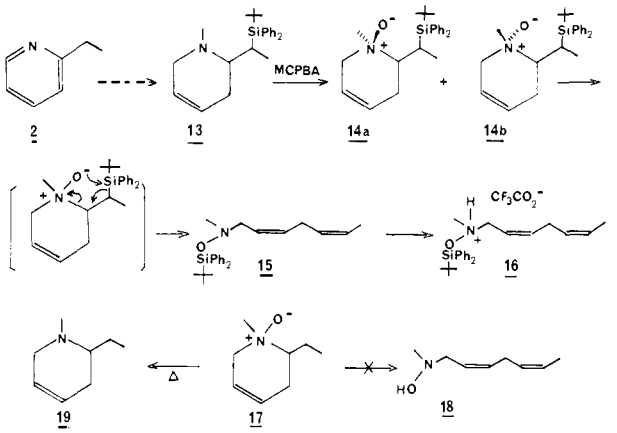
Scheme III



iodide in methanol gave rise to the tetrahydropyridinium salt **8**. With the requisite substrate in hand, its fragmentation was examined. Treatment of **8** with CsF (10 equiv) in refluxing acetonitrile for 4 h led smoothly by a stereoselective fragmentation[8] to the (2*Z*,5*E*)-1-(dimethylamino)heptadiene **9** (77%; Scheme I). It is noteworthy that the silicon-induced fragmentation was the sole reaction observed excluding Hoffmann elimination of the allylic proton on C_3.[4]

The geometry of the two double bonds was established by a careful double-irradiation experiment at 400 MHz[7] of the corresponding ammonium salt **10**. The stereoselectivity of the fragmentation led to the assignment of the 2*R*,1′*S* relative configurations to the tetrahydropyridine **5**, if an antielimination could be assumed by analogy with other desilicohalogenation reactions.[9] Furthermore, examination of the molecular model of the 3,6 dihydropyridinium intermediate **11** and consideration of the steric interactions could account for the stereospecific attack of hydride ion during the reduction step affording compound **5** (Scheme II). In addition, hydrogenation of the tetrahydropyridines **5** and **6** led to the same piperidine, **7**, showing that these three products presented the same relative configurations at C_2 and $C_{1'}$.

With the desired diene ammonium salt **10** in hand, the synthesis of the (9*Z*,12*E*)-tetradecadien-1-yl acetate (**1**) was achieved in three steps: alkylation with the Grignard reagent **12** in the presence of lithium tetrachlorocuprate[10] (THF, −30 °C, 4 h), deprotection of the alcohol (TsOH, MeOH, reflux), and acetylation (Ac_2O, pyridine) afforded the acetate **1** (74%) after purification (preparative TLC, SiO_2–NO_3Ag (15%), 90:10 hexane–AcOEt; Scheme I). This compound was identical with an authentic sample of (9*Z*,12*E*)-tetradecadien-1-yl acetate.

The behavior of the *N*-oxide **14** has been examined in order to make a comparison with the results obtained from the previous fragmentation process. By analogy with 1,3-silicon migration,[11] a "sila-Cope" elimination was expected to occur by a syn elimination which could afford the (*Z*,*Z*)-1,4-dienamine derivative **15**.

The tetrahydropyridine **13** was prepared as previously in three steps from 2-ethylpyridine **2** (overall yield 71%). Oxidation with MCPBA led to diastereoisomeric *N*-oxides **14a** and **14b**, which could not be separated. Even with the more stable diphenyl *tert*-butylsilicon group,[12] these two *N*-oxides were found to be unstable and gave rise spontaneously to a sila Cope elimination leading to the diene hydroxylamine derivative **15** (65%;[13] Scheme III). The *Z*,*Z* configuration of the two double bonds was established after careful examination of the 400-MHz NMR spectrum of the corresponding ammonium salt **16**.[7] As far as we know, this is the first example of this type of elimination.

It is noteworthy that the related *N*-oxide **17** did not give rise to the corresponding diene hydroxylamine **18**, but under more drastic conditions (toluene reflux) led to the tetrahydropyridine **19** (40%). The formation of this product is clearly the result of an intermolecular oxidation–reduction process observed already in the piperidine series by Cope and Lebel.[14]

Further work directed toward the synthesis of pheromones and other natural products including a (*Z*,*Z*)-1,4-diene unit is in progress in our laboratory.

Acknowledgment. We thank J. Cavallaro for the preparation of compound **15**, Drs. F. Guêritte and Z. Andriamialisoa for 400-MHz spectrometry, Dr. J.-Y. Lallemand for helpful discussion, and Dr. C. Descoins for providing an authentic sample of pheromone **1**.

