Polyhedral Phosphaborane Chemistry: Crystal and Molecular Structure of the Diphenylphosphido-bridged *arachno*-Decaboranyl Cluster Compound $[PMePh_3]$-$[6,9\text{-}\mu\text{-}(PPh_2)B_{10}H_{12}]$ *

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$[PMePh_3][B_{10}H_{12}(PPh_2)]$ crystallizes in the orthorhombic space group $Pca2_1$, with a = 3 316.9(4), b = 1 397.2(2), c = 1 469.6(1) pm, and Z = 8; the structure has been solved and refined to R = 0.0673, R' = 0.0743, for 4 104 independent reflections. The crystal contains two nearly identical $[B_{10}H_{12}(PPh_2)]^-$ units in the unit cell. The ten-boron cage structure of the $[B_{10}H_{12}(PPh_2)]^-$ anion resembles that of $[B_{10}H_{14}]^{2-}$, but it has a bridging PPh_2 group between the B(6) and B(9) positions instead of *endo*-terminal hydrides. The bonding about phosphorus is approximately tetrahedral with phosphorus–boron bond lengths averaging 189.5 pm. The unusual 'remote' *arachno* 11-vertex structure is briefly discussed in comparison with some other isoelectronic *arachno*-type 11-vertex species.

Multielement n.m.r. spectroscopy has suggested that the anionic species $[B_{10}H_{12}(PPh_2)]^-$ has an *arachno*-decaboranyl structure in which opposing 6,9-positions on the open face are bridged by the PPh_2 moiety.[1] We now report the confirmation of this structure by a single-crystal *X*-ray diffraction analysis of the triphenylphosphonium salt $[PMePh_3][B_{10}H_{12}(PPh_2)]$.

Experimental

Preparation.—The neutral phosphinoborane 5,6-μ-(PPh_2)-$B_{10}H_{13}$ was made from $B_{10}H_{14}$ and $PClPh_2$ by published methods.[2] Deprotonation was effected by treatment of a stirred aqueous suspension of $B_{10}H_{13}(PPh_2)$ with an excess of dilute aqueous sodium hydroxide solution (total [NaOH] *ca.* 0.3 mol dm^{-3}). After 3 h the suspension was filtered to remove the insoluble unreacted $B_{10}H_{13}(PPh_2)$. Cation exchange was effected by treatment of the filtrate with a saturated aqueous solution of $[PMePh_3]Br$ to yield $[PMePh_3][B_{10}H_{12}(PPh_2)]$ as a colourless precipitate. Crystals of this compound suitable for a single-crystal *X*-ray diffraction analysis were grown at room temperature by diffusion of cyclohexane into a solution in dichloromethane.

Crystallographic Studies.—Unit-cell and intensity data were obtained using a CAD4 diffractometer operating in the ω/2θ scan mode and using nickel-filtered Cu-K_α radiation (λ = 154.178 pm) following a procedure described elsewhere in detail.[3]

Crystal data. $C_{31}H_{40}B_{10}P_2$, M = 582.67, orthorhombic, a = 3 316.9(4), b = 1 397.2(2), c = 1 469.6(1) pm, U = 6.811 nm^3, space group $Pca2_1$, Z = 8, D_c = 1.14 g cm^{-3}, μ(Cu-K_α) = 11.99 cm^{-1}, $F(000)$ = 2 400, T = 290 K. Scan width ω = 0.85 + 0.15 tan θ, scan speeds 1.35—6.77° min^{-1}, $2.0 \leqslant \theta \leqslant 60°$. 5 891 Data were collected, 4 104 were considered observed $[I > 1.5\sigma(I)]$.

