ion.[1,2] Neutral ligands, in contrast, frequently co-ordinate to the B_5 framework initially, and cause a rearrangement of the hydrogen atoms. Neutral adducts isolated include $B_5H_9{\cdot}L^2$ (L^2 = dppm,[3] dppe,[3] and tmen [3,4]) ‡ and $B_5H_9{\cdot}2L^1$ (L^1 = NMe_3 [5,6] and PMe_3 [5,7,8]). These neutral species often react further causing degradation of the borane framework, and with trimethylamine in particular, $BH_3{\cdot}NMe_3$ and $B_4H_6{\cdot}NMe_3$ have been formulated as products.[6,7] In some cases immediate degradation occurs, *e.g.* with ammonia where the bis-ammoniate appears to be best represented as $[BH_2(NH_3)_2]^+[B_4H_7]^-$,[9-11] and with (dimethylamino)difluorophosphine, $PF_2(NMe_2)$, where a diborane(4) adduct $B_2H_4{\cdot}2PF_2(NMe_2)$, as well as $B_3H_5{\cdot}2PF_2(NMe_2)$, are among the products.[11] Similarly, when pentaborane(9) is treated with excess of trimethylphosphine above 0 °C, it gives both $B_2H_4{\cdot}2PMe_3$ and $B_3H_5{\cdot}3PMe_3$.[8,12] Tetraborane(8) derivatives, *e.g.* $B_4H_8{\cdot}$tmen, have also been obtained from the adduct $B_5H_9{\cdot}$tmen by a methanolic degradative reaction,[4] and a recent n.m.r. study on this compound suggests that it is a fluxional *hypho*-borane whose structure is related to that of $B_5H_9{\cdot}$tmen, by removal of a single BH unit and rearrangement of two hydrogen atoms.[13]

Since the $B_5H_9{\cdot}L^2$ and $B_5H_9{\cdot}2L^1$ systems are isoelectronic with the hypothetical *hypho*-$B_5H_{11}^{2-}$ ion, and contain $(n + 4)$ skeletal electron pairs,[14] we have studied the structures of $B_5H_9{\cdot}L^2$ [L^2 = dppm (1); dppe (2); tmen (3)], and also $B_4H_8{\cdot}$tmen (4), to obtain more information on the configurations adopted by such species. There is relatively little structural information available on other compounds; only $B_5H_9{\cdot}2PMe_3$, and the related $B_6H_{10}{\cdot}2PMe_3$, have been fully characterised by *X*-ray data.[7,15]

Of the other known examples of *hypho*-species most have been prepared and characterised using ^1H and ^{11}B n.m.r. spectra, although this method cannot define the very open skeletal structures. In some cases, because of poor data on the fluxional behaviour of the open framework of these species, several postulated structures could equally well fit the experimental evidence. Some aspects of this work have been reported previously.[3]

Experimental

Standard vacuum-line techniques were used for the handling of pentaborane(9) and other volatile compounds. All solvents were rigorously dried before use and degassed before storing in suitable vessels on the vacuum line. The solid products were handled in a conventional glove-box under pure dry nitrogen. I.r. spectra were run as Nujol (or hexchlorobutadiene) mulls, and were recorded using a Perkin-Elmer 580B spectrophotometer. The ^{11}B n.m.r. spectra were recorded at 28.9 MHz using a Bruker WH90 spectrometer with $BF_3{\cdot}Et_2O$ as an external standard, downfield shifts being quoted as positive.

Preparation of Adducts.—The adducts (1), (2), and (3) were obtained by a method similar to that used originally for the adduct (3). The procedure used for (2) is typical: dppe (1.92 g, 5 mmol) was dissolved in dry tetrahydrofuran (thf) (30 cm³) in a round-bottomed flask, and pentaborane(9) (0.32 g, 5 mmol) distilled into the flask at −196 °C using a vacuum line. The flask was warmed slowly (0.5 h) to room temperature, and the contents stirred magnetically for 12 h. All the volatile material was then pumped off from the white solid which had precipitated from solution. The yield was essentially quantitative. Recrystallisation from thf gave long needle-like crystals; slow recrystallisation over 48 h resulted in the incorporation of a half-molecule of disordered solvent into the lattice. It was found advantageous for (3) to use a slight excess of ligand in the reaction, and in this case it was best recrystallised from a CH_2Cl_2–hexane mixture (or acetonitrile–diethyl ether) containing some free ligand, to limit any decomposition of the adduct. Since (3) decomposes slowly in air it was mounted immediately after purification in a Lindemann capillary which was then sealed. The corresponding reactions of pentaborane(9) with arsenic ligands $Ph_2As(CH_2)_nAsPh_2$ (n = 1 or

---

† *Supplementary data available* (No. SUP 23374; 62 pp.): structure factors, thermal parameters, complete bond distance and angle data for compounds (1) and (2), atomic co-ordinates for (4). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ dppm = Bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, tmen = *NNN'N'*-tetramethylethylenediamine.

Table 1. Crystal data

	(1)	(2)	(3)	(4)
Formula	$C_{25}H_{31}B_5P_2\cdot\frac{1}{2}C_4H_4O$	$C_{26}H_{33}B_5P_2$	$C_6H_{25}B_5N_2$	$C_6H_{24}B_4N_2$
System	orthorhombic	orthorhombic	orthorhombic	monoclinic
Absences	$h00, h \neq 2n; 0k0, k \neq 2n; 00l, l \neq 2n$	$h0l, l \neq 2n; 0kl, k \neq 2n; hk0, h \neq 2n$	as for (1)	$hkl, h + k \neq 2n; h0l, l \neq 2n$
Space group	$P2_12_12_1$	*Pbca*	$P2_12_12_1$	*Cc*
a/Å	7.931(4)	14.297(4)	12.940(2)	7.654(2)
b/Å	16.816(5)	16.492(6)	12.911(3)	12.937(2)
c/Å	23.271(8)	22.280(9)	15.046(2)	12.536(2)
β/Å	90	90	90	107.78(2)
U/Å^3	3 105(2)	5 253(3)	2 513.9(8)	1 182.0(5)
M	481.5	461.6	179.3	167.5
D_c/g cm^{-3}	1.03	1.17	0.95	0.94
Z	4	8	8	4
F(000)	1 016	1 952	800	376
Range (2θ) about $\alpha_1 - \alpha_2$/°	±0.7	±1.0	±0.9	±1.2
Total reflections	3 031	3 700	2 858	853
Observed reflections [$I/\sigma(I) \geq 3.0$]	1 850	2 643	1 200	576
Final *R*	0.069	0.047	0.055	0.134

2) yield only high melting point polymeric materials.[16] The anions $[B_5H_8L^2]^-$ (L^2 = dppm or dppe) were prepared by treating (1) and (2) with either n-butyl-lithium or potassium hydride in thf solution; the reactions are slow at room temperature and often take several days to go to completion.

Analytical data were obtained by Butterworths Laboratories Ltd. Initial attempts to determine the hydrolysable hydrogen showed that hydrolysis was usually slow, especially for (1) and (2). For example, a sample of (1) was heated in a sealed flask with dilute hydrochloric acid for 8 days at 80 °C, followed by 16 days at 100 °C, and still only 91% of the total hydrolysable hydrogen was recovered. Compound (1), found: C, 66.9; H, 7.1; B, 11.85; P, 13.8. Calc. for $C_{25}H_{31}B_5P_2$: C, 67.1; H, 7.0; B, 12.1; P, 13.85%. Compound (2), found: C, 67.5; H, 7.05; B, 11.75; P, 13.15. Calc. for $C_{26}H_{33}B_5P_2$: C, 67.65; H, 7.2; B, 11.7; P, 13.4%. Compound (3), found: C, 39.9; H, 13.9; B, 29.8. Calc. for $C_6H_{25}B_5N_2$: C, 40.2; H, 14.0; B, 30.1%.

A suspension of (3) in acetonitrile rapidly evolved hydrogen (1 mol per mol of adduct) on the addition of methanol at room temperature, and the resulting white solid was identified as $B_4H_8\cdot$tmen from its ^{11}B n.m.r. spectrum.[13] After filtering off, washing with acetonitrile, and drying *in vacuo*, the solid was recrystallised from acetonitrile–diethyl ether or dimethylformamide to produce colourless crystals, although these were always of rather poor quality.

Data Collection.—Crystal data for compounds (1)—(4) are in Table 1. Three-dimensional *X*-ray data for all four compounds were collected on a Syntex $P2_1$ diffractometer using Mo-K_α radiation (λ = 0.710 69 Å). In each case, the cell constants were obtained by least-squares refinement of the diffracting positions of up to 15 high-angle reflections. Three standard reflections were monitored every 75 reflections, and showed only statistical fluctuations [apart from a generator failure during collection for (1) which required the later deletion of 124 reflections]. Data were collected to a maximum 2θ of 50° [45° for (4)]. Reflections were measured using θ—2θ scans with a variable scan rate of 1° min^{-1} to 29.3° min^{-1}, depending on the intensity of a preliminary 2 s count. Background counts were recorded at each end of the scan, each for one quarter of the scan time. Lorentz and polarisation (but not absorption) corrections were applied. The structure of (1) was solved using MULTAN.[17] Using rigid phenyl groups in the calculation of normalised structure factors for the 3 031 data collected, the final statistics and the distribution of the *E* values clearly showed the absence of a centre of symmetry. The *E* map based on the phase set with highest figure of merit showed 19 atoms of the expected structure. These atoms gave $R = 0.344$ after two cycles of least-squares refinement and the remaining non-hydrogen atoms were located in the subsequent Fourier synthesis. These non-hydrogen atoms were refined for several cycles of least squares, first with isotropic then anisotropic thermal parameters so that the *R* factor dropped to 0.15. At this point the difference-Fourier map contained several peaks attributable to hydrogen atoms and several elongated peaks of sufficient height to be half-weight carbon atoms (also to be seen in the initial *E* map). These were attributed to a half-molecule of thf solvent in a general position, and the best agreement was given when the molecule was assumed to be disordered. The model chosen to represent the disorder consists of two separate orientations of the thf molecule rotated by approximately 30°. Each peak has an occupancy of 0.25 giving overall half a solvent molecule per general position. The atomic positions for each orientation were chosen from difference-Fourier maps and were not refined.

