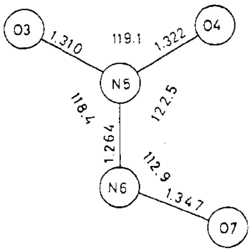

Figure 1. Distances and angles. Esd's are about 0.005 Å and 0.3°, respectively.

that found in azobenzenes.[13] The N-O distances are all quite long compared to those in the nitrate[14] and nitrite[15] ions (~1.24 Å), whereas the situation observed in potassium *syn*-methyldiazotate[16] appears to correspond more closely to that found in the present case. This would indicate a high degree of charge localization on the oxygen atoms in Angeli's salt.

The angle N5-N6-O7 (112.9°) is nearly the same as that found in azobenzenes[13] or in azoxy compounds,[17] also testifying to a similarity in electronic structure.

The interesting question of the position of the protons in the free acid cannot be unambiguously answered on the basis of our results. However, the geometry around N6 indicates a preference for an N-O single bond, and it seems reasonable to assume that O7 is the site of one proton. We also see no reason why there would be an absolute preference of one of the remaining oxygen atoms over the other, so that we envision a case of tautomerism involving these two atoms.

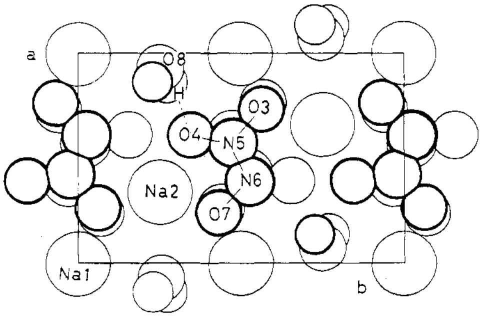

Figure 2. Packing diagram showing the structure projected along *c*.

The O4· · ·H-O8 hydrogen bond (2.784 Å) indicates a rather weak bond.

The Na^+ ions at centers of symmetry have six oxygen contacts ranging from 2.35 (O7′) to 2.49 Å (H_2O), averaging 2.42 Å. The Na^+ ions on the twofold axis have seven oxygen contacts in the range 2.51 (O7)-2.62 Å (H_2O), for an average of 2.55 Å. We note that the presumably most negative oxygen atom, O7, also is the one which makes the shortest Na-O contacts. The difference in average Na-O distance for six- and seven-coordination corresponds to earlier observations.[18]

Registry No. $Na_2N_2O_3 \cdot H_2O$, 37035-81-7.

Acknowledgment. The authors are pleased to acknowledge the financial support of this study by the National Science Foundation.

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(18) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 4.1.1.

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Crystal and Molecular Structure of 5,6-μ-Diphenylphosphino-decaborane(14)[1]

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The compound 5,6-μ-diphenylphosphino-decaborane(14), $B_{10}H_{13}P(C_6H_5)_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 7.39$ (1), $b = 12.59$ (1), $c = 20.02$ (2) Å, $Z = 4$, $\rho_{\text{calcd}} = 1.093$ g/cm^3, and $\rho_{\text{exptl}} = 1.09$ (1) g/cm^3. The structure of the molecule was determined using the heavy-atom technique and refined by the full-matrix least-squares method to a conventional R factor of 10.2% for 833 independent observed photographic data. The phosphorus atom of the diphenylphosphino group occupies a bridging position between B5 and B6 of a distorted B_{10} icosahedral fragment, confirming for the first time the substitution of a nonmetallic atom in a bridge hydrogen position in the decaborane(14) molecule.

Introduction

Several years ago the diphenylphosphino derivative of decaborane(14), formulated $B_{10}H_{13}P(C_6H_5)_2$, was prepared independently in two laboratories. Muetterties and Aftandilian obtained $B_{10}H_{13}P(C_6H_5)_2$ from the reaction of the decaboranyl Grignard reagent with diphenylchlorophosphine[2]

$$B_{10}H_{13}MgI + (C_6H_5)_2PCl \rightarrow B_{10}H_{13}P(C_6H_5)_2 + NaCl$$

while Schroeder prepared the compound by treating sodium

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(1) Presented in part at the International Meeting on Boron Compounds, Liblice, Czechoslovakia, June 21-25, 1971.

(2) (a) E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962); (b) V. D. Aftandilian, U. S. Patent 3,013,041 (1961); (c) E. L. Muetterties, U. S. Patent 3,118,932 (1964).

tridecahydrodecaborate(1−) with diphenylchlorophosphine[3]

$$NaB_{10}H_{13} + (C_6H_5)_2PCl \rightarrow B_{10}H_{13}P(C_6H_5)_2 + NaCl$$

Muetterties and Aftandilian concluded, on the basis of comparative solubilities and absence of P-H stretching absorption in the infrared spectrum, that diphenylphosphinodecaborane(14) was correctly formulated as a substituted decaborane rather than as a member of the $B_{10}H_{12}L$ class of compounds[4,5] with $L = P(C_6H_5)_2H$. Both groups investigated the availability of the extra pair of electrons presumably present on the phosphorus atom in $B_{10}H_{13}P(C_6H_5)_2$, found no tendency for quaternization of the phosphorus atom with reagents such as methyl iodide or for reaction of the compound with Lewis acids, and so concluded that the extra pair of electrons provided by the phosphorus atom was involved in bonding with the decaborane cage.