Structure solution and refinement. The structure was determined by direct methods using the SHELX program.[4] The top four peaks in the *E*-map were assigned as phosphorus atoms and these were developed into two pairs of anions and cations using successive Fourier difference maps. Once all non-hydrogen atoms had been located the structure was refined by blocked full-matrix least-squares (a cation and anion in each block) using SHELX. Only the phosphorus atoms were assigned anisotropic thermal parameters; all other non-hydrogen atoms were refined with individual isotropic thermal parameters. The phenyl rings were included in refinement as rigid bodies with hexagonal symmetry (C–C 139.5 pm). All phenyl and methyl hydrogen atoms were then included in calculated positions (C–H 108 pm) using the AFIX routine in SHELX, with each group refined with an overall isotropic thermal parameter. The hydrogen atoms on both boron cages were located in the subsequent Fourier difference map and these were refined with individual isotropic thermal parameters. The weighting scheme $1/[\sigma^2(F_o) + 0.000\,15(F_o)^2]$ was applied at the end of refinement in order to obtain acceptable agreement analyses. The final R values were R = 0.0673 and R' = 0.0743. Final atomic co-ordinates are listed in Tables 1 and 2.

Results

The solid form of $[PMePh_3][B_{10}H_{12}(PPh_2)]$ examined contained two crystallographically distinct $[B_{10}H_{12}(PPh_2)]^-$ entities in the unit cell, but the dimensions of these were nevertheless found to be very similar. Selected interatomic distances and angles for the anions are given in Tables 3 and 4 respectively; dimensions within the two distinct anionic moieties (molecule a and molecule b) are designated by the descriptors a and b and horizontal rows in the Tables contain dimensions that would be identical if each of the molecules conformed to the C_{2v} symmetry to which it approximates. A packing diagram is given in Figure 1, and a more detailed view of one of the $[B_{10}H_{12}(PPh_2)]^-$ anions (molecule b) is given in Figure 2. The numbering system is that conventionally used for the *nido*- and *arachno*-ten-vertex species $B_{10}H_{14}$ and $[B_{10}H_{14}]^{2-}$.

Discussion

The molecular structure of the $[B_{10}H_{12}(PPh_2)]^-$ anion is seen to be that of an *arachno*-decaboranyl unit bridged between the B(6) and B(9) positions by a PPh_2 unit [structure (**2**), Scheme 1]. This contrasts to the configuration of its conjugate acid precursor $B_{10}H_{13}(PPh_2)$ [structure (**1**)] which has substantial

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* Methyltriphenylphosphonium 6,9-μ-diphenylphosphido-*arachno*-decaborate.

Supplementary data available (No. SUP 56393, 10 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Non-hydrogen atom co-ordinates (× 10^4) for $[PMePh_3][B_{10}H_{12}(PPh_2)]$