With these atoms fixed and using anisotropic thermal parameters for all non-hydrogen atoms, the final least-squares refinement in five blocks eventually converged to $R = 0.069$ and $R' = 0.082$. The weights (w) were given by $w = XY$ where $X = \sin\theta/0.3$ if $\sin\theta < 0.3$ or $X = 0.4/\sin\theta$ if $\sin\theta > 0.4$, otherwise $X = 1$; $Y = F/9.5$ if $F < 9.5$ or $Y = 20.0/F$ if $F > 20.0$, otherwise $Y = 1$. In the final cycle no shift was greater than 0.50 of its standard deviation for a non-hydrogen atom (largest shift/error for a hydrogen atom was 1.4) and the final Fourier synthesis contained a few residual peaks up to 1 e Å^{-3} mainly around the disordered solvent.

For (2), initial structure solution was by MULTAN using a data set of poor quality for which refinement terminated at $R = 0.17$. This was replaced with a recollected set, and starting from the previous co-ordinates, two cycles of isotropic refinement reduced *R* to 0.085. Anisotropic thermal parameters for all non-hydrogen atoms reduced this further to 0.054. After repositioning several hydrogen atoms (ring hydrogens in calculated positions, C–H = 0.95 Å), and including corrections for extinction and dispersion effects, the refinement in five blocks eventually converged to $R = 0.047$ and $R' = 0.063$. The weights used were given by $w = (A + F + B^*F^2)^{\frac{1}{2}}$ where $A = 14.6$ and $B = 0.0073$.

For (3), structure solution was again by MULTAN, and the E map of highest figure of merit showed 25 of the expected 26 non-hydrogen atoms (though with a number of spurious peaks). Fourier syntheses and isotropic refinement reduced R to 0.15.

The thermal parameters of the second tmen molecule were in general high ($U = 0.06$—0.13), and it became clear that the carbon atoms of this group were disordered, existing in two separate conformations of equal weight. Adopting this model enabled the hydrogen atoms attached to this tmen molecule to be located, some with unit population parameters. Keeping these atoms fixed during the final refinement cycles and allowing anisotropic thermal parameters for all atoms except the carbon atoms of the disordered tmen, the least squares refinement in five blocks eventually converged to $R = 0.055$ and $R' = 0.049$. The weights used were given by $w = XY[1/\sigma(F)]^2$ where $X = \sin\theta/0.245$ if $\sin\theta < 0.245$, otherwise $X = 1$; $Y = F/5.0$ if $F < 5.0$ or $Y = 18.0/F$ if $F > 18.0$, otherwise $Y = 1$. Six reflections with large $w(\Delta F)^2$ after the application of this scheme were rejected from subsequent refinement cycles. In the final refinement cycle no parameter shift was greater than 33% of its standard deviation and the final difference-Fourier map was featureless.

For (4), data were collected on a poor crystal with large angular spread and were expected to be of poor quality. The space group *Cc* in preference to *C*2/*c* was chosen on the basis of the intensity statistics. MULTAN showed the molecule clearly in the solution with highest figure of merit, but refinement of this was affected by the data quality. Even with anisotropic thermal parameters for B, C, and N atoms the R value could not be reduced below 0.13 and the hydrogen atoms could not be reliably identified. Refinement was terminated at this figure.

Final refinement for all structures used the *X*-RAY system [18] on a Burroughs B6700 computer. Scattering factors were taken from ref. 19, used in the analytical form. Final positional parameters are in Table 2 [except for those for (4) and the disordered solvent of (1) which are included with the deposited material]. Bond lengths and angles (Tables 3 and 4) and deviations from molecular planes (Table 5) are presented for (1)—(3).

Analysis of the molecular packing shows that all intermolecular contacts are at van der Waals distances, and there are no features of particular interest. Packing diagrams are therefore not included.

Results and Discussion

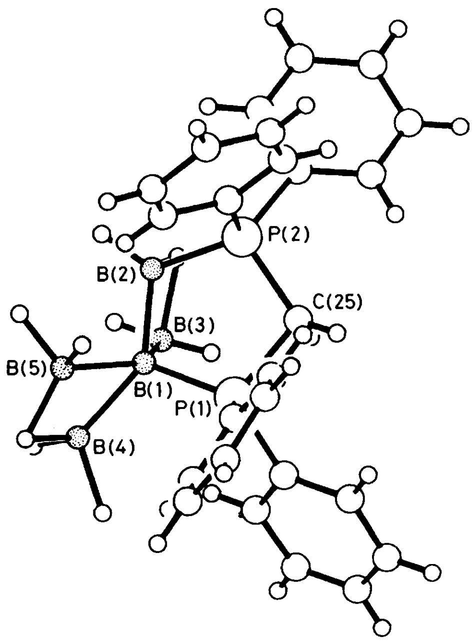


Figure 1. The structure of B_5H_9·dppm (1), showing principal atomic numbering; boron atoms are stippled

The adducts (1) and (2) are obtained as colourless crystalline solids from direct interaction of the ligands with pentaborane-(9), and are remarkably stable in air showing no visible change over a period of many months. There is no further reaction with excess ligand to afford cleavage products, such as $H_3B·Ph_2PCH_2PPh_2·BH_3$, as has been observed when trialkyl-amines or -phosphines are used as ligands. The i.r. spectra of (1) and (2) show, apart from absorptions associated with the ligands, bands at 2 510—2 490 and 2 410—2 400 cm^{-1} from the terminal B–H and B–H$_2$ groups, and weaker absorptions at 1 900—1 850 cm^{-1} from the B–H–B groups, but the overall complexity of the spectra offers little chance of obtaining any structural details. We were unable to obtain good quality ^{11}B n.m.r. spectra on the compounds (1) and (2); in solvents such as thf, dichloromethane, and 1,2-dichlorethane only very broad resonances (*ca.* 200 Hz wide at half-height) were obtained at approximately −22 (relative intensity 4) and −55 (1) p.p.m. for (1), and −21 (4) and −51 (1) p.p.m. for (2). However, the spectra were not always reproducible, and other resonances (*e.g.* a sharp signal at +1 p.p.m.) appeared in some spectra, indicative of decomposition processes. The ^{31}P spectrum of (1) in thf showed a complicated signal at +17—19 p.p.m. (relative to H_3PO_4 as external standard). We were able to reproduce the previously reported ^{11}B spectrum for (3),[4,13] and an obvious difference from the spectra for (1) and (2) is that the low-field resonance in (3), assigned to the HB·tmen group in B_5H_9·tmen, is not present in the spectra of (1) and (2) as expected.

Both (1) and (2) show some properties similar to B_5H_9 itself, namely that on treatment with either potassium hydride or n-butyl-lithium in thf solution one mol of hydrogen (or butane) per mol of (1), or (2), is evolved slowly over a period of about 2 days at room temperature. The resulting species, *e.g.* $K^+[B_5H_8(Ph_2PCH_2PPh_2)]^-$, are soluble in thf, and the ^{11}B n.m.r. spectrum of the derivative from (1) shows again two broad resonances at −23 and −53 p.p.m. In contrast to $K^+[B_5H_8]^-$, which decomposes in solution evolving hydrogen, the derivatives from (1) and (2) appear to be more stable and evolve only small quantities of hydrogen on standing at room temperature for several days.

Structural Results.—In both (1) and (2) the B_5H_9 moieties have become shallow pyramids with rearrangement of the hydrogen atoms to give basal ' BH$_2$ ' groups and two symmetrical hydrogen bridges (Figures 1 and 2). Within the B$_5$ frameworks there are two triangular BBB faces sharing a vertex, with the B–B distances in the faces ranging from 1.745 to 1.829 Å (comparable to B–B distances in other B_5H_9 derivatives). The distances and angles in the two frameworks in (1) and (2) are almost the same. The largest discrepancy occurs in the B · · · B non-bonded distances between basal atoms. In (1) these are 2.770(15) and 2.746(16) Å, whilst in (2) they are 2.723(7) and 2.755(7) Å. Although full structural parameters have not been published for the B_5H_9 group in $B_5H_9·2PMe_3$, it is apparently similar to (1) and (2) with normal B–B distances, although the average non-bonded

Table 2. Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

(*a*) B_5H_9·dppm (1)