Registry No. 1, 30507-70-1; **2**, 100-71-0; **3**, 83862-20-8; **4**, 83862-21-9; **5**, 83862-22-0; **6**, 83862-23-1; **7**, 83862-24-2; **8**, 83862-25-3; **9**, 83862-26-4; **10**, 83862-27-5; **13**, 83862-28-6; **14a**/**14b**, 83862-29-7; **15**, 838-30-0; **16**, 83862-31-1; **17**, 83862-32-2; **19**, 5126-34-0; *tert*-butyldimethylchlorosilane, 18162-48-6; 2-[(7-chloroheptyl)oxy]tetrahydro-2*H*-pyran, 55944-71-3.

(8) For a related fragmentation see: Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476.

(9) (a) Miller, R. B.; Mc Garvey, G. *J. Org. Chem.* **1978**, *43*, 4424. (b) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020. (c) Chan, T. H.; Massuda, D. *Ibid.* **1977**, *99*, 936. (d) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442.

(10) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303.

(11) (a) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (b) Kocienski, P. J. *Tetrahedron Lett.* **1980**, *21*, 1559. (c) Ager, D. J.; Cookson, R. C. *Ibid.* **1980**, *21*, 1677.

(12) Hanessian, S.; Lavallee, P. *Can. J. Chem.* **1975**, *53*, 2975.

(13) MCPBA (2.7 mmol) was added to a solution of amine **13** (1.07 mmol) in CH_2Cl_2 (30 mL) at −20 °C. After 5 min, the reaction mixture was poured into a 10% aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The residue obtained after evaporation of the organic layer was refluxed in CH_3CN (10 mL) for 30 min. After evaporation of the solvent, the resulting diene was purified by TLC (SiO_2, 90–10 hexane–AcOEt).

(14) (a) Cope, A. C.; Lebel, N. A. *J. Am. Chem. Soc.* **1960**, *82*, 4656. (b) Laughlin, R. G. *Ibid.* **1973**, *95*, 3295.

Chiral Allenylboronic Esters: A Practical Reagent for Enantioselective Carbon–Carbon Bond Formation

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Condensations of aldehydes with chiral allenylboronic esters provide β-acetylenic alcohols with an exceptionally high degree of enantioselectivity (Scheme I.)[1,2]

The present investigation originates from the assumption that the chiral allenyl anion may react with aldehydes via a transition state of type **1**.[3] The structure **1** appears less sterically constrained than that of its diastereomer, in which the position of the H and R groups are interchanged. Thus, if the reaction is stereospecific it will result *in predictable transfer of chirality from chiral auxiliary ligand (easily obtainable from (+)- or (−)-dialkyl tartrate) to a newly formed carbon–carbon bond.*[4] Verification of this hypothesis has been obtained as illustrated in Table I.

The following experiment provides details of the new process: A 1-L round-bottomed flask, equipped with a magnetic stirring

(1) Recent applications of allenyl anions for organic synthesis: Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225.

(2) Condensations of aldehydes with enantiomerically enriched allylboranes were shown to provide homoallylic alcohols with 50–85% ee: Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330. See also: Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. Recently, reactions of allenic and propargylic boranes were reported: Pearson, N. R.; Hahn, G.; Zweifel, G. *J. Org. Chem.* **1982**, *47*, 3364.

(3) (a) Saniere-Karila, M.; Capmau, M. L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1973**, 3371. (b) Favre, E.; Gaudemar, M. *J. Organomet. Chem.* **1975**, *92*, 17. (c) For a recent general review, see: Moreau, J.-L. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; pp 363–414. (d) Reference 1.

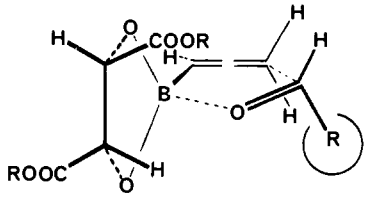
(4) Dialkyl tartrate is an effective catalyst for asymmetric epoxidation; see: Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5976. See also ref 12b.