Boron-11 nmr studies led Schroeder to conclude tentatively that the diphenylphosphino group was bonded to B6 of the decaborane framework,[3] while Muetterties and Aftandilian noted the difficulty of an unambiguous interpretation of the ^{11}B nmr spectrum for the compound.[2a] Both groups observed the easy removal of a proton from $B_{10}H_{13}P(C_6H_5)_2$ by Lewis bases such as triethylamine, yielding salts of the very stable diphenylphosphinododecahydrodecaborate(1−) ion

$$B_{10}H_{13}P(C_6H_5)_2 + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+B_{10}H_{12}P(C_6H_5)_2^-$$

and both groups discovered the hydrolytic degradation of $B_{10}H_{13}P(C_6H_5)_2$ to diphenylphosphine-nonaborane(13)

$$B_{10}H_{13}P(C_6H_5)_2 \xrightarrow[\text{or ROH}]{H_2O} B_9H_{13}P(C_6H_5)_2H$$

The degradation product *did* show an infrared absorption assigned to the P-H stretch, consistent with the formulation of this compound as a member of the $B_9H_{13}L$ class.[4] Finally, Muetterties and Aftandilian studied the reaction of the decaboranyl Grignard reagent with several other group V compounds and isolated a number of decaborane derivatives, such as $B_{10}H_{13}N(CH_3)_2$, $B_{10}H_{13}As(C_6H_5)_2$, and $B_{10}H_{13}P(C_2H_5)(CH_3)$,[2] which are presumably structurally analogous to $B_{10}H_{13}P(C_6H_5)_2$.

As part of a general investigation of the structural properties of decaborane(14)-phosphine derivatives, we have conducted a single-crystal X-ray diffraction study of $B_{10}H_{13}P(C_6H_5)_2$. We find that the phosphorus atom of the diphenylphosphino group is four-coordinated and occupies a bridging position between B5 and B6 of a distorted B_{10} icosahedral fragment.

Experimental Section

The compound $B_{10}H_{13}P(C_6H_5)_2$ was prepared from the reaction of $NaB_{10}H_{13}$ and $(C_6H_5)_2PCl$, following the procedure of Schroeder,[3] and after recrystallization was found to melt at 144°. Other physical properties of the white crystalline solid were in agreement with those recorded in the literature.[2,3] Crystals suitable for the X-ray study were grown from dichloromethane–hexane solutions. Preliminary Weissenberg and precession photographs taken with Cu Kα radiation showed systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, uniquely consistent with orthorhombic space group $P2_12_12_1$ (D_2^4). Lattice constants of $a = 7.39$ (1), $b = 12.59$ (1), and $c = 20.02$ (2) Å were determined from Weissenberg and precession photographs taken at 22°, where the lattice parameter errors are standard deviations from the mean value determined from films calibrated with aluminum powder diffraction lines. A density of 1.093 g cm^{-3} was calculated on the assumption that four molecules with molecular weight 306.42 occupy the unit cell. This calculated value is in excellent agreement with the experimental crystal density of 1.09 (1) g cm^{-3} determined by the flotation technique in mixtures of hexane and chlorobenzene.

Intensity data were collected from a needlelike crystal of approximate dimensions 0.08 × 0.1 × 0.6 mm which was sealed in a thin-walled glass capillary with the long dimension (a) parallel to the capillary walls. Multiple-film equiinclination Weissenberg photographs ($0kl$–$6kl$) were prepared using Ni-filtered Cu Kα radiation (λ 1.5418 Å), and relative intensities of diffraction maxima were determined by visual comparison with an intensity scale prepared from the same crystal. A total of 1048 unique diffraction maxima, including 215 below the lower limit of observation (unobserved reflections), were measured and were scaled according to exposure times for the various Weissenberg levels. Lorentz and polarization corrections were applied[6] to the data, but corrections for spot extension and absorption were not made. The linear absorption coefficient for $B_{10}H_{13}P(C_6H_5)_2$ is 11.52 cm^{-1} (Cu Kα radiation), and the corresponding transmission factors on a given Weissenberg level are estimated to vary from 0.86 to 0.89. Atomic scattering factors for all atoms were obtained from the usual source,[7] and except as noted below all reflections were given unit weight throughout the data analysis.[8]

Solution and Refinement of the Structure

The positional parameters of the phosphorus atom in the asymmetric unit were deduced from a three-dimensional sharpened Patterson function. A structure factor calculation based upon the P atom only, followed by an electron density calculation, showed possible positions for several of the carbon and boron atoms. Inclusion of the three most likely C atoms in the structure factor calculation gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.446$. An electron density map based upon this model confirmed locations for six additional C atoms, and an additional structure factor–electron density cycle located the remaining three C atoms and all ten B atoms in the molecule. A structure factor calculation at this stage gave $R = 0.298$. Three cycles of full-matrix least-squares refinement of positional parameters and individual isotropic temperature factors (assigned initial values of 5.10 by the data scaling program) gave $R = 0.147$. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$, and the unobserved reflections were not included in this or subsequent refinements.