Atom	*x*	*y*	*z*
P(1)	7 705.7(26)	4 351.6(11)	740.3(8)
P(2)	8 465.5(24)	4 542.6(11)	1 949.3(8)
C(1)	7 483(11)	3 275(4)	704(3)
C(2)	8 840(13)	2 802(5)	845(4)
C(3)	8 636(16)	1 972(5)	821(5)
C(4)	7 146(17)	1 657(6)	661(4)
C(5)	5 816(16)	2 118(6)	528(5)
C(6)	6 009(12)	2 947(6)	542(4)
C(7)	6 415(12)	4 757(4)	169(3)
C(8)	7 168(14)	4 801(6)	−376(4)
C(9)	6 156(17)	5 090(8)	−827(4)
C(10)	4 622(14)	5 380(7)	−739(4)
C(11)	3 916(12)	5 347(7)	−198(4)
C(12)	4 857(12)	5 032(6)	247(3)
C(13)	8 175(10)	3 719(4)	2 349(3)
C(14)	9 223(13)	3 609(6)	2 818(4)
H(1)	9 568(88)	5 416(45)	593(29)
H(2)	10 856(115)	4 422(58)	529(38)
H(3)	9 343(75)	6 005(37)	1 197(25)
H(4)	11 612(114)	5 952(50)	1 016(34)
H(5)	13 063(87)	4 269(43)	1 968(30)
H(6)	11 898(95)	5 138(46)	2 482(33)
H(7)	9 796(189)	2 908(82)	3 578(56)
H(8)	11 672(127)	3 500(56)	1 694(40)
H(9)	13 008(131)	3 945(65)	1 254(45)
H(21)	10 049(171)	4 006(72)	2 843(52)
H(31)	3 226(95)	3 317(47)	1 771(31)
H(41)	7 433(125)	1 920(53)	3 213(36)
H(51)	5 951(122)	2 242(55)	2 545(39)
H(61)	6 271(122)	3 201(54)	1 905(39)
H(81)	5 590(146)	4 984(68)	2 654(45)
H(91)	4 801(140)	5 887(60)	3 332(42)
C(15)	9 129(15)	2 923(7)	3 155(4)
C(16)	7 937(16)	2 360(5)	3 009(5)
C(17)	6 911(17)	2 473(6)	2 549(5)
C(18)	6 981(14)	3 161(5)	2 219(4)
C(19)	7 877(10)	5 414(4)	2 463(3)
C(20)	6 394(12)	5 332(6)	2 775(4)
C(21)	5 918(14)	5 932(7)	3 158(4)
C(22)	6 936(16)	6 591(6)	3 216(4)
C(23)	8 371(17)	6 669(5)	2 917(4)
C(24)	8 874(13)	6 066(5)	2 537(4)
C(25)	6 803(10)	4 702(5)	1 408(3)
B(1)	10 522(12)	4 753(5)	1 516(4)
B(2)	10 009(12)	4 682(6)	788(4)
B(3)	10 397(14)	5 650(6)	1 120(4)
B(4)	12 301(14)	4 941(7)	1 963(6)
B(5)	12 050(14)	3 995(6)	1 616(5)
H(101)	6 373(146)	6 951(64)	3 498(43)
H(111)	9 137(157)	7 038(74)	3 104(52)
H(121)	245(109)	1 113(48)	2 728(32)
H(141)	10 073(128)	2 930(56)	988(38)
H(151)	9 555(146)	1 707(68)	886(46)
H(161)	6 970(113)	1 204(49)	696(37)
H(171)	5 148(157)	1 706(70)	358(48)
H(181)	4 984(174)	3 108(78)	490(51)
H(201)	7 720(247)	4 283(112)	−474(75)
H(211)	6 817(129)	5 168(61)	−1 225(39)
H(221)	3 514(313)	5 533(138)	−867(95)
H(231)	2 849(132)	5 648(60)	−148(42)
H(241)	3 930(235)	4 938(112)	500(71)
H(251)	6 415(94)	5 231(48)	1 373(30)
H(252)	5 876(165)	4 368(80)	1 520(51)

(*b*) B_5H_9·dppe (2)

Atom	*x*	*y*	*z*
P(1)	3 538.7(6)	197.5(6)	2 820.6(4)
P(2)	2 532 3(6)	443.6(6)	4 165.2(4)
C(1)	3 875(2)	423(2)	2 168(2)
C(2)	3 373(3)	346(3)	1 632(2)
C(3)	3 539(3)	865(3)	1 156(2)
C(4)	4 207(3)	1 475(3)	1 212(2)
C(5)	4 707(3)	1 559(2)	1 730(2)
C(6)	4 556(2)	1 028(2)	2 208(2)
C(7)	3 406(3)	−1 215(2)	2 499(2)
C(8)	4 155(3)	−1 540(3)	2 174(2)
C(9)	4 127(4)	−2 339(3)	1 972(2)
C(10)	3 352(4)	−2 815(3)	2 074(2)
C(11)	2 614(4)	−2 499(3)	2 367(2)
C(12)	2 628(3)	−1 700(2)	2 589(2)
C(13)	2 229(2)	1 235(2)	4 703(2)
C(14)	1 608(3)	1 857(2)	4 565(2)
C(15)	1 439(3)	2 474(3)	4 974(2)
C(16)	1 885(3)	2 470(3)	5 520(2)
C(17)	2 490(3)	1 858(3)	5 665(2)
C(18)	2 673(3)	1 237(3)	5 261(2)
C(19)	1 754(2)	−409(2)	4 282(2)
C(20)	2 100(3)	−1 186(2)	4 256(2)
C(21)	1 499(3)	−1 848(3)	4 285(3)
C(22)	552(3)	−1 734(3)	4 335(2)
C(23)	197(3)	−960(3)	4 367(2)
C(24)	785(3)	−297(3)	4 336(2)
C(25)	2 323(2)	149(2)	2 951(2)
C(26)	2 217(2)	816(2)	3 420(2)
B(1)	4 350(3)	−159(3)	3 525(2)
B(2)	3 846(3)	156(3)	4 201(2)
B(3)	4 603(3)	837(3)	3 773(2)
B(4)	5 502(3)	−494(3)	3 297(3)
B(5)	4 763(3)	−1 151(3)	3 740(2)
H(1)	4 173(26)	859(22)	4 296(16)
H(2)	4 030(25)	−125(22)	4 615(16)
H(3)	4 262(29)	1 316(27)	3 543(19)
H(4)	5 305(31)	985(25)	3 935(18)
H(5)	5 493(31)	−1 285(28)	3 433(20)
H(6)	6 127(27)	−214(22)	3 550(17)
H(7)	5 585(28)	−517(24)	2 782(18)
H(8)	5 003(25)	−1 244(23)	4 191(17)
H(9)	4 299(27)	−1 659(23)	3 583(16)
H(21)	2 878(27)	−57(22)	1 591(18)
H(31)	3 232(31)	741(25)	768(19)
H(41)	4 324(25)	1 795(21)	883(16)
H(51)	5 194(28)	1 980(24)	1 792(17)
H(61)	4 871(22)	1 071(19)	2 555(15)
H(81)	4 695(31)	−1 222(28)	2 078(20)
H(91)	4 592(29)	−2 557(25)	1 735(18)
H(101)	3 379(34)	−3 390(30)	1 898(21)
H(111)	2 112(30)	−2 724(27)	2 438(21)
H(121)	2 081(21)	−1 460(29)	2 818(13)
H(141)	1 324(20)	1 839(17)	4 195(13)
H(151)	1 094(24)	2 890(20)	4 884(16)
H(161)	1 777(29)	2 869(23)	5 811(17)
H(171)	2 779(31)	1 816(27)	6 019(20)
H(181)	3 086(26)	877(22)	5 339(16)
H(201)	2 772(31)	−1 272(28)	4 222(19)
H(211)	1 753(33)	−2 349(28)	4 238(21)
H(221)	117(28)	−2 205(25)	4 341(17)
H(231)	−463(34)	−828(28)	4 415(21)
H(241)	571(29)	181(25)	4 394(19)

Table 2. (*continued*)

(*c*) B_5H_9·tmen (3)

Atom	*x*	*y*	*z*
N(11)	3 718(3)	4 102(3)	4 543(3)
N(12)	3 129(3)	4 865(3)	5 991(3)
N(21)	2 180(3)	840(3)	−1 546(3)
N(22)	1 353(3)	706(3)	−45(3)
C(11)	3 432(6)	3 014(5)	4 257(4)
C(12)	4 553(5)	4 471(5)	3 941(4)
C(13)	2 766(5)	4 769(6)	4 456(4)
C(14)	2 767(5)	5 472(5)	5 213(5)
C(15)	2 295(5)	4 199(6)	6 371(6)
C(16)	3 477(5)	5 618(5)	6 687(4)
B(11)	4 384(5)	3 053(5)	6 106(4)
B(12)	4 119(4)	4 200(5)	5 599(4)
B(13)	4 860(6)	3 475(7)	7 173(5)
B(14)	5 298(6)	2 364(7)	6 662(5)
B(15)	5 566(5)	2 668(6)	5 533(5)
B(21)	164(5)	1 721(5)	−1 380(4)
B(22)	1 339(4)	1 515(5)	−913(4)
B(23)	509(6)	2 694(6)	−2 208(5)
B(24)	−688(6)	2 661(6)	−1 678(5)
B(25)	−454(6)	2 506(6)	−513(5)
C(21A)	1 715(9)	22(10)	−2 049(8)
C(22A)	2 780(10)	1 527(10)	−2 122(8)
C(23A)	2 900(9)	416(10)	−844(8)
C(24A)	2 145(13)	−63(13)	−112(11)
C(25A)	1 533(10)	1 492(11)	807(9)
C(26A)	400(11)	130(11)	200(10)
C(21B)	1 761(9)	517(11)	−2 451(8)
C(22B)	3 103(10)	1 592(11)	−1 752(9)
C(23B)	2 541(10)	−105(11)	−1 072(9)
C(24B)	2 470(11)	185(11)	−129(10)
C(25B)	1 308(12)	1 154(13)	781(11)
C(26B)	528(11)	−128(11)	−164(10)
H(11)	3 773(33)	2 451(35)	6 065(28)
H(12)	4 702(24)	4 784(26)	5 538(20)
H(13)	5 182(41)	4 175(46)	7 090(31)
H(14)	4 385(41)	3 445(41)	7 851(36)
H(15)	5 704(40)	2 806(38)	7 331(32)
H(16)	5 198(34)	1 608(44)	6 854(27)
H(17)	6 116(47)	2 473(43)	6 213(40)
H(18)	5 576(36)	2 034(38)	5 109(32)
H(19)	6 071(34)	3 505(41)	5 326(28)
H(21)	−203(33)	1 058(36)	−1 601(27)
H(22)	1 757(28)	2 225(32)	−720(24)
H(23)	1 171(30)	3 100(30)	−1 896(23)
H(24)	436(28)	2 473(28)	−2 934(28)
H(25)	−90(38)	3 492(42)	−2 082(28)
H(26)	−1 390(37)	2 436(35)	−1 954(27)
H(27)	−851(35)	3 221(39)	−1 013(32)
H(28)	37(42)	2 966(38)	−147(33)
H(29)	−1 126(35)	2 185(32)	−85(29)
H(111)	3 221(24)	3 026(25)	3 682(20)
H(112)	2 893(37)	2 718(37)	4 726(30)
H(113)	4 138(43)	2 650(39)	4 266(34)
H(121)	4 920(37)	5 186(38)	4 097(30)
H(122)	4 326(31)	4 293(33)	3 347(24)
H(123)	5 150(67)	3 766(69)	3 903(57)
H(131)	2 677(39)	5 063(42)	3 883(32)
H(132)	2 105(37)	4 081(39)	4 644(29)
H(141)	2 104(27)	5 831(30)	5 317(21)
H(142)	3 467(43)	6 128(43)	4 874(34)
H(151)	2 028(45)	3 676(52)	5 963(40)
H(152)	2 516(37)	3 904(37)	6 912(33)
H(153)	1 735(39)	4 780(41)	6 613(31)
H(161)	3 006(33)	6 101(31)	6 792(25)
H(162)	3 597(50)	5 190(54)	7 091(39)
H(163)	4 019(38)	6 151(36)	6 377(32)
H(21AB)	1 118	49	−2 396
H(22AB)(1)	3 486	1 100	−2 044
H(22AB)(2)	2 805	2 185	−2 024
H(23AB)	3 362	−175	−1 164
H(24AB)	2 531	−289	482
H(25AB)	719	1 797	768
H(26AB)(1)	−109	438	98
H(26AB)(2)	369	−599	−158
H(21A)(1)	2 347	−347	−2 394
H(21A)(2)	1 256	−640	−1 813
H(22A)(3)	2 401	1 370	−2 736
H(23A)(2)	3 369	1 074	−514
H(24A)(2)	1 877	−850	−355
H(25A)(1)	1 560	959	1 445
H(25A)(2)	2 180	1 921	593
H(26A)(3)	424	−116	934
H(21B)(1)	2 494	137	−2 786
H(21B)(3)	1 446	1 196	−2 820
H(22B)(3)	3 442	1 929	−1 187
H(23B)(2)	2 342	−724	−1 436
H(24B)(1)	2 994	667	132
H(25B)(1)	1 108	629	1 298
H(25B)(3)	1 972	1 388	960