Atom	*x*	*y*	*z*
P(1)	1 318(1)	4 545(2)	8 047(0.5)
P(2)	1 575(1)	5 586(2)	2 132(2)
P(3)	1 159(1)	9 659(2)	8 461(2)
P(4)	999(1)	700(2)	4 399(2)
C(111)	937(1)	4 644(4)	8 955(4)
C(112)	794(1)	5 534(4)	9 242(4)
C(113)	509(1)	5 589(4)	9 937(4)
C(114)	366(1)	4 754(4)	10 346(4)
C(115)	509(1)	3 864(4)	10 059(4)
C(116)	794(1)	3 809(4)	9 363(4)
C(121)	1 752(2)	4 134(4)	8 717(4)
C(122)	2 029(2)	4 792(4)	9 063(4)
C(123)	2 345(2)	4 480(4)	9 615(4)
C(124)	2 384(2)	3 510(4)	9 821(4)
C(125)	2 107(2)	2 852(4)	9 475(4)
C(126)	1 791(2)	3 164(4)	8 923(4)
B(1a)	1 478(4)	4 811(9)	5 613(9)
B(2a)	1 365(4)	5 843(9)	6 262(9)
B(3a)	968(4)	5 215(10)	5 811(10)
B(4a)	1 118(4)	4 017(9)	5 971(10)
B(5a)	1 780(4)	5 168(8)	6 560(8)
B(6a)	1 425(3)	5 708(8)	7 438(7)
B(7a)	918(4)	5 768(9)	6 855(9)
B(8a)	746(4)	4 489(9)	6 644(10)
B(9a)	1 158(4)	3 697(8)	7 112(9)
B(10a)	1 606(4)	3 888(8)	6 403(8)
C(211)	1 071(2)	5 708(5)	2 490(5)
C(212)	874(2)	4 985(5)	2 970(5)
C(213)	477(2)	5 117(5)	3 260(5)
C(214)	277(2)	5 972(5)	3 069(5)
C(215)	474(2)	6 696(5)	2 589(5)
C(216)	871(2)	6 564(5)	2 300(5)
C(221)	1 884(2)	6 258(3)	2 901(4)
C(222)	2 275(2)	6 507(3)	2 645(4)
C(223)	2 516(2)	7 045(3)	3 232(4)
C(224)	2 366(2)	7 335(3)	4 074(4)
C(225)	1 974(2)	7 087(3)	4 330(4)
C(226)	1 734(2)	6 549(3)	3 744(4)
C(231)	1 705(2)	4 351(4)	2 119(4)
C(232)	1 493(2)	3 752(4)	1 530(4)
C(233)	1 593(2)	2 784(4)	1 471(4)
C(234)	1 906(2)	2 416(4)	2 000(4)
C(235)	2 118(2)	3 015(4)	2 589(4)
C(236)	2 018(2)	3 982(4)	2 649(4)
C(24)	1 640(3)	6 038(7)	1 019(7)
C(311)	742(1)	10 211(3)	7 863(4)
C(312)	476(1)	9 640(3)	7 367(4)
C(313)	162(1)	10 060(3)	6 878(4)
C(314)	114(1)	11 052(3)	6 885(4)
C(315)	381(1)	11 623(3)	7 381(4)
C(316)	694(1)	11 203(3)	7 870(4)
C(321)	1 529(2)	9 547(4)	7 587(4)
C(322)	1 727(2)	10 367(4)	7 278(4)
C(323)	2 025(2)	10 292(4)	6 611(4)
C(324)	2 125(2)	9 399(4)	6 253(4)
C(325)	1 927(2)	8 579(4)	6 562(4)
C(326)	1 629(2)	8 654(4)	7 229(4)
B(1b)	967(3)	9 199(8)	10 896(8)
B(2b)	1 370(4)	9 991(9)	10 610(8)
B(3b)	1 474(3)	8 762(8)	10 692(8)
B(4b)	1 054(3)	8 231(8)	10 191(8)
B(5b)	880(3)	10 217(8)	10 229(8)
B(6b)	1 358(3)	10 396(7)	9 466(8)
B(7b)	1 716(4)	9 481(8)	9 901(8)
B(8b)	1 505(3)	8 263(8)	9 589(8)
B(9b)	1 008(3)	8 497(7)	9 016(8)
B(10b)	670(3)	9 032(8)	9 899(8)
C(411)	705(1)	1 428(3)	3 685(4)
C(412)	787(1)	1 479(3)	2 755(4)
C(413)	547(1)	2 045(3)	2 191(4)
C(414)	225(1)	2 561(3)	2 557(4)
C(415)	144(1)	2 511(3)	3 487(4)
C(416)	384(1)	1 944(3)	4 051(4)
C(421)	750(2)	−406(4)	4 607(4)
C(422)	959(2)	−1 075(4)	5 129(4)
C(423)	785(2)	−1 961(4)	5 321(4)
C(424)	402(2)	−2 178(4)	4 990(4)
C(425)	192(2)	−1 509(4)	4 468(4)
C(426)	366(2)	−623(4)	4 276(4)
C(431)	1 481(2)	459(4)	3 949(4)
C(432)	1 815(2)	967(4)	4 260(4)
C(433)	2 200(2)	734(4)	3 946(4)
C(434)	2 250(2)	−8(4)	3 321(4)
C(435)	1 915(2)	−517(4)	3 010(4)
C(436)	1 531(2)	−283(4)	3 324(4)
C(44)	1 065(4)	1 275(8)	5 497(8)

elements of *nido*-decarboranyl character.[5] The overall dimensions of the $B_{10}H_{12}$ subcluster in the anion are very similar to those of *arachno*-$[B_{10}H_{14}]^{2-}$ and related *arachno*-ten-vertex species such as $B_{10}H_{12}(SMe_2)_2$.[6,7] In particular there are bridging hydrogen atoms at the B(5)–B(10) and B(7)–B(8) positions, and the corresponding interboron distances are some 10 pm shorter than the corresponding diagnostically long *nido*-decaboranyl interboron distances of *ca.* 200 pm.[8]