A difference map was calculated in an attempt to locate positions of hydrogen atoms, but the map could not be interpreted unambiguously. Consequently, the positions of the 10 phenyl H atoms were calculated,[6] assuming C–H distances of 1.08 Å, and introduced into the model. One cycle of refinement of position and isotropic temperature factors for P, C, and B atoms (H atom parameters were *not* refined) gave $R = 0.143$, and a difference map at this stage allowed the location of the 13 remaining H atoms per molecule. Positional parameters were refined one cycle for all 46 atoms; then anisotropic temperature factors were introduced for P, C, and B atoms, individual isotropic temperature factors of 4.00 were introduced for H atoms, and after two cycles of refinement of positional and anisotropic temperature factors for the nonhydrogen atoms, the value of R was 0.102. In the final cycle the average shift per error for the 208 refined parameters was 0.277, and the standard deviation of an

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[3] H. Schroeder, *Inorg. Chem.*, 2, 390 (1963).

[4] M. F. Hawthorne in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, Somerset, N. J., 1967, pp 223-323.

[5] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, 20, 66 (1961).

[6] Most of the calculations in this study were conducted using the "X-Ray System of Crystallographic Programs" compiled by J. M. Stewart, *et al.*, University of Maryland, and made commercially available by the Control Data Corp. Programs used from this system include: DATRDN and DATFIX, data reduction and scaling programs; FOURR, a general Fourier synthesis program; FC, a program for calculation of structure factors; ORFLS, a modified version of the Busing, Martin, and Levy full-matrix least-squares program; BONDLA, a program to calculate bond distances and angles; LSQPL, a least-squares plane and line program. Phenyl hydrogen positions were calculated using the program PLHA, by E. B. Fleischer, *et al.*, University of Chicago. Amplitudes of vibration and the thermal ellipsoid plot were obtained using the program ORTEP written by C. K. Johnson.

[7] "International Tables for X-Ray Crystallography," Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1968, pp 202-203, Table 3.3.1 A.

[8] Upon completion of the refinement using unit weights, a variable-weighting scheme was introduced and further refinement of a limited number of parameters was carried out. No significant changes in these parameters resulted, and because computing funds were limited, further refinement with variable weights was not attempted.

Table I
Atomic Parameters for $B_{10}H_{13}P(C_6H_5)_2$ Positional Parameters[a]

Atom	x	y	z
P	0.0710 (4)	0.0203 (2)	0.1347 (1)
B1	0.1702 (25)	0.1472 (12)	0.2768 (7)
B2	0.9529 (20)	0.0978 (10)	0.2568 (6)
B3	0.0631 (23)	0.0523 (11)	0.3303 (6)
B4	0.3173 (23)	0.0479 (10)	0.3211 (7)
B5	0.1509 (18)	0.1351 (9)	0.1906 (5)
B6	0.8958 (18)	0.9838 (9)	0.2039 (6)
B7	0.9375 (21)	0.9612 (10)	0.2864 (5)
B8	0.1857 (20)	0.9360 (10)	0.3217 (6)
B9	0.3824 (20)	0.9537 (12)	0.2722 (7)
B10	0.3551 (18)	0.0894 (12)	0.2341 (6)
C1	0.9402 (15)	0.0714 (8)	0.0668 (5)
C2	0.8123 (17)	0.1456 (8)	0.0798 (5)
C3	0.6941 (17)	0.1899 (8)	0.0288 (6)
C4	0.7265 (16)	0.1515 (8)	0.9660 (6)
C5	0.8538 (16)	0.0806 (8)	0.9502 (6)
C6	0.9725 (15)	0.0405 (8)	−0.0001 (5)
C1′	0.2266 (15)	0.9282 (8)	0.1021 (4)
C2′	0.2010 (17)	0.8210 (10)	0.1125 (5)
C3′	0.3281 (21)	0.7496 (10)	0.0885 (6)
C4′	0.4781 (18)	0.7804 (11)	0.0562 (6)
C5′	0.5124 (17)	0.8877 (11)	0.0474 (6)
C6′	0.3811 (17)	0.9622 (8)	0.0689 (6)
H(B1)	0.253 (13)	0.199 (7)	0.270 (4)
H(B2)	0.821 (14)	0.136 (8)	0.260 (4)
H(B3)	0.107 (13)	0.064 (7)	0.389 (4)
H(B4)	0.458 (12)	0.064 (7)	0.344 (4)
H(B5)	0.075 (14)	0.181 (7)	0.168 (4)
H(B6)	0.711 (12)	0.013 (7)	0.167 (4)
H(B7)	0.793 (12)	0.950 (7)	0.305 (4)
H(B8)	0.189 (12)	0.876 (7)	0.351 (4)
H(B9)	0.505 (14)	0.906 (8)	0.264 (5)
H(B10)	0.486 (13)	0.143 (7)	0.199 (4)
H(B6B7)	0.003 (12)	0.901 (7)	0.229 (4)
H(B8B9)	0.488 (12)	0.032 (7)	0.225 (4)
H(B9B10)	0.297 (14)	0.921 (8)	0.272 (5)
H(C2)	0.778 (12)	0.183 (7)	0.112 (5)
H(C3)	0.591 (14)	0.262 (6)	0.050 (4)
H(C4)	0.596 (13)	0.181 (7)	−0.063 (4)
H(C5)	0.957 (14)	0.064 (7)	−0.118 (4)
H(C6)	0.057 (13)	0.988 (7)	0.002 (4)
H(C2′)	0.155 (15)	0.800 (9)	0.110 (6)
H(C3′)	0.359 (13)	0.670 (8)	0.099 (4)
H(C4′)	0.588 (14)	0.728 (7)	0.050 (4)
H(C5′)	0.628 (14)	0.924 (8)	0.027 (5)
H(C6′)	0.357 (13)	0.034 (7)	0.061 (5)