B · · · B contact distance of 2.95 Å is *ca.* 0.2 Å longer.[7] These values should be compared to a B · · · B non-bonded distance of 2.97 Å in B_5H_{11}.[20]

The phosphorus atoms of the ligands dppm and dppe bridge apical and basal positions of these B_5 groups, giving five- and six-membered rings respectively. The configurations of the ligands are shown in Figure 3 and the torsion angles in the five- and six-membered chelate rings are in Table 6. Both these ligands are very flexible due to rotations about both P–C and (in the case of dppe) C–C bonds, and can exist in a number of conformations. Furthermore, both ligands can act as both chelating bidentate ligands or as bridging bidentate ligands providing that there are no steric constraints of both. In both ligands the PBBP planes are approximately planar, so that the conformation in the chelate rings can be characterised by the atomic displacements of the backbone carbon atoms from this plane. In B_5H_9·dppm C(25) is 0.56 Å from this plane, whilst in the dppe complex, atoms C(25) and C(26) deviate by 0.05 and 0.83 Å respectively from the corresponding plane.

In the dppe complex and to a lesser extent in the dppm complex, there is considerable strain in the ligands. The need to form a six-membered chelate ring in (2) results in much larger P(1)–B(1)–B(2) and P(2)–B(2)–B(1) angles [117.2(3) and 115.9(3)° respectively, compared to the corresponding angles of 107.7(6) and 107.4(6)° in compound (1)], a much larger ligand bite [P · · · P distance of 3.49 Å, *cf.* 2.92 Å in (1)]. Both compounds show considerable repulsive interactions between the phenyl rings, as can be seen from several parameters. The two P–C–C (*ipso*) angles in each ring are non-equivalent, one angle being greater and the other less than the expected 120° by 1 or 2°. Furthermore, the P–C bonds make angles of a few degrees (3.2—6.6°) with the least-squares planes of the phenyl rings. Clearly the phenyl rings, as they are being forced apart, are bending and also slightly rotating about each P–C bond (more deformable than the C–C and C–H bonds).

In the dppm ligand in (1), the C–C distances in the phenyl rings are in the range 1.326(18)—1.408(15) Å (weighted average 1.375 Å), with the corresponding angles varying from

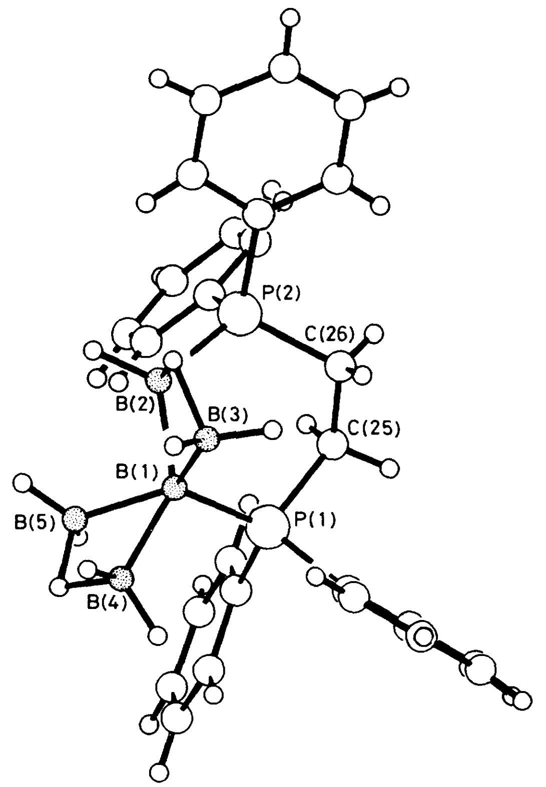


Figure 2. The structure of B_5H_9·dppe (2), showing principal atomic numbering; boron atoms are stippled

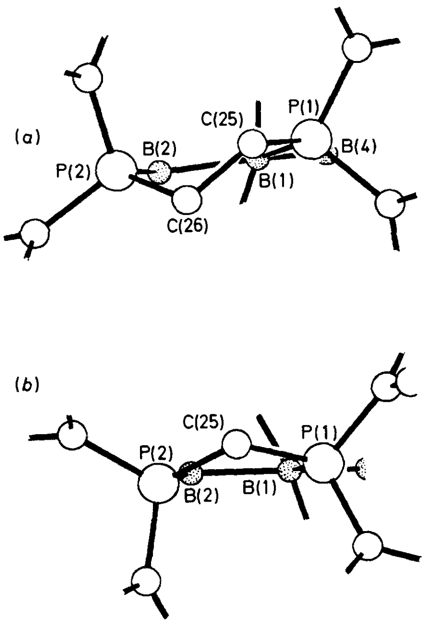


Figure 3. Conformations of chelate rings in (a) B_5H_9·dppe and (b) B_5H_9·dppm

116.7(10) to 122.1(8)° (average 119.18°). For the dppe ligand in (2) the corresponding C–C distances and CCC angles are in the ranges 1.346(8)—1.407(6) Å (average 1.385 Å) and 117.9(4)—121.5(5)° (average 119.99°), respectively. The corresponding P–C (Ph) distances in (1) average 1.821 Å; in (2) they average 1.828 Å. These should be compared to the normal range of P–C(sp^2) distances of 1.807(3) to 1.829(6) Å found in phosphines.[21] Possibly because of the strains in the chelate ring and between the phenyl rings, there is no distinct difference in the P–C(Ph) and P–C(sp^3) distances in either compound.

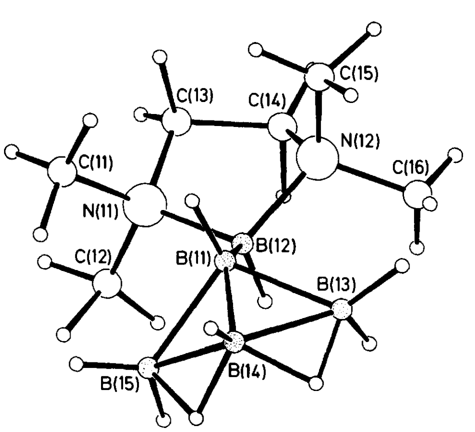


Figure 4. The ordered molecule of B_5H_9·tmen (3) showing the principal atomic numbering

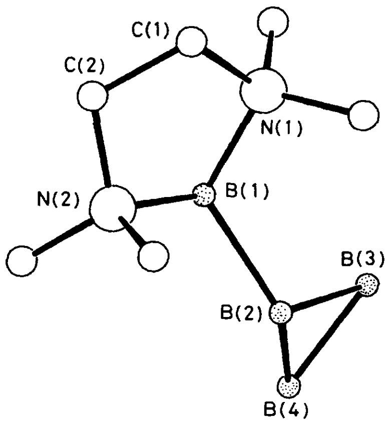


Figure 5. The structure of B_4H_8·tmen (4), showing the atomic numbering; hydrogen positions were not determined

In compound (3) both independent molecules contain a B_5 framework which is markedly different from those in compounds (1) and (2) (Figure 4). Both nitrogen atoms donate to the same ' basal ' boron atom forming a five-membered chelate ring with average B–N distance of 1.673 Å and N–B–N angle of 97.1°. In molecule 2 of compound (3), the chelate ring is disordered, existing in two separate conformations. It is worth noting that a structure involving the tmen ligand chelating at a single boron position was previously favoured over several possibilities on the basis of i.r. and n.m.r. evidence, although the arrangement of boron and hydrogen atoms was uncertain.[4]

For B_4H_8·tmen, the poor X-ray data prevented refinement to a low R value but despite this the overall structure is clear (Figure 5). It confirms the proposal [13] that both nitrogen atoms co-ordinate to a single boron atom, giving a parallel structure to that of B_5H_9·tmen (3).