The boron–phosphorus distances of *ca.* 190 pm are 3—4 pm shorter than those of the neutral precursor $B_{10}H_{13}(PPh_2)$, but the relative significance of this is difficult to assess because there are limited data for comparison. The distance of 190 pm is, however, towards the lower end of the range (188—198 pm) commonly found for tertiary phosphine ligands bound *exo* to borane and metallaborane clusters,[9–16] and is also shorter than the distances of *ca.* 193 pm found for the two-electron, two-centre σ bonds in $BH_3(PH_3)$ and $BH_3(PMe_3)$,[17,18] this may be an indication of relatively strong boron–phosphorus bonding in the $[B_{10}H_{12}(PPh_2)]^-$ anion. The phosphorus–carbon distances in the anion, at *ca.* 181 pm (mean), are somewhat longer than those in the neutral precursor (*ca.* 178 pm),[5] and slightly shorter than those in the neutral phosphine PPh_3 (*ca.* 183 pm).

The angles around phosphorus (100—115°) deviate somewhat from the ideal tetrahedral, but this deviation is not severe, and far less marked than in the neutral precursor $B_{10}H_{13}(PPh_2)$,[5] in which they range between 88 and 122°. The differences in the phosphorus binding for the two compounds are also reflected in the difference of 88 p.p.m.[1] in the ^{31}P n.m.r. nuclear shielding between the two species.

The stability of the bridged structure in $[B_{10}H_{12}(PPh_2)]^-$ must derive at least in part from the strong localizing effect of the bonds to the more electronegative phosphorus atom, although an additional factor in the overall stability will be the ideal bite-size of the ten-boron cluster manifested in the short boron–phosphorus bond lengths and the near-tetrahedral angles at the phosphorus atom.

The PB_{10} heavier-atom geometry is unusual because it has a 'remote' *arachno* configuration notionally derived by the removal of two non-adjacent vertices from a closed 13-vertex C_{2v} deltahedron, whereas conventional *arachno* configurations are derived by the removal of two adjacent vertices. Although this remote *arachno*-type configuration was postulated for many early 11-vertex metalladecaboranes, most of these are now known to have more reasonable *nido* configurations.[15] In this context it may be noted that extended Hückel molecular