Anisotropic Thermal Parameters for P, B, and C Atoms[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	314 (13)	79 (4)	25 (1)	9 (7)	7 (4)	1 (2)
B1	535 (108)	138 (30)	42 (9)	−18 (50)	−49 (28)	−18 (14)
B2	379 (75)	92 (22)	36 (8)	43 (38)	23 (23)	3 (11)
B3	366 (71)	114 (24)	41 (8)	2 (42)	−15 (24)	−1 (12)
B4	470 (87)	79 (21)	48 (10)	−4 (38)	5 (26)	5 (12)
B5	383 (74)	96 (20)	30 (7)	−21 (33)	−36 (19)	−10 (9)
B6	342 (71)	97 (19)	37 (7)	41 (36)	14 (36)	14 (11)
B7	406 (67)	117 (23)	23 (6)	−14 (43)	−34 (18)	1 (10)
B8	348 (72)	109 (23)	39 (8)	34 (37)	−38 (21)	21 (11)
B9	360 (85)	113 (27)	58 (11)	−8 (38)	−51 (26)	10 (14)
B10	316 (69)	170 (30)	28 (7)	−14 (39)	−17 (18)	0 (13)
C1	246 (49)	89 (16)	36 (7)	−4 (27)	12 (16)	−5 (9)
C2	375 (65)	90 (18)	40 (7)	24 (32)	11 (19)	−17 (10)
C3	473 (74)	109 (19)	34 (7)	70 (34)	−14 (19)	−15 (10)
C4	406 (69)	88 (18)	38 (8)	24 (31)	−19 (19)	12 (10)
C5	329 (61)	99 (19)	45 (8)	14 (30)	−16 (19)	−9 (11)
C6	371 (60)	72 (15)	34 (6)	49 (27)	−4 (17)	−7 (8)
C1′	313 (60)	103 (19)	20 (5)	−10 (27)	8 (14)	5 (8)
C2′	358 (67)	103 (21)	45 (8)	−3 (33)	25 (19)	−3 (11)
C3′	444 (84)	130 (24)	51 (10)	42 (41)	22 (24)	7 (13)
C4′	467 (81)	133 (25)	44 (8)	78 (36)	51 (21)	−8 (12)
C5′	419 (77)	119 (22)	54 (9)	28 (35)	61 (20)	19 (12)
C6′	399 (69)	76 (17)	48 (8)	9 (31)	27 (19)	3 (10)

[a] The numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. The coordinates are expressed as fractions of the unit cell parameters.
[b] Anisotropic temperature factors are defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and are ×10⁴.

Table II. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max	Atom	Min	Intermed	Max
P	0.224	0.250	0.297	C2	0.226	0.314	0.328
B1	0.239	0.349	0.406	C3	0.236	0.281	0.391
B2	0.247	0.264	0.348	C4	0.230	0.299	0.344
B3	0.279	0.302	0.327	C5	0.269	0.284	0.330
B4	0.249	0.313	0.361	C6	0.214	0.265	0.337
B5	0.203	0.289	0.345	C1′	0.197	0.285	0.300
B6	0.240	0.272	0.341	C2′	0.275	0.288	0.339
B7	0.195	0.304	0.350	C3′	0.302	0.309	0.380
B8	0.196	0.326	0.344	C4′	0.225	0.330	0.407
B9	0.261	0.299	0.388	C5′	0.253	0.299	0.410
B10	0.228	0.302	0.371	C6′	0.246	0.288	0.355
C1	0.246	0.262	0.289				

observation of unit weight, defined as $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ where n is the number of observations and m is the number of variables, is 1.48.

A final difference map showed a number of peaks which could not be assigned as atom residuals, but the largest of these peaks was of the order of magnitude of the peaks assigned to H atoms and approximately one-tenth the size of a peak expected for a B or C atom.

A table of observed and calculated structure factors is available.[9] Final atomic coordinates expressed in fractions of unit cell dimensions, and anisotropic temperature factors for P, B, and C atoms are contained in Table I. Table II lists root-mean-square amplitudes of vibration for the nonhydrogen atoms, and Figure 1 gives a visual representation of the thermal ellipsoids. Tables III and IV contain bond distances and selected angles in $B_{10}H_{13}P(C_6H_5)_2$, and Figure 2 is a drawing of the molecule which includes H atoms.