The average value of 1.673 Å for the B–N distances in (3) can be compared to values of 1.636(4), 1.610(6), 1.60(2), and 1.58(3) Å in the trimethylamine adducts with boron trifluoride, trichloride, tribromide, and tri-iodide,[22] and values of 1.609

Table 3. Bond distances (Å) and bond angles (°), with standard deviations in parentheses, for **B_5H_9·dppm (1)** and **B_5H_9·dppe (2)**

(*a*) Distances

(*i*) B_5H_9 moiety

	(1)	(2)		(1)	(2)
P(1)-B(1)	1.927(9)	1.953(4)	B(2)-H(1)	1.36(8)	1.27(4)
P(2)-B(2)	1.913(10)	1.939(4)	B(3)-H(1)	1.45(7)	1.32(4)
B(1)-B(2)	1.745(13)	1.747(6)	B(2)-H(2)	1.01(9)	1.06(4)
B(1)-B(3)	1.769(14)	1.768(6)	B(3)-H(3)	1.04(6)	1.06(4)
B(1)-B(4)	1.781(15)	1.810(6)	B(3)-H(4)	1.12(9)	1.09(4)
B(1)-B(5)	1.774(14)	1.804(6)	B(4)-H(5)	1.28(7)	1.34(5)
B(2)-B(3)	1.827(14)	1.829(7)	B(5)-H(5)	1.24(7)	1.27(4)
B(4)-B(5)	1.794(16)	1.806(7)	B(4)-H(6)	1.29(8)	1.15(4)
B(2) · · · B(5)	2.770(15)	2.723(7)	B(4)-H(7)	1.07(8)	1.16(4)
B(3) · · · B(4)	2.746(16)	2.755(7)	B(5)-H(8)	0.90(10)	1.07(4)
			B(5)-H(9)	1.14(11)	1.12(4)

(*ii*) Ligand

	(1)	(2)		(1)	(2)
P(1)-C(1)	1.825(7)	1.841(4)	C(25)-C(26)		1.525(5)
P(1)-C(7)	1.826(8)	1.834(4)	C(25)-H(251)	0.94	0.92(3)
P(2)-C(13)	1.821(7)	1.824(4)	C(25)-H(252)	0.96	0.99(4)
P(2)-C(19)	1.811(8)	1.812(4)	C(26)-H(261)		0.95(3)
P(1)-C(25)	1.827(8)	1.853(4)	C(26)-H(262)		0.95(4)
P(2)-C(25)	1.809(8)				
P(2)-C(26)		1.827(4)			

(*iii*) Phenyl rings

B_5H_9·dppm (1) 1.326(18)—1.408(15); weighted average 1.375
B_5H_9·dppe (2) 1.346(8)—1.407(6); weighted average 1.385

(*b*) Angles

(*i*) B_5H_9 moiety

	(1)	(2)		(1)	(2)
P(1)-B(1)-B(2)	107.7(6)	117.2(3)	B(2)-B(3)-H(1)	47.4(30)	43.9(16)
P(1)-B(1)-B(3)	107.9(6)	113.7(3)	B(2)-B(3)-H(3)	116.6(34)	115.9(23)
P(1)-B(1)-B(4)	112.4(6)	107.8(3)	B(2)-B(3)-H(4)	117.4(43)	120.4(22)
P(1)-B(1)-B(5)	116.1(6)	112.2(3)	H(1)-B(3)-H(3)	86.4(44)	100.9(28)
P(2)-B(2)-B(1)	107.4(6)	115.9(3)	H(1)-B(3)-H(4)	109.4(50)	97.3(27)
P(2)-B(2)-B(3)	116.4(6)	113.7(3)	H(3)-B(3)-H(4)	117.9(56)	114.6(32)
B(2)-B(1)-B(3)	62.6(6)	62.7(3)	B(2)-H(1)-B(3)	81.1(38)	89.9(23)
B(4)-B(1)-B(5)	60.6(6)	60.0(3)	B(1)-B(4)-H(5)	102.9(32)	103.1(19)
B(2)-B(1)-B(5)	103.8(7)	100.1(3)	B(1)-B(4)-H(6)	113.3(34)	116.5(19)
B(3)-B(1)-B(4)	101.3(7)	100.6(3)	B(1)-B(4)-H(7)	114.0(41)	112.4(20)
B(2)-B(1)-B(4)	139.7(8)	135.0(3)	B(5)-B(4)-H(5)	43.6(32)	44.6(19)
B(3)-B(1)-B(5)	136.0(8)	133.8(3)	B(5)-B(4)-H(6)	128.3(35)	115.2(19)
B(1)-B(2)-B(3)	59.3(5)	59.2(3)	B(5)-B(4)-H(7)	114.5(42)	125.7(20)
B(1)-B(3)-B(2)	58.0(5)	58.1(3)	H(5)-B(4)-H(6)	109.5(47)	106.7(27)
B(1)-B(4)-B(5)	59.5(6)	59.9(3)	H(5)-B(4)-H(7)	101.7(53)	101.1(27)
B(1)-B(5)-B(4)	59.9(6)	60.2(3)	H(6)-B(4)-H(7)	114.1(53)	114.8(28)
P(2)-B(2)-H(1)	89.9(30)	98.0(17)	B(1)-B(5)-H(5)	105.3(34)	106.5(21)
P(2)-B(2)-H(2)	118.5(54)	112.4(19)	B(1)-B(5)-H(8)	117.5(64)	118.9(20)
B(1)-B(2)-H(1)	108.8(30)	105.3(17)	B(1)-B(5)-H(9)	114.3(54)	113.5(20)
B(1)-B(2)-H(2)	117.2(52)	121.1(20)	B(4)-B(5)-H(5)	45.6(33)	47.8(21)
B(3)-B(2)-H(1)	51.5(30)	46.2(17)	B(4)-B(5)-H(8)	139.8(61)	114.3(20)
B(3)-B(2)-H(2)	122.0(55)	125.0(19)	B(4)-B(5)-H(9)	108.9(55)	128.4(19)
H(1)-B(2)-H(2)	111.5(62)	99.3(26)	H(5)-B(5)-H(8)	115.3(70)	102.6(28)
B(1)-B(3)-H(1)	103.6(30)	101.8(16)	H(5)-B(5)-H(9)	94.9(62)	100.8(28)
B(1)-B(3)-H(3)	116.3(34)	116.6(24)	H(8)-B(5)-H(9)	107.6(83)	112.0(28)
B(1)-B(3)-H(4)	117.0(44)	119.8(22)	B(4)-H(5)-B(5)	90.9(46)	87.7(28)

(*ii*) Ligand

	(1)	(2)		(1)	(2)
B(1)-P(1)-C(1)	117.1(4)	117.4(2)	C(19)-P(2)-C(25)	106.5(4)	
B(1)-P(1)-C(7)	119.4(4)	113.9(2)	C(19)-P(2)-C(26)		103.9(2)
B(1)-P(1)-C(25)	104.1(4)	114.9(2)	P(1)-C(1)-C(2)	116.1(6)	119.3(3)
C(1)-P(1)-C(7)	103.8(3)	103.1(2)	P(1)-C(1)-C(6)	123.9(6)	121.9(3)
C(1)-P(1)-C(25)	107.9(4)	101.4(2)	P(1)-C(7)-C(8)	119.2(6)	118.3(3)
C(7)-P(1)-C(25)	103.2(4)	104.2(2)	P(1)-C(7)-C(12)	120.4(6)	123.7(3)
B(2)-P(2)-C(13)	112.6(4)	112.3(2)	P(2)-C(13)-C(14)	119.2(7)	122.2(3)

Table 3. (*continued*)

(*ii*) Ligand

	(1)	(2)		(1)	(2)
B(2)-P(2)-C(19)	118.2(4)	113.5(2)	P(2)-C(13)-C(18)	120.3(7)	118.6(3)
B(2)-P(2)-C(25)	103.5(4)		P(2)-C(19)-C(20)	116.3(7)	119.7(3)
B(2)-P(2)-C(26)		111.0(2)	P(2)-C(19)-C(24)	123.7(6)	121.1(3)
C(13)-P(2)-C(19)	106.6(4)	108.3(2)	P(1)-C(25)-P(2)	106.8(4)	
C(13)-P(2)-C(25)	109.0(4)		P(1)-C(25)-C(26)		115.0(2)
C(13)-P(2)-C(26)		107.4(2)	P(2)-C(26)-C(25)		110.9(3)

(*iii*) Phenyl rings

B_5H_9·dppm (1) 116.7(10)—122.1(8); weighted average 119.18
B_5H_9·dppe (2) 117.9(4)—121.5(5); weighted average 119.99

Å and 1.578(8) Å ($B-NH_3$) in BH_3·NMe_3 and NH_3·BH_2·NCS respectively.[23] Distances and angles in the ligand are normal, and there is no evidence of strain.

Boron Polyhedra.—In forming the skeletal arrangements in compounds (1) and (2) the apical hydrogen atom of B_5H_9 has migrated to a basal position following the introduction of four bonding electrons from the phosphorus atoms into the molecular orbitals of the B_5 polyhedron. With nine skeletal electron pairs to accommodate in the *hypho*-B_5 skeleton, the five boron atoms should occupy all but three vertices of an eight-vertex polyhedron according to the rules of Wade[14] and Rudolph. Although the dodecahedron is the most common eight-vertex polyhedron, the present B_5 geometry more closely resembles a hexagonal bipyramid with B(1) at the apex, missing two *trans* equatorial atoms and the other apex. This has a centre to apex height of 0.64 Å and edge lengths of 1.81 Å (equatorial) and 1.77 Å (apex to base) for (1); the corresponding values in (2) are 0.69, 1.82, and 1.78 Å. The angle between the opposite triangular B_3 faces is 130.4° (1), and 126.5° (2) compared with angles of 90—91° between opposite faces in B_5H_9.

In each molecule of (3) the basal boron atom bonded to the tmen ligand becomes, on rearrangement, singly bonded [B(1)-B(2) 1.699 Å average] to the apical boron atom of the B_4H_8 and is separated from the basal atoms B(3) and B(5) by non-bonded contact distances of 2.708 Å [B(2) · · · B(3)] and 2.721 Å [B(2) · · · B(5)]. Within the triangular faces of the two B_4H_8 groups, the B-B distances range from 1.699 to 1.835 Å although, interestingly, the shortest is B(1)-B(4) (1.700 Å average) suggesting a possible three-centre system, B(2)-B(1)-B(4). The arrangement of hydrogen atoms bears some similarity to the original B_5H_9, with B-H single bonds still occurring at B(1) and B(4) [BH_2 groups at B(3) and B(5)]. The two hydrogen bridges are within experimental error symmetric (average B-H 1.32 Å and B-H-B 84°), although the individual values do seem to indicate that there is some difference between the bridge to H(5) compared to that to H(7). The parent polyhedron for (3) can again be regarded as a hexagonal bypyramid with the angles B(3)-B(4)-B(5) = 107.9(6)° and 107.5(5)° in the two independent molecules, slightly smaller than the ideal value of 120°. The dihedral angles between the faces B(1),B(3),B(4) and B(1),B(3),B(5) (129.4 and 127.4°) are, however, higher than the value of 118.1° found between analogous faces of B_4H_{10}.[20]

In the structure of (4), the open nature of the framework makes a match with a B_7 polyhedron easy, but not very discriminating.