Table 2. Hydrogen atom co-ordinates (× 10^4) for $[PMePh_3][B_{10}H_{12}(PPh_2)]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H(112)	905(1)	6 180(4)	8 925(4)	H(312)	513(1)	8 872(3)	7 362(4)
H(113)	399(1)	6 278(4)	10 159(4)	H(313)	−43(1)	9 618(3)	6 494(4)
H(114)	145(1)	4 797(4)	10 884(4)	H(314)	−128(1)	11 378(3)	6 506(4)
H(115)	398(1)	3 218(4)	10 375(4)	H(315)	343(1)	12 391(3)	7 386(4)
H(116)	904(1)	3 120(4)	9 141(4)	H(316)	900(1)	11 645(3)	8 254(4)
H(122)	1 999(2)	5 543(4)	8 903(4)	H(322)	1 650(2)	11 058(4)	7 555(4)
H(123)	2 559(2)	4 989(4)	9 883(4)	H(323)	2 177(2)	10 926(4)	6 371(4)
H(124)	2 629(2)	3 268(4)	10 248(4)	H(324)	2 355(2)	9 341(4)	5 736(4)
H(125)	2 138(2)	2 101(4)	9 635(4)	H(325)	2 004(2)	7 887(4)	6 284(4)
H(126)	1 577(2)	2 655(4)	8 656(4)	H(326)	1 477(2)	8 019(4)	7 468(4)
H(1a)	1 678(18)	4 746(24)	4 967(24)	H(1b)	904(15)	9 170(22)	11 609(23)
H(2a)	1 333(20)	6 544(24)	5 975(24)	H(2b)	1 485(18)	10 553(23)	11 099(24)
H(3a)	790(18)	5 273(23)	5 267(24)	H(3b)	1 664(16)	8 480(23)	11 343(23)
H(4a)	1 040(18)	3 326(24)	5 651(23)	H(4b)	943(18)	7 486(23)	10 304(24)
H(5a)	2 121(15)	5 429(22)	6 429(22)	H(5b)	706(18)	10 886(23)	10 320(23)
H(6a)	1 451(19)	6 291(24)	7 912(24)	H(6b)	1 449(14)	11 127(22)	9 333(22)
H(7a)	683(17)	6 384(23)	6 948(23)	H(7b)	2 060(16)	9 732(22)	9 925(22)
H(8a)	466(19)	4 263(23)	6 724(24)	H(8b)	1 678(17)	7 552(23)	9 455(23)
H(9a)	1 115(21)	3 109(24)	7 275(24)	H(9b)	803(17)	8 037(23)	8 532(23)
H(10a)	1 807(16)	3 438(23)	6 182(23)	H(10b)	364(18)	9 035(23)	9 927(23)
H(78a)	713(18)	5 027(23)	7 285(24)	H(78b)	1 668(17)	8 940(23)	9 067(23)
H(51a)	1 796(18)	4 326(23)	7 183(23)	H(51b)	673(16)	9 910(22)	9 517(23)
H(212)	1 028(2)	4 322(5)	3 118(5)	H(412)	1 036(1)	1 079(3)	2 472(4)
H(213)	324(2)	4 557(5)	3 631(5)	H(413)	610(1)	2 084(3)	1 471(4)
H(214)	−30(2)	6 075(5)	3 293(5)	H(414)	40(1)	2 999(3)	2 120(4)
H(215)	320(2)	7 358(5)	2 441(5)	H(415)	−105(1)	2 910(3)	3 770(4)
H(216)	1 023(2)	7 124(5)	1 928(5)	H(416)	320(1)	1 905(3)	4 771(4)
H(222)	2 392(2)	6 282(3)	1 993(4)	H(422)	1 256(2)	−907(4)	5 384(4)
H(223)	2 819(2)	7 237(3)	3 033(4)	H(423)	947(2)	−2 479(4)	5 725(4)
H(224)	2 552(2)	7 752(3)	4 528(4)	H(424)	267(2)	−2 864(4)	5 139(4)
H(225)	1 858(2)	7 312(3)	4 982(4)	H(425)	−105(2)	−1 676(4)	4 212(4)
H(226)	1 431(2)	6 356(3)	3 942(4)	H(426)	204(2)	−104(4)	3 872(4)
H(232)	1 251(2)	4 037(4)	1 120(4)	H(432)	1 777(2)	1 542(4)	4 744(4)
H(233)	1 429(2)	2 321(4)	1 015(4)	H(433)	2 459(2)	1 127(4)	4 187(4)
H(234)	1 983(2)	1 667(4)	1 954(4)	H(434)	2 547(2)	−189(4)	3 078(4)
H(235)	2 360(2)	2 729(4)	2 999(4)	H(435)	1 954(2)	−1 091(4)	2 526(4)
H(236)	2 182(2)	4 446(4)	3 105(4)	H(436)	1 271(2)	−677(4)	3 083(4)
H(241)	1 562(3)	6 788(7)	1 000(7)	H(441)	1 083(4)	733(8)	6 019(8)
H(242)	1 452(3)	5 649(7)	546(7)	H(442)	809(4)	1 734(8)	5 630(8)
H(243)	1 953(3)	5 952(7)	832(7)	H(443)	1 338(4)	1 697(8)	5 498(8)