Description and Discussion of the Structure

The outstanding feature of the molecular structure of $B_{10}H_{13}P(C_6H_5)_2$ (Figures 1 and 2) is the presence of a four-coordinated phosphorus atom which bridges B5 and B6 of the decaborane framework. The P-B5 and P-B6 distances (Table III) are 1.92 (1) and 1.95 (1) Å, respectively, in good agreement with P-B distances of 1.93 Å found in H_3PBH_3[10a] and $(CH_3)_3PBH_3$.[10b] Bond angles centered about the P atom (Table IV) fall into three groups. Three of the angles, C1-P-C1′, C1-P-B6, and C1-P-B5, are close to the expected tetrahedral angle. However, the two angles C1′-P-B5 and C1′-P-B6 are close to 120°, while the B5-P-B6 angle is a surprisingly low 88.2 (5)°. This distortion from tetrahedral geometry may be attributed to the significant size difference between the P atom and the B atoms which it bridges. A decrease in the B5-P-B6 angle and concomitant increases in the C1′-P-B5 and C1′-P-B6 angles are apparently necessary in order for the diphenylphosphino group to fit into the bridging position.

Some distortion also exists in the B_{10} fragment, and consistent with the observation above, the distortion is greatest in the vicinity of B5, B6, and B7. The B5-B6 distance is 2.69 (2) Å and the B6-B7 distance is 1.70 (2) Å, while the comparable B8-B9 and B9-B10 distances on the opposite side of the molecule are 1.77 (2) and 1.88 (2) Å, respectively. Analogous B-B distances in X-ray and neutron diffraction studies of $B_{10}H_{14}$ range from 1.76 to 1.79 Å.[11] The B7-B8 distance of 1.99 (2) Å agrees well with the comparable dis-

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(9) A table of the final values of $10|F_o|$ and $10|F_c|$ for the 1048 reflections will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-288.

(10) (a) E. L. McGandy, *Diss. Abstr.*, 22, 754 (1961); (b) R. Thomas and K. Eriks, paper presented at the Meeting of the American Crystallographic Association, July 1959.

(11) (a) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, 3, 436 (1950); (b) E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, 27, 27 (1957); (c) A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 8, 464 (1969).

Table III. Bond Distances (Å) for $B_{10}H_{13}P(C_6H_5)_2$

i	j	D_{ij}	i	j	D_{ij}
P	B5	1.92 (1)	C1	C2	1.36 (2)
P	B6	1.95 (1)	C2	C3	1.46 (2)
P	C1	1.79 (1)	C3	C4	1.37 (2)
P	C1′	1.76 (1)	C4	C5	1.33 (2)
			C5	C6	1.42 (2)
B1	B2	1.77 (2)	C6	C1	1.42 (2)
B1	B3	1.79 (2)			
B1	B4	1.88 (2)	C1′	C2′	1.38 (2)
B1	B5	1.74 (2)	C2′	C3′	1.39 (2)
B1	B10	1.77 (2)	C3′	C4′	1.34 (2)
			C4′	C5′	1.39 (2)
B2	B3	1.78 (2)	C5′	C6′	1.42 (2)
B2	B5	2.03 (2)	C6′	C1′	1.39 (2)
B2	B6	1.83 (2)			
B2	B7	1.82 (2)	B1	H(B1)	0.90 (19)
			B2	H(B2)	1.09 (20)
B3	B4	1.89 (2)	B3	H(B3)	1.22 (16)
B3	B7	1.72 (2)	B4	H(B4)	1.16 (17)
B3	B8	1.73 (2)	B5	H(B5)	0.92 (19)
			B6	H(B6)	1.60 (17)
B4	B8	1.71 (2)	B7	H(B7)	1.15 (18)
B4	B9	1.61 (2)	B8	H(B8)	0.96 (17)
B4	B10	1.84 (2)	B9	H(B9)	1.10 (20)
			B10	H(B10)	1.38 (18)
B5	B6	2.69 (2)			
B5	B10	1.84 (2)	B6	H(B6B7)	1.40 (17)
			B7	H(B6B7)	1.46 (17)
B6	B7	1.70 (2)	B8	H(B8B9)	1.30 (21)
			B9	H(B8B9)	1.39 (19)
B7	B8	1.99 (2)	B9	H(B9B10)	1.57 (18)
			B10	H(B9B10)	1.23 (18)
B8	B9	1.77 (2)			
			C2	H(C2)	0.84 (18)
B9	B10	1.88 (2)	C3	H(C3)	1.27 (17)
			C4	H(C4)	1.18 (18)
			C5	H(C5)	1.58 (17)
			C6	H(C6)	0.91 (18)
			C2′	H(C2′)	1.10 (18)
			C3′	H(C3′)	1.05 (19)
			C4′	H(C4′)	1.06 (19)
			C5′	H(C5′)	1.06 (20)
			C6′	H(C6′)	0.94 (18)

tance of 1.973 Å reported for $B_{10}H_{14}$,[11c] but the B5-B10 distance is only 1.84 (2) Å, illustrating further the distortion in the B_{10} cage.