Discussion of the Structures.—The most striking result of the structural study is the existence of isomeric forms of the B_5H_9·L^2 species (L^2 = dppm, dppe, and tmen).

In comparing compounds (1) and (2) with (3) and (4), it could be expected that an open *hypho*-framework would be rather flexible and might not correspond precisely to the rigid geometry of the corresponding closed parent polyhedron. It is somewhat unexpected to find it capable of the gross rearrangements observed here. In understanding this, one possible explanation is steric, that the chelating bisphosphine ligand is unable to co-ordinate both atoms to a single small boron atom. This is supported by the evidence noted above for strain in the ligand, but on balance it is probably unlikely, as the P-B distances are no shorter than those that might be found with, for example, carbon in the ring. Alternatively, the ability of phosphorus compared with nitrogen to accept electron density into its empty 3*d* orbitals might account for the bridging mode of the phosphine ligands and the preferential co-ordination of a phosphorus atom at the apical position (especially as in B_5H_9 there is a residual negative charge at the apical boron atom).[24] Since any electron density removed by the phosphorus atoms can be further delocalised in phenyl ring orbitals, this process could be very effective.

Since nitrogen has no low-lying *d* orbitals, no d_π character can be associated with the B-N bonds. Hence the co-ordination of the ligand tmen in chelating mode at a basal position could be predicted. The different framework arrangement in (3) then reflects a need to delocalise the greater electron density left on the B_5 skeleton by the tmen. Part of this electron density is located in the short B(1)-B(2) bond which is close to a two-centre, two-electron bond rather than the three-centre, three-electron bonds in the triangular faces of the frameworks in (1) and (2). The integral B_4 unit in (3) may be better at delocalising the remaining framework electrons than the two three-centre systems in (1) and (2) connected *via* the apical atom. Similar arguments apply to (4), and lead to the prediction that the corresponding bis-phosphine complex should have base-apex co-ordination.

Further support for the suggestion that the *d* orbitals on phosphorus are involved in charge delocalisation can be seen from electron diffraction measurements on monosubstituted pentaboranes, B_5H_8X (X = SiH_3 or CH_3).[25] With the silyl compounds, there is a very significant shortening of the B-Si bond length when the substituent is apical [1.981(5) *cf.* 2.006(4) Å], whilst in the corresponding methyl-substituted derivatives there is no difference in B-C lengths [1.595(5) *cf.* 1.592(5) Å] even though, in the latter compounds, it is known that the 2-substituted isomer is chemically more stable. Both B_5H_8Me-1 and $B_5H_7Me_2$-1,2 rearrange to products with the methyl groups basal due to the negative charge at the apex. The absence of a 2,4-isomer in the rearrangement of $B_5H_7Me_2$-1,2 is attributable to H(methyl) · · · H(bridge) repulsions in the intermediate for the rearrangement.[2,26] The shortening of the apical B-Si bond is consistent with the suggestion that

Table 4. Bond distances (Å) and bond angles (°), with standard deviations in parentheses, for B_5H_9·tmen (3)

(*a*) Distances

(*i*) B_5H_9 moiety

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
N(1)-B(2)	1.677(7)	1.689(7)	B(1)-H(1)	1.111(45)	1.033(46)
N(2)-B(2)	1.651(7)	1.673(7)	B(2)-H(2)	1.071(33)	1.102(40)
B(1)-B(2)	1.700(9)	1.697(8)	B(3)-H(3)	1.003(59)	1.109(39)
B(1)-B(3)	1.804(10)	1.824(10)	B(3)-H(4)	1.192(54)	1.133(42)
B(1)-B(4)	1.701(10)	1.699(10)	B(3)-H(5)	1.418(51)	1.303(53)
B(1)-B(5)	1.825(10)	1.835(10)	B(4)-H(5)	1.271(50)	1.456(51)
B(3)-B(4)	1.723(13)	1.742(11)	B(4)-H(6)	1.026(46)	1.040(47)
B(4)-B(5)	1.778(11)	1.789(11)	B(4)-H(7)	1.264(61)	1.252(49)
B(2) · · · B(3)	2.720(10)	2.696(10)	B(5)-H(7)	1.272(60)	1.297(49)
B(2) · · · B(5)	2.726(10)	2.716(9)	B(5)-H(8)	1.038(49)	1.029(52)
B(3) · · · B(5)	2.830(12)	2.848(11)	B(5)-H(9)	1.301(51)	1.160(45)

(*ii*) Ligand

Molecule 1				Molecule 2			
N(11)-C(11)	1.515(8)	C(13)-H(131)	0.95(5)	N(21)-C(21A)	1.432(13)	N(21)-C(21B)	1.524(13)
N(11-C(12)	1.488(7)	C(13)-H(132)	1.27(5)	N(21)-C(22A)	1.464(13)	N(21)-C(22B)	1.570(14)
N(11)-C(13)	1.508(8)	C(14)-H(141)	0.99(4)	N(21)-C(23A)	1.511(13)	N(21)-C(23B)	1.488(15)
N(12)-C(14)	1.485(8)	C(14)-H(142)	1.34(6)	N(22)-C(24A)	1.430(17)	N(22)-C(24B)	1.599(15)
N(12)-C(15)	1.494(9)	C(15)-H(151)	0.97(16)	N(22)-C(25A)	1.652(15)	N(22)-C(25B)	1.372(17)
N(12)-C(16)	1.499(8)	C(15)-H(152)	0.94(5)	N(22)-C(26A)	1.486(15)	N(22)-C(26B)	1.526(15)
C(13)-C(14)	1.457(9)	C(15)-H(153)	1.10(5)	C(23A)-C(24A)	1.596(20)		
C(11)-H(111)	1.06(5)	C(16)-H(161)	0.89(4)				
C(11)-H(112)	1.03(5)	C(16)-H(162)	0.84(6)				
C(11)-H(113)	0.91(3)	C(16)-H(163)	1.09(5)				
C(12)-H(121)	1.06(5)						
C(12)-H(122)	0.97(4)						
C(12)-H(123)	1.19(9)						

(*b*) Angles

(*i*) B_5H_9 moiety

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
N(1)-B(2)-N(2)	97.9(4)	96.3(4)	H(3)-B(3)-H(4)	110.4(39)	126.2(27)
N(1)-B(2)-N(1)	115.0(4)	115.1(4)	H(3)-B(3)-H(5)	104.5(37)	91.4(30)
N(2)-B(2)-B(1)	116.7(4)	115.5(4)	H(4)-B(3)-H(5)	103.5(33)	106.8(27)
B(2)-B(1)-B(3)	101.8(5)	99.9(4)	B(1)-B(4)-H(5)	116.3(23)	107.0(20)
B(2)-B(1)-B(4)	144.7(5)	143.3(5)	B(1)-B(4)-H(6)	123.2(25)	118.2(22)
B(2)-B(1)-B(5)	101.2(4)	100.5(4)	B(1)-B(4)-H(7)	105.2(27)	108.2(22)
B(3)-B(1)-B(4)	58.8(4)	59.1(4)	B(3)-B(4)-H(5)	53.8(23)	47.1(20)
B(3)-B(1)-B(5)	102.5(5)	102.2(5)	B(3)-B(4)-H(6)	128.7(25)	126.8(24)
B(4)-B(1)-B(5)	60.4(4)	60.7(4)	B(3)-B(4)-H(7)	115.0(26)	120.1(22)
B(1)-B(3)-B(4)	57.6(4)	56.9(4)	B(5)-B(4)-H(5)	125.3(23)	113.7(18)
B(1)-B(4)-B(3)	63.6(5)	64.0(4)	B(5)-B(4)-H(6)	120.2(25)	120.5(24)
B(1)-B(4)-B(5)	63.2(4)	63.4(4)	B(5)-B(4)-H(7)	45.7(27)	46.5(22)
B(1)-B(5)-B(4)	56.3(4)	55.9(4)	H(5)-B(4)-H(6)	104.9(33)	120.1(30)
B(3)-B(4)-B(5)	107.9(6)	107.5(5)	H(5)-B(4)-H(7)	91.6(36)	89.9(29)
B(2)-B(1)-H(1)	116.2(23)	114.5(25)	H(6)-B(4)-H(7)	111.2(36)	109.4(32)
B(3)-B(1)-H(1)	120.3(22)	117.6(23)	B(3)-H(5)-B(4)	79.7(28)	78.1(29)
B(4)-B(1)-H(1)	99.0(23)	102.1(25)	B(1)-B(5)-H(7)	98.2(28)	98.9(22)
B(5)-B(1)-H(1)	112.4(23)	119.1(24)	B(1)-B(5)-H(8)	121.1(26)	115.5(30)
N(1)-B(2)-H(2)	100.9(17)	105.2(19)	B(1)-B(5)-H(9)	107.9(21)	121.6(22)
N(2)-B(2)-H(2)	102.2(18)	108.0(20)	B(4)-B(5)-H(7)	45.3(28)	44.4(22)
B(1)-B(2)-H(2)	120.7(18)	114.8(20)	B(4)-B(5)-H(8)	114.6(27)	124.4(28)
B(1)-B(3)-H(3)	107.7(28)	103.0(20)	B(4)-B(5)-H(9)	120.6(20)	117.2(23)
B(1)-B(3)-H(4)	125.2(26)	117.7(19)	H(7)-B(5)-H(8)	109.3(27)	98.3(35)
B(1)-B(3)-H(5)	103.3(20)	107.5(21)	H(7)-B(5)-H(9)	94.4(32)	106.2(30)
B(4)-B(3)-H(3)	123.9(30)	120.3(20)	H(8)-B(5)-H(9)	120.1(33)	111.8(36)
B(4)-B(3)-H(4)	121.6(26)	111.2(19)	B(4)-H(7)-B(5)	89.1(39)	89.1(31)
B(4)-B(3)-H(5)	46.5(20)	54.9(22)			