Table 3. Selected interatomic distances (pm) for the anion $[B_{10}H_{12}(PPh_2)]^-$, with estimated standard deviations in parentheses

(*i*) Interboron distances

a	B(1)–B(3)	180.9(20)						
b		181.4(17)						
a	B(1)–B(2)	176.8(19)	B(1)–B(4)	171.4(20)	B(2)–B(3)	171.6(20)	B(3)–B(4)	176.2(20)
b		178.7(18)		172.7(17)		175.6(18)		174.2(17)
a	B(1)–B(5)	178.4(19)	B(1)–B(10)	178.6(19)	B(3)–B(7)	172.6(20)	B(3)–B(8)	175.2(21)
b		175.2(18)		178.1(17)		173.4(18)		176.9(18)
a	B(2)–B(5)	172.5(19)	B(4)–B(10)	175.0(20)	B(2)–B(7)	172.3(19)	B(4)–B(8)	171.4(21)
b		174.9(18)		174.8(17)		170.7(19)		173.9(17)
a	B(2)–B(6)	175.1(18)	B(4)–B(9)	174.1(20)				
b		177.4(18)		177.4(18)				
a	B(5)–B(6)	190.3(20)	B(6)–B(7)	189.0(18)	B(9)–B(10)	183.5(18)	B(8)–B(9)	188.8(20)
b		195.8(18)		186.0(17)		186.9(17)		188.0(17)
a	B(5)–B(10)	189.3(18)	B(7)–B(8)	190.0(20)				
b		186.0(17)		189.7(17)				

(*ii*) Other distances

a	P(1)–B(6)	188.8(13)	P(1)–B(9)	189.0(14)	B–H (terminal)	87(4)–121(5)
b	P(3)–B(6)	191.8(13)	P(3)–B(9)	188.4(12)		102(6)–121(4)
a	P(1)–C(111)	184.3(7)	P(1)–C(121)	183.7(7)	B–H (bridge)	120(4)–149(4)
b	P(3)–C(311)	181.1(6)	P(3)–C(321)	178.5(8)		133(4)–145(4)

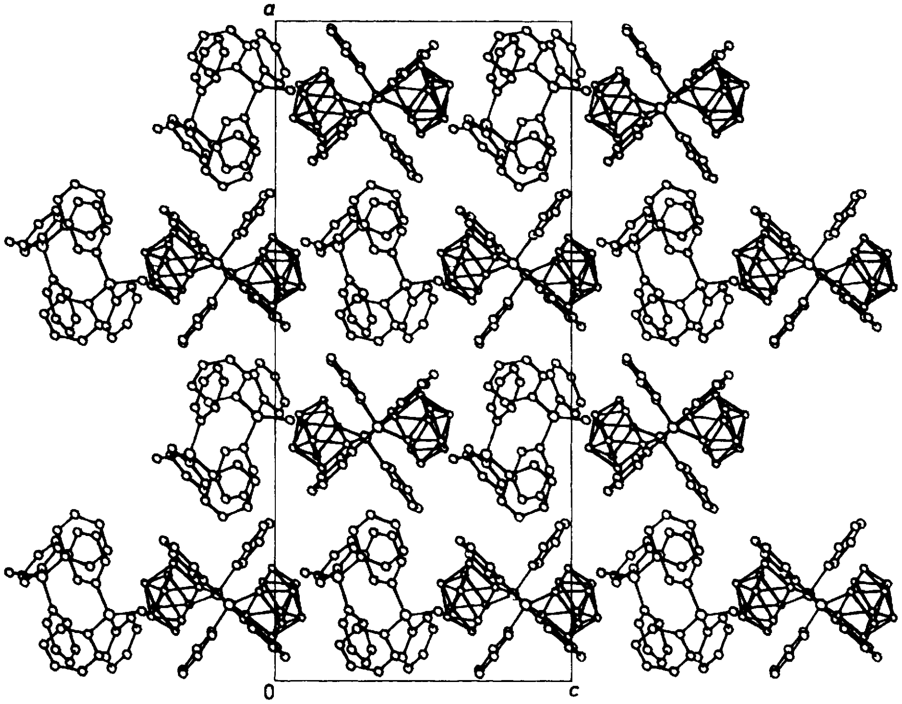


Figure 1. Packing diagram for $[PMePh_3][B_{10}H_{12}(PPh_2)]$; view direction [010]