The B10-B5-B6 angle of 107.8 (7)° is substantially smaller than comparable angles in other parts of the molecule which average[12] 123.1 (9)°, and the B5-B6-B7 angle of 95.0 (8)° also is significantly smaller than the B8-B9-B10 angle of 104.6 (9)°. However, the folding angle between the planes B3, B1, B10 and B1, B3, B7 is 74.0 (12)°, which falls between the values 76 and 71.8 (3)° reported in the literature[11a,c] for $B_{10}H_{14}$. The external angle between the planes defined by B5, P, B6 and B5, B2, B6 is 185.5 (12)°, in reasonable agreement with the external angle of 182.2° observed in the bridge-substituted pentaborane derivative, 1-Br-μ-$(CH_3)_3SiB_5H_7$.[13]

The P-C1 and P-C1′ bond distances are 1.79 (1) and 1.76 (1) Å, respectively, slightly shorter than the average value of 1.829 (3) Å found in $P(C_6H_5)_3$.[14] The C-C distances are somewhat variable but average 1.39 (2) Å, in good agreement with the accepted value of 1.392 Å for the C-C distance in benzene.[14] The P-C-C and C-C-C angles taken together average 119 (2)°, sufficiently close to the expected value of 120.0°.

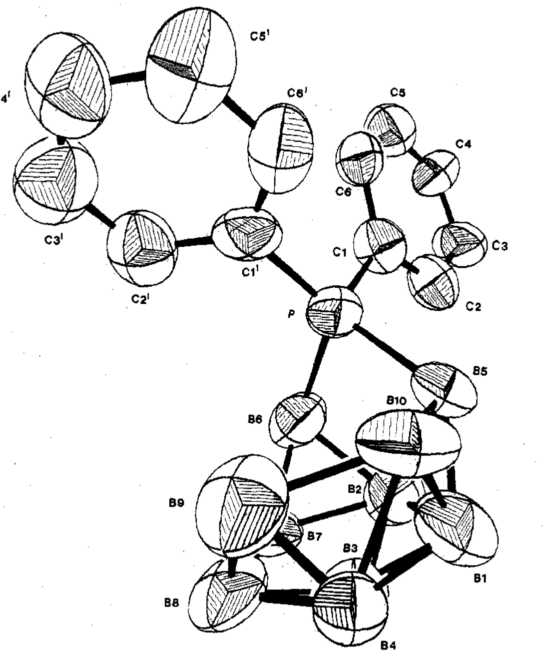

Figure 1. A perspective drawing of the nonhydrogen atoms in 5,6-μ-diphenylphosphino-decaborane(14). The thermal ellipsoids represent 50% probability distributions.

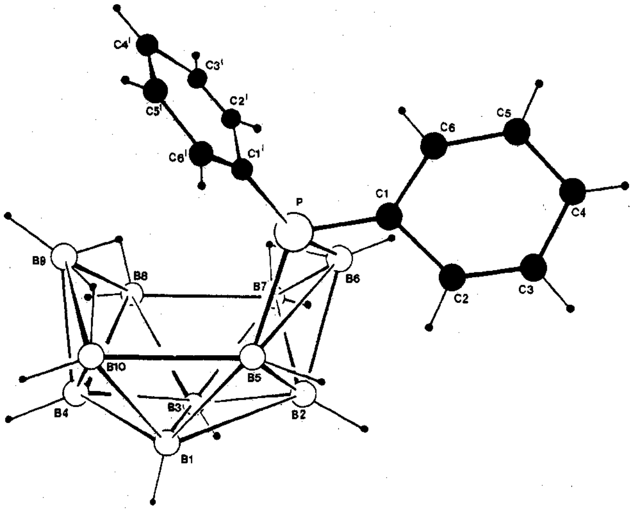

Figure 2. The molecular structure of, and numbering system for, 5,6-μ-diphenylphosphino-decaborane(14). Boron atoms are represented by open circles, carbon atoms by shaded circles, and hydrogen atoms by small shaded circles; the phosphorus atom is represented by the large open circle. The lines between *boron* atoms are not intended to represent chemical bonds but simply to show the framework structure of that portion of the molecule. Hydrogen atoms are numbered according to the carbon or boron atom(s) to which they are bonded; *e.g.*, H(B1) is bonded to B1, H(C3′) to C3′; H(B8B9) is bonded to both B8 and B9.

Finally, the B-H(terminal) bond distances average 1.2 (2) Å, the B-H(bridge) distances average 1.4 (2) Å, and the C-H distances average 1.0 (2) Å. However, as implied above in the description of the refinement procedure and in Table III, the H atoms are not considered to have been accurately located.

This structural study provides the first unambiguous evidence for substitution of a single-bridge H atom in a decaborane(14) derivative by a nonmetallic atom (other than

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(12) The estimated errors listed for the average value here and below are either the mean of the standard deviations or the root-mean-square deviation, whichever is larger in each case.