(*ii*) Ligand

Molecule 1							
B(12)-N(11)-C(11)	114.5(4)	H(121)-C(12)-H(123)	112.5(50)	N(11)-C(13)-C(14)	106.7(5)	N(12)-C(15)-H(151)	114.4(36)
B(12)-N(11)-C(12)	101.1(4)	H(122)-C(12)-H(123)	88.4(48)	N(12)-C(14)-C(13)	106.7(5)	N(12)-C(15)-H(152)	110.1(30)
B(12)-N(11)-C(13)	107.0(4)	N(11)-C(13)-H(131)	114.0(31)	N(11)-C(11)-H(111)	109.2(21)	N(12)-C(15)-H(153)	102.1(27)
C(11)-N(11)-C(12)	107.5(4)	N(11)-C(13)-H(132)	97.6(23)	N(11)-C(11)-H(112)	101.8(29)	H(151)-C(15)-H(152)	111.8(48)
C(11)-N(11)-C(13)	107.8(5)	C(14)-C(13)-H(131)	117.4(32)	N(11)-C(11)-H(113)	107.8(26)	H(151)-C(15)-H(153)	116.5(44)

Table 4. (*continued*)

(*ii*) Ligand

Molecule 1

C(12)-N(11)-C(13)	111.0(4)	C(14)-C(13)-H(132)	105.2(21)	H(111)-C(11)-H(112)	116.1(33)	H(152)-C(15)-H(153)	100.9(39)
B(12)-N(12)-C(14)	103.8(4)	H(131)-C(13)-H(132)	113.7(37)	H(111)-C(11)-H(113)	106.7(35)	N(12)-C(16)-H(161)	112.0(27)
B(12)-N(12)-C(15)	113.5(5)	N(12)-C(14)-H(141)	113.4(20)	H(112)-C(11)-H(113)	114.2(39)	N(12)-C(16)-H(162)	97.7(45)
B(12)-N(12)-C(16)	110.8(4)	N(12)-C(14)-H(142)	114.8(23)	N(11)-C(12)-H(121)	117.9(26)	N(12)-C(16)-H(163)	107.7(25)
C(14)-N(12)-C(15)	112.2(5)	C(13)-C(14)-H(141)	114.5(21)	N(11)-C(12)-H(122)	105.4(24)	H(161)-C(16)-H(162)	117.6(51)
C(14)-N(12)-C(16)	107.6(4)	C(13)-C(14)-H(142)	95.6(23)	N(11)-C(12)-H(123)	104.8(42)	H(161)-C(16)-H(163)	94.4(37)
C(15)-N(12)-C(16)	108.8(5)	H(141)-C(14)-H(142)	110.6(33)	H(121)-C(12)-H(122)	122.9(35)	H(162)-C(16)-H(163)	127.6(52)

Molecule 2

	Conformation			Conformation	
	A	B		A	B
B(22)-N(21)-C(21)	114.1(5)	114.6(6)	B(22)-N(22)-C(25)	102.9(6)	116.3(8)
B(22)-N(21)-C(22)	111.3(6)	106 4(6)	B(22)-N(22)-C(26)	119.8(6)	110.0(6)
B(22)-N(21)-C(23)	101.0(5)	110.8(6)	C(24)-N(22)-C(25)	112.3(8)	106.7(9)
C(21)-N(21)-C(22)	110.9(7)	105.3(7)	C(24)-N(22)-C(26)	105.4(9)	109.0(8)
C(21)-N(21)-C(23)	111.2(7)	108.4(8)	C(25)-N(22)-C(26)	103.4(8)	111.9(9)
C(22)-N(21)-C(23)	107.8(7)	111.3(8)	N(21)-C(23)-C(24)	104.2(9)	103.5(10)
B(22)-N(22)-C(24)	112.8(7)	102.2(6)	N(22)-C(24)-C(23)	102.6(11)	103.9(10)

Table 5. Angles between least-squares planes and lines and displacements of atoms from them

(*a*) B_5H_9·dppm (1)

Plane	Defining atoms	Plane	Defining atoms	Line	Defining atoms
1	B(1), B(2), B(3)	6	P(1), P(2), B(1), B(2)	11	P(1)-C(1)
2	B(1), B(4), B(5)	7	C(1)—C(6)	12	P(1)-C(7)
3	B(1), B(2), B(5)	8	C(7)—C(12)	13	P(2)-C(13)
4	B(1), B(3), B(4)	9	C(13)—C(18)	14	P(2)-C(19)
5	B(2), B(3), B(4), B(5)	10	C(19)-C(24)		

Angles (°) between planes or lines

(1)—(2)	130.43	(2)—(3)	40.23	(3)—(5)	35.80	(7)—(8)	84.27
(1)—(3)	45.05	(2)—(4)	43.21	(3)—(6)	61.16	(9)—(10)	85.61
(1)—(4)	39.40	(2)—(5)	24.51	(4)—(5)	34.35	(7)—(11)	0.31
(1)—(5)	25.06	(2)—(6)	73.64	(4)—(6)	63.24	(8)—(12)	1.59
(1)—(6)	73.94	(3)—(4)	109.85	(5)—(6)	89.58	(9)—(13)	0.75
(10)—(14)	0.35						

Significant atomic displacements (Å)

Plane 5:	B(1)	0.635	Plane 7:	P(1)	−0.022
	P(1)	1.532	Plane 8:	P(1)	−0.059
	P(2)	2.902	Plane 9:	P(2)	−0.027
Plane 6:	C(25)	0.556	Plane 10:	P(2)	0.001

(*b*) B_5H_9·dppe (2)

Plane	Defining atoms	Plane	Defining atoms	Line	Defining atoms
1	B(1), B(2), B(3)	6	P(1), P(2), B(1), B(2)	11	P(1)-C(2)
2	B(1), B(4), B(5)	7	C(1)—C(6)	12	P(1)-C(7)
3	B(1), B(2), B(5)	8	C(7)—C(12)	13	P(2)-C(13)
4	B(1), B(3), B(4)	9	C(13)—C(18)	14	P(2)-C(19)
5	B(2), B(3), B(4), B(5)	10	C(19)—C(24)		

Angles (°) between planes or lines

(1)—(2)	126.45	(2)—(3)	43.38	(3)—(5)	37.25	(7)—(8)	80.32
(1)—(3)	45.64	(2)—(4)	45.20	(3)—(6)	58.05	(9)—(10)	70.83
(1)—(4)	44.55	(2)—(5)	26.18	(4)—(5)	37.19	(7)—(11)	6.65
(1)—(5)	27.38	(2)—(6)	73.79	(4)—(6)	61.01	(8)—(12)	48.86
(1)—(6)	76.31	(3)—(4)	105.55	(5)—(6)	88.52	(9)—(13)	3.19
(10)—(14)	5.67						

Significant atom displacements (Å)

Plane 5:	B(1)	−0.690	Plane 7:	P(1)	0.221
	P(1)	−2.637	Plane 8:	P(1)	0.168
	P(2)	−1.287	Plane 9:	P(2)	0.104
Plane 6:	C(25)	0.050	Plane 10:	P(2)	−0.180
	C(26)	0.829			

Table 5. (*continued*)

(*c*) B_5H_9·tmen (3) *

Plane	Defining atoms	Plane	Defining atoms
1	N(11), B(12), N(12) [N(21), B(22), N(22)]	5	B(11), B(13), B(15) [B(21), B(23), B(25)]
2	B(11), B(12), B(14) [B(21), B(22), B(24)]	6	B(12), B(13), B(14) [B(22), B(23), B(24)]
3	B(11), B(13), B(14) [B(21), B(23), B(24)]	7	B(12), B(14), B(15) [B(22), B(24), B(25)]
4	B(11), B(14), B(15) [B(21), B(24), B(25)]	8	B(13), B(14), B(15) [B(23), B(24). B(25)]

Angles (°) between planes

(1)—(2)	87.9 [89.6]	(2)—(7)	75.1 [76.0]	(3)—(8)	46.5 [47.5]	(5)—(7)	55.1 [56.8]
(2)—(3)	63.8 [62.1]	(2)—(8)	89.2 [88.2]	(4)—(5)	42.6 [43.7]	(5)—(8)	76.6 [78.5]
(2)—(4)	65.6 [66.1]	(3)—(4)	129.3 [128.2]	(4)—(7)	19.2 [19.9]	(7)—(7)	148.4 [147.8]
(2)—(5)	90.0 [89.1]	(3)—(5)	43.6 [44.5]	(4)—(8)	46.7 [47.8]	(6)—(8)	27.6 [28.1]
(2)—(6)	73.2 [71.8]	(3)—(6)	18.9 [19.4]	(5)—(6)	55.5 [57.0]	(7)—(8)	27.5 [27.9]

Significant atomic displacements (Å)

Plane 1:	C(13)	0.18 [C (23A), 0.85; C(23B), 0.02]	Plane 2:	B(13)	1.38 [B(23), −1.38]
	C(14)	0.71 [C (24A), 0.23; C (24B), 0.70]		B(15)	−1.45 [B(25), 1.46]
Plane 2:	N(11)	−1.26 [N(21), −1.28]	Plane 5:	B(12)	1.61 [B(22), 1.63]
	N(12)	1.26 [N(22), 1.23]		B(14)	−1.00 [B(24), −1.02]
	C(13)	−0.63 [C (23A), −0.69; C (23B), −0.77]	Plane 8:	B(11)	−1.11 [B(21), −1.13]
	C(14)	0.59 [C (24A), 0.75; C (24B), 0.53]		B(12)	−1.26 [B(22), −1.27]

* Atoms and values in square brackets relate to Molecule 2.