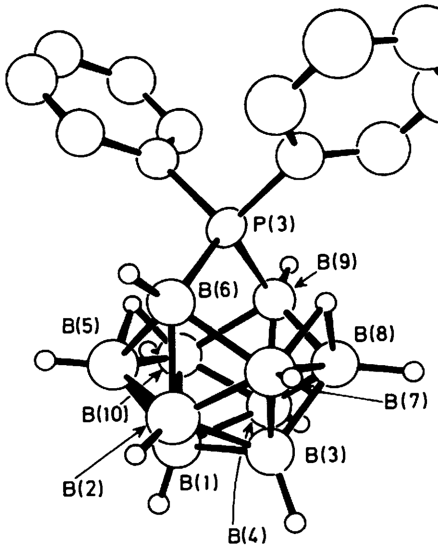
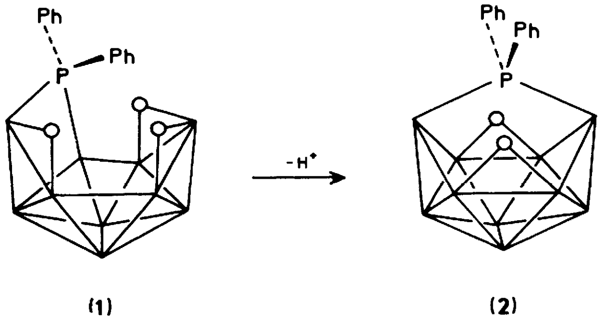
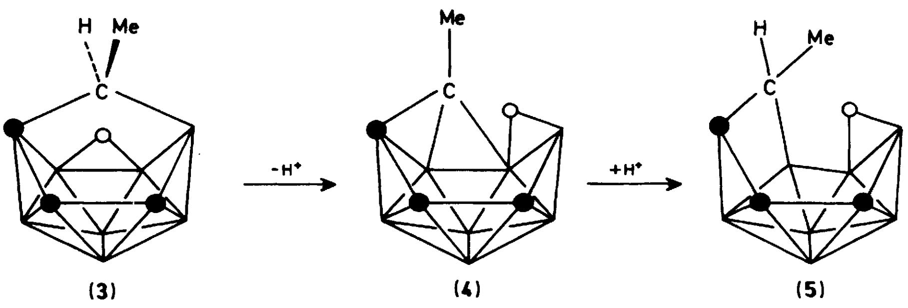


Figure 2. ORTEP drawing of one of the $[B_{10}H_{12}(PPh_2)]^-$ anions (molecule b), with phenyl hydrogen atoms omitted



Scheme 1.



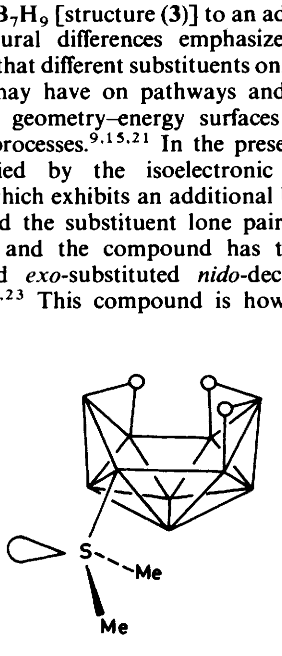
Scheme 2.