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Table IV. Selected Angles (Degrees) for $B_{10}H_{13}P(C_6H_5)_2$

Atoms	Angle	Atoms	Angle
C1-P-C1′	107.9 (5)	B10-B5-P	107.0 (8)
C1-P-B6	105.4 (6)	B7-B6-P	127.4 (9)
C1-P-B5	109.7 (5)		
C1′-P-B6	122.9 (5)	B5-B6-P	45.4 (4)
C1′-P-B5	120.7 (6)	B6-B5-P	46.4 (4)
B5-P-B6	88.2 (5)		
		B10-B5-B6	107.8 (7)
P-C1-C2	118.6 (8)	B8-B7-B6	122.5 (10)
P-C1-C6	122.0 (8)	B7-B8-B9	122.4 (8)
C2-C1-C6	119.3 (9)	B5-B10-B9	124.5 (9)
P-C1′-C2′	120.0 (8)	B5-B6-B7	95.0 (8)
P-C1′-C6′	120.8 (8)	B8-B9-B10	104.6 (9)
C2′-C1′-C6′	119.1 (10)		
		B5-B2-B7	118.4 (9)
C1-C2-C3	123.3 (9)	B8-B4-B10	109.0 (9)
C2-C3-C4	113.9 (10)		
C3-C4-C5	125.3 (11)		
C4-C5-C6	120.4 (10)		
C5-C6-C1	117.5 (10)		
C1′-C2′-C3′	119.4 (11)		
C2′-C3′-C4′	122.6 (12)		
C3′-C4′-C5′	119.7 (12)		
C4′-C5′-C6′	118.8 (11)		
C5′-C6′-C1′	120.3 (10)		

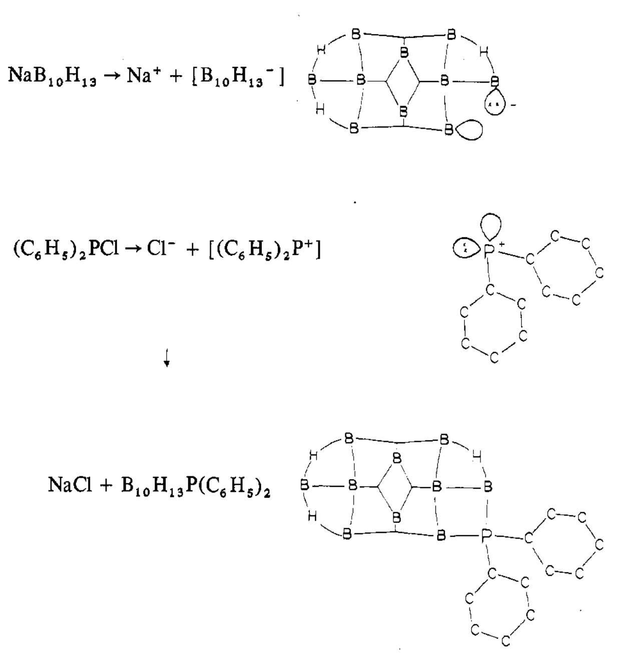

Figure 3. A schematic representation for the formation of $B_{10}H_{13}P(C_6H_5)_2$. A reactive $B_{10}H_{13}^-$, produced from the dissociation of $NaB_{10}H_{13}$, reacts with $(C_6H_5)_2P^+$ from $(C_6H_5)_2PCl$ to form $B_{10}H_{13}P(C_6H_5)_2$. The small crosses represent electrons involved in the B-P bonds.

deuterium). Bridge substitution by the oxygen atom of an ethoxy group in $B_{10}H_{13}OC_2H_5$ was proposed on the basis of 12.8-MHz ^{11}B nmr studies,[15] but more recent nmr studies of this compound at 32.1 MHz are interpreted in terms of terminal substitution of OC_2H_5 at B5.[16]

A cadmium derivative of the dodecahydrodecaborate(2−) ion, $[CdB_{10}H_{12}\cdot 2(C_2H_5)_2O]_2$, has been shown to consist of two $B_{10}H_{12}^{2-}$ ligands bridged by two Cd^{2+} ions such that each Cd occupies a bridge hydrogen position in both of the B_{10} fragments simultaneously.[17] In addition, there are numerous examples of insertions of atoms such as boron,[4] carbon,[18a] sulfur,[18b] phosphorus,[18c] aluminum, gallium, and thallium,[18d] and germanium and tin,[18e] as well as nickel, cadmium, zinc, and several other transition metal ions[19] into decaborane fragments yielding 11-atom icosahedral fragment molecules and ions, but in these cases the inserted atom is presumed to occupy the eleventh site of the icosahedral fragment rather than the bridging site of a decaborane(14) molecule. Recent X-ray studies have confirmed two such structures.[20] Bridge substitution in the diborane(6) system has been known for some time[4] and recently has been established for the pentaborane(9) system.[13,21] In addition, the compound $(C_2H_5)NH_2B_8H_{11}NH(C_2H_5)$ is known to have an $NH(C_2H_5)$ group occupying a bridging position in a hypothetical $B_8H_{13}^-$ ion structure.[22]