Table 6. Torsion angles (°) * in the chelate rings

(*a*) B_5H_9·dppm (1)

P(1)-C(25)-P(2)-B(2)	+32.98
C(25)-P(2)-B(2)-B(1)	−26.23
P(2)-B(2)-B(1)-P(1)	−9.46
B(2)-B(1)-P(1)-C(25)	−10.51
B(1)-P(1)-C(25)-P(2)	+27.42

(*b*) B_5H_9·dppe (2)

P(1)-C(25)-C(26)-P(2)	−66.10
C(25)-C(26)-P(2)-B(2)	+64.74
C(26)-P(2)-B(2)-B(1)	−28.48
P(2)-B(2)-B(1)-P(1)	−0.76
B(2)-B(1)-P(1)-C(25)	−2.34
B(1)-P(1)-C(25)-C(26)	+56.70

(*c*) B_5H_9·tmen (3)

Molecule 1		Molecule 2			
B(12)-N(11)-C(13)-C(14)	−17.82	B(22)-N(21)-C(23A)-C(24A)	−48.56	C(23A)-C(24A)-N(22)-B(22)	−17.50
N(11)-C(13)-C(14)-N(12)	−39.28	B(22)-N(21)-C(23A)-C(24B)	−35.32	C(23A)-C(24B)-N(22)-B(22)	+9.28
C(13)-C(14)-N(12)-B(12)	+43.82	B(22)-N(21)-C(23B)-C(24A)	+8.12	C(23B)-C(24A)-N(22)-B(22)	+15.99
C(14)-N(12)-B(12)-N(11)	−29.42	B(22)-N(21)-C(23B)-C(24B)	+28.42	C(23B)-C(24B)-N(22)-B(22)	+47.28
N(12)-B(12)-N(11)-C(13)	+7.34	N(21)-C(23A)-C(24A)-N(22)	+42.46	C(24A)-N(22)-B(22)-N(21)	−10.11
		N(21)-C(23A)-C(24B)-N(22)	+17.04	C(24B)-N(22)-B(22)-N(21)	−26.79
		N(21)-C(23B)-C(24A)-N(22)	−14.98	N(22)-B(22)-N(21)-C(23A)	+34.97
		N(21)-C(23B)-C(24B)-N(22)	−46.75	N(22)-B(22)-N(21)-C(23B)	+0.63

* Defined as in R. Bucourt, *Topics Stereochem.*, 1974, **8**, 159.

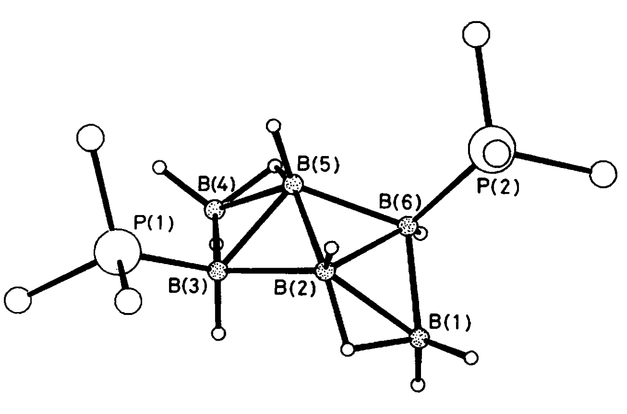


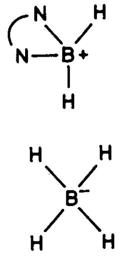
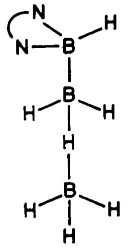
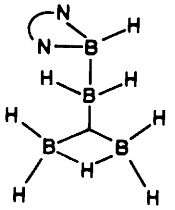
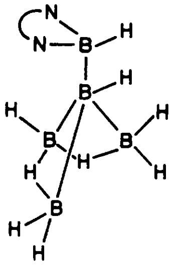
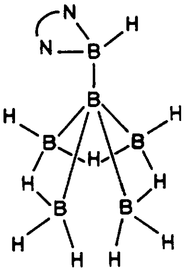
Figure 6. The structure of B_6H_{10}·2PMe$_3$, redrawn from ref. 15, omitting the methyl hydrogen atoms

the negative charge at the apex is delocalised into the empty Si 3*d* orbitals, giving a partial double bond at the apical position.

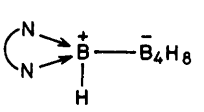
We can compare the rearrangements of B_5H_9 with those found for B_6H_{10} when it is converted into B_6H_{10}·2PMe$_3$.[15] The resulting structure (Figure 6) can be derived from the attachment of the two PMe$_3$ groups to adjacent equatorial boron atoms, followed by breaking of this B–B bond. An apex–base B–B bond also has to break before the boron skeleton can flatten to the structure observed. This open framework resembles the equatorial belt of an icosahedron rather than occupying all but three vertices of a nine-vertex polyhedron, such as a tricapped trigonal prism. It is noticeable that the PMe$_3$ groups are well separated, and we can expect B_6H_{10}·dppe (or B_6H_{10}·dppm) to have a significantly different structure.

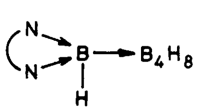
The atomic arrangement of the boron atoms in B_5H_9·tmen (3) is still of *hypho*-type, although the structure can be interpreted in two different ways: a zwitterionic form (I) and a valence structure (II) (N–N = tmen), depending on the view of the isolated B–B bond. The B_4 fragment can be seen as

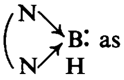
Table 7. Known or postulated structures for tmen adducts of the boron hydrides

Full formula	$[BH_2{\cdot}tmen]^+[BH_4]^-$	$B_3H_7{\cdot}tmen$	$B_4H_8{\cdot}tmen$	$B_5H_9{\cdot}tmen$	$B_6H_{10}{\cdot}tmen$
Status	Known with other ligands and as individual ions		This work	This work	Postulated
Formulation *	BH_5L	B_2H_6L	B_3H_7L	B_4H_8L	B_5H_9L
No. of H atoms on apical boron	4	3 (2 terminal, 1 bridging)	2 terminal	1 terminal	0
Structure					

* L = BH·tmen.

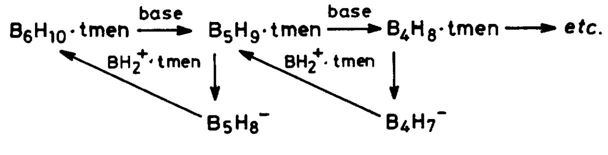

(I)


(II)

$B_4H_9^-$, either by considering (N–N)BH^+ as a one-electron donor group equivalent to H in form (I), or by replacing a ligand L by H^- in $L \longrightarrow B_4H_8$. Paradoxically, this is an *arachno*-form. The reason is, that with the isolated HB·tmen group, we have removed two skeletal electron pairs; this group is formally equivalent to BH_3^{2-}. As $B_4H_8{\cdot}$tmen (4) also has a structure with an isolated boron atom, we can suggest that tmen is always a chelating ligand, donating to one atom. By regarding this group  as a ligand L, itself donating to an *arachno*-borane, we can place the known or postulated tmen–borane adducts in sequence (see Table 7).

An obvious structural change along the series concerns the apical boron atom. Starting with no terminal hydrogen atoms in $B_6H_{10}{\cdot}$tmen, these are added one by one until the apex is a saturated BH_4^-, and the adduct has dissociated into ions.

This series suggests a systematic route to borane interconversions, as well as being a plausible geometric sequence. Degradation with base, *e.g.* methanol, has the effect of removing one boron atom, converting, for example, $B_5H_9{\cdot}$tmen to $B_4H_8{\cdot}$tmen. It is possible to add a boron (cluster expansion) atom by the reaction between borane anions and B_2H_6 and it may be possible to do this directly within the *hypho*-sequence by using $BH_2^+{\cdot}$tmen instead of B_2H_6. The resulting reactions would form a sequence of the type shown. It remains to demonstrate the practicality of the cluster expansion step.



Acknowledgements

We thank S.R.C. for a research studentship (to J. F. S.), and post-doctoral support (to G. H. and H. M. C.). We also thank Dr. R. E. Williams for a generous gift of pentaborane-(9).

References

1 D. F. Gaines, *Acc. Chem. Res.*, 1973, **6**, 416 and refs. therein.
2 M. A. Nelson and G. Kodama, *Inorg. Chem.*, 1981, **20**, 3579.
3 N. W. Alcock, H. M. Colquhoun, G. Harran, J. F. Sawyer, and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1977, 368.
4 N. E. Miller, H. C. Miller, and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 866.
5 C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1973, 179.
6 A. B. Burg, *J. Am. Chem. Soc.*, 1957, **79**, 2129.
7 A. V. Fratini, G. W. Sullivan, M. L. Denniston, K. R. Hertz, and S. G. Shore, *J. Am. Chem. Soc.*, 1974, **96**, 3013.
8 M. Kameda and G. Kodama, *Inorg. Chem.*, 1980, **19**, 2288.
9 G. Kodama, *J. Am. Chem. Soc.*, 1970, **92**, 3482.
10 G. Kodama, U. Engelhardt, C. Lafrenz, and R. W. Parry, *J. Am. Chem. Soc.*, 1972, **94**, 407.
11 E. R. Lory and D. M. Ritter, *Inorg. Chem.*, 1970, **9**, 1847.
12 R. K. Hertz, M. L. Denniston, and S. G. Shore, *Inorg. Chem.*, 1978, **17**, 2673.
13 H. M. Colquhoun, *J. Chem. Res.*, 1978, 451.
14 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
15 M. Mangion, R. K. Hertz, M. L. Denniston, J. R. Long, W. R. Clayton, and S. G. Shore, *J. Am. Chem. Soc.*, 1976, **98**, 449.
16 C. G. Savory and M. G. H. Wallbridge, unpublished work.
17 P. Main and M. M. Woolfson, MULTAN computer program, University of York, 1972.
18 J. M. Stewart, *X*-RAY 72, Technical Report TR-192, Computer Science Centre, University of Maryland, 1972.
19 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
20 E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, 1957, **27**, 209.

21 A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, 1975, **31**, 1630.
22 P. H. Clippard, J. C. Hansen, and R. C. Taylor, *J. Cryst. Mol. Struct.*, 1971, **1**, 363.
23 C. Glidewell, *Inorg. Chim. Acta*, 1974, **11**, 257 and refs. therein.
24 W. N. Lipscomb, 'Boron Hydrides,' W. A. Benjamin Inc., New York, 1963, ch. 3, p. 110.
25 J. D. Wieser, D. C. Moody, J. C. Huffman, R. L. Hilderbrand, and R. Schaeffer, *J. Am. Chem. Soc.*, 1975, **97**, 1074.
26 L. B. Friedman and W. N. Lipscomb, *Inorg. Chem.*, 1966, **5**, 1752.

Received 23rd *March* 1982; *Paper* 2/508