Table 4. Selected interatomic angles (°) for the anion $[B_{10}H_{12}(PPh_2)]^-$, with estimated standard deviations in parentheses

(*i*) Boron–boron–phosphorus								
a	B(2)–B(6)–P(1)	122.6(8)	B(4)–B(9)–P(1)	124.1(9)				
b	B(2)–B(6)–P(3)	124.5(8)	B(4)–B(9)–P(3)	125.4(8)				
a	B(5)–B(6)–P(1)	95.5(6)	B(7)–B(6)–P(1)	95.0(7)	B(10)–B(9)–P(1)	95.4(7)	B(8)–B(9)–P(1)	95.8(8)
b	B(5)–B(6)–P(3)	95.4(7)	B(7)–B(6)–P(3)	96.6(7)	B(10)–B(9)–P(3)	96.7(7)	B(8)–B(9)–P(3)	96.3(7)
(*ii*) Boron–boron–boron								
a	B(6)–B(5)–B(10)	105.6(9)	B(6)–B(7)–B(8)	107.4(9)	B(5)–B(10)–B(9)	108.3(9)	B(7)–B(8)–B(9)	106.3(9)
b	B(6)–B(5)–B(10)	105.5(9)	B(6)–B(7)–B(8)	107.3(8)	B(5)–B(10)–B(9)	108.3(8)	B(7)–B(8)–B(9)	106.0(8)
a	B(5)–B(6)–B(7)	105.1(8)	B(8)–B(9)–B(10)	107.1(9)				
b	B(5)–B(6)–B(7)	103.5(8)	B(8)–B(9)–B(10)	106.5(8)				
Other intracluster B–B–B angles:	a 56.2(7)—66.4(8) and 102.6(10)—121.7(10)							
	b 55.6(7)—67.5(8) and 102.6(8)—120.4(10)							
(*iii*) Angles at phosphorus								
a	C(121)–P(1)–B(6)	112.1(5)	C(121)–P(1)–B(9)	114.5(5)	C(111)–P(1)–B(6)	114.0(5)	C(111)–P(1)–B(9)	112.4(5)
b	C(321)–P(3)–B(6)	111.4(5)	C(321)–P(3)–B(9)	114.8(5)	C(311)–P(3)–B(6)	114.0(5)	C(311)–P(3)–B(9)	111.9(5)
a	C(121)–P(1)–C(111)	100.0(4)						
b	C(321)–P(3)–C(311)	102.3(4)						
a	B(6)–P(1)–B(9)	104.3(6)						
b	B(6)–P(3)–B(9)	102.8(6)						

orbital calculations on a number of ideal triangulated *arachno*-$[B_nH_n]^{6-}$ fragments imply that the remote configurations are in fact the more stable, but that progressive open-face protonation ultimately stabilizes adjacent *arachno*-type structures, the crossover occurring at 2—3 open-face bridging protons.[19] This would therefore be in accord with the deprotonation of the neutral precursor $B_{10}H_{13}(PPh_2)$ (which has an adjacent *arachno*-type structure with three face-bridging hydrogen atoms) to give the remote *arachno*-$[B_{10}H_{12}(PPh_2)]^-$ anion (which has only two face-bridging hydrogen atoms) (Scheme 1). Conversely, however, in the *arachno*-11-vertex-C_4B_7 system it has been proposed that it is the adjacent *arachno*-type isomers that are the more stable [configurations (**4**) and (**5**), Scheme 2], and that prototropic processes convert the remote *arachno* isomer of $Me_4C_4B_7H_9$ [structure (**3**)] to an adjacent one.[20]

These behavioural differences emphasize the differential stabilizing effects that different substituents on, and constituents of, the clusters may have on pathways and minima on the multidimensional geometry–energy surfaces associated with cluster reaction processes.[9,15,21] In the present system this is further exemplified by the isoelectronic neutral species $B_{10}H_{12}(SMe_2)$, which exhibits an additional behavioural type. In this compound the substituent lone pair is not active in cluster bonding, and the compound has the properties of a straightforward *exo*-substituted *nido*-decaboranyl cluster [structure (**6**)].[22,23] This compound is however believed to have a more 'reactive' isomer,[24–26] which could in principle adopt any of the configurations analogous to (**1**)—(**5**), although others could also be envisaged.[27]



(**6**)

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