The lack of availability of the extra pair of electrons presumed to be on the P atom of diphenylphosphinodecaborane(14)[2,3] now may be understood in terms of the bridging position occupied by the diphenylphosphino group in this compound. The P-B distances suggest that these bonds be considered normal electron pair bonds, while the very long B5-B6 distance suggests that little direct bonding interaction occurs between these two B atoms. Moreover, no other B atom is sufficiently close to the P atom to justify additional P-B bonding; the P-B2 distance of 2.77 (1) Å is the shortest nonbonded P-B distance. The two P-B bonds may be described in terms of one orbital from each of B5 and B6 of a $B_{10}H_{13}^-$ and two orbitals from the P atom of a $(C_6H_5)_2P^+$. A total of four electrons are available in these orbitals, sufficient for the formation of ordinary electron-pair bonds between P and B5 and P and B6. Figure 3 illustrates schematically the formation of $B_{10}H_{13}P(C_6H_5)_2$ from $NaB_{10}H_{13}$ and $(C_6H_5)_2PCl$. The topological description of $B_{10}H_{13}^-$ given in this figure is in agreement with the reported X-ray study,[23] but the bonding arrangement includes open three-center B-B-B bonds which recently have fallen into disfavor.[24]

The recently reported[18c] formation of the phosphaundecaboranes, $B_{10}H_{12}P(C_6H_5)$ and $B_{10}H_{12}P(CH_3)$, from the reaction of $NaB_{10}H_{13}$ with $(C_6H_5)PCl_2$ and $(CH_3)PCl_2$ may involve an intermediate analogous to $B_{10}H_{13}P(C_6H_5)_2$. The first step of this reaction may be simply the reaction of $NaB_{10}H_{13}$ with $RPCl_2$ to yield a bridge-substituted decaborane, as follows for the reaction with $(C_6H_5)PCl_2$

$$NaB_{10}H_{13} + (C_6H_5)PCl_2 \rightarrow [B_{10}H_{13}P(C_6H_5)Cl] + NaCl$$

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The following step could be intramolecular in character consisting of elimination of a bridge hydrogen as H^+ from between B9 and B10 of the borane and a Cl^- from the bonded $P(C_6H_5)Cl$, followed by bond formation among the P atom, B9, and B10 *via* the three freed orbitals and the single pair of electrons

$$[B_{10}H_{13}P(C_6H_5)Cl] \rightarrow B_{10}H_{12}P(C_6H_5) + HCl$$

Such a reaction scheme would be expected to yield an 11-atom icosahedral fragment molecule, which is the structure proposed for the two phosphaundecaboranes and supported by ^{11}B nmr studies.[18c]

The very stable $B_{10}H_{12}P(C_6H_5)_2^-$ ion prepared by Muetterties and Aftandilian[2] and by Schroeder[3] from $B_{10}H_{13}P(C_6H_5)_2$ is probably a bridge-substituted $B_{10}H_{13}^-$ ion. This conclusion is supported by the observation that the P atom in $B_{10}H_{12}P(C_6H_5)_2^-$ could not be quaternized, and by the lack of P-H absorption in the infrared spectrum of the ion.[2] It is interesting to note that $B_{10}H_{12}P(C_6H_5)_2^-$, which contains two more electrons distributed among the bonds involving boron atoms than does the $B_{10}H_{13}^-$ ion, is substantially more stable hydrolytically and less reactive toward electron pair donors[2] than is the $B_{10}H_{13}^-$ ion. This suggests that at least some delocalization of electron density from the P-B bonds into the borane fragment does occur. The formulation of the hydrolytic degradation product of $B_{10}H_{13}P(C_6H_5)_2$ as $B_9H_{13}P(C_6H_5)_2H$, a member of the $B_9H_{13}L$ class of borane derivatives,[4] is supported by several physical properties of the degradation product.[2,3] This formulation requires that the diphenylphosphino group be shifted in the degradation process from a bridging position in $B_{10}H_{13}P(C_6H_5)_2$ to a terminal position in $B_9H_{13}P(C_6H_5)_2H$, in which the fourth coordination site of P is occupied by an H atom. A cleavage of the P-B5 bond leaving the bonding electron pair on the P atom, followed by spatial rearrangement at B6 and addition of H^+ to the P atom, seems to be a simple and obvious step to suggest for the degradation mechanism. Removal of B9 from the borane fragment and rearrangement and addition of H atoms as well as rearrangement of B-B bonds would be required to yield the structure established for the $B_9H_{13}L$ system.[22] These other necessary steps and indeed the sequential order of all of the steps in the degradation are not so obvious, but proposals for possible degradation pathways in such systems have been presented.[25]

The establishment of a bridging substituent in 5,6-μ-diphenylphosphinodecaborane(14) suggests that numerous other decaborane(14) derivatives may have such a structural feature. It seems likely that some, if not all, of the group V derivatives prepared from the Grignard derivative of decaborane(14)[2] are bridge substituted. Moreover, several other products of the reactions of the decaboranyl Grignard reagent or the sodium salt of the tridecahydrodecaborate(1−) ion, such as $B_{10}H_{13}CH_2C_6H_5$, $B_{10}H_{13}CH_2CH_3$, $B_{10}H_{13}CH_3$, and $B_{10}H_{13}Si(CH_3)_3$, which heretofore have been characterized[26] as 6-, 5-, or 1-substituted decaboranes, may prove to be bridge substituted or may arise from the rearrangement of a bridge-substituted intermediate.

Registry No. $B_{10}H_{13}P(C_6H_5)_2$, 37037-00-6.

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