0002-7863/82/1504-7667$01.25/0

Table 1. Asymmetric Alkylation of Carbonyl Compounds by Chiral Allenylboronic Esters[a]

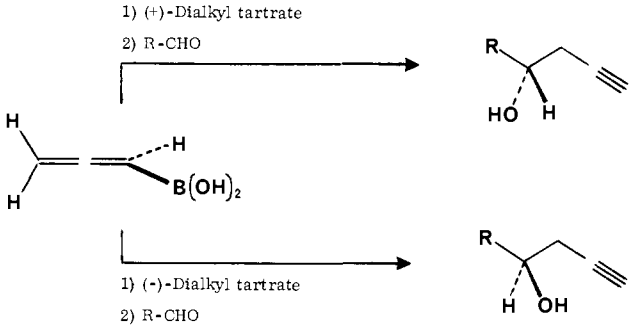
entry	tartrate[b]	aldehyde (equiv)	rxn conditions: T, °C (time, h)	product: yield,[c] %	product: $[\alpha]^{25}_D$, deg (c in methanol)	product: ee % (configuration)
1	L(+)-DET	cyclohexanecarbaldehyde (1.0)	−78 (9), −20 (12)	85	+7.28 (7.4)	86[e] (S)[f]
2	L(+)-DET	cyclohexanecarbaldehyde (1.5)	−78 (9), −20 (12)	56[d]	+7.78 (3.1)	92[e] (S)[f]
3	D(−)-DET	cyclohexanecarbaldehyde (1.5)	−78 (44)	74[d]	−7.08 (4.1)	87[e] (R)
4	L(+)-DIPT	cyclohexanecarbaldehyde (1.5)	−78 (24)	42[d]		90[e] (S)[f]
5	D(−)-DIPT	cyclohexanecarbaldehyde (1.0)	−78 (22)	70		91[e] (R)
6	D(−)-DIPT	cyclohexanecarbaldehyde (1.5)	−78 (22)	81[d]	−7.68 (1.7)	95[e] (R)
7	L(+)-DET	hexanal (1.5)	−78 (6), −20 (14)	75[d]	+19.72 (3.7)	88[e] (S)[g]
8	L(+)-DIPT	hexanal (1.5)	−78 (22)	63[d]	+20.98 (5.9)	>95[e] (S)[g]
9	L(+)-DET	trimethylacetaldehyde (1.5)	−78 (46)	53[d]	−36.33 (1.8)	88[e]
10	L(+)-DIPT	trimethylacetaldehyde (1.5)	−78 (22)	47[d]	−38.28 (3.6)	93[e]
11	L(+)-DET	benzaldehyde (1.5)	−78 (9), −20 (12)	52[d]		60[h] (S)[i]
12	D(−)-DET	benzaldehyde (1.5)	−78 (44)	70[d]	+7.36 (3.8)	63[h] (R)
13	L(+)-DIPT	benzaldehyde (1.5)	−78 (44)	43[d]	−9.21 (3.5)	79[h] (S)[i]
14	L(+)-DET	*p*-nitrobenzaldehyde (1.5)	−78 (6), −20 (14)	58[d]	+2.82 (3.9)	72[h]
15	L(+)-DET	*p*-methoxybenzaldehyde (1.5)	−78 (6), −20 (14)	66[d]	−3.60 (4.1)	72[h]
16	L(+)-DET	2-furaldehyde (1.5)	−78 (46)	50[d]	+5.04 (1.6)	70[h]
17	L(+)-DET	*trans*-2-hexenal (1.0)	−78 (9), −20 (12)	66	+13.45 (5.2)	62[j] (S)[g]
18	L(+)-DIPT	*trans*-2-hexenal (1.0)	−78 (12), −20 (24)	39	+14.04 (1.4)	66[j] (S)[g]
19	L(+)-DET	*trans*-cinnamaldehyde (1.5)	−78 (6), −20 (14)	67[d]	+28.32 (4.0)	79[h]
20	L(+)-DET	1-perillaldehyde (1.5)	−78 (22)	52[d]	−66.45 (7.0)	>95[k]

[a] Unless otherwise noted, all reactions were performed as described in text. [b] L(+)-Diethyl tartrate (DET) and L(+)-diisopropyl tartrate (DIPT) were purchased from Tokyo Kasei Co. and used without further purifications. D(−)-DET was prepared from a previous procedure: Austin, P. C. *J. Chem. Soc.* 1928, 1831. D(−)-DIPT was generously donated from Dr. T. Katsuki at Kyushu University. [c] Isolated yields. All new compounds gave appropriate analytical and spectral data. [d] Yields are based on allenylboronic acid, and the remainder was only unreacted carbonyl compound. [e] Determined by GC analyses of the ester from (*S*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride; see ref 9. [f] Absolute configuration was determined by the conversion to (*S*)-1-cyclohexyl-1-butanol (Pd-C, H_2): Levene, P. A.; Rothen, A. *J. Org. Chem.* 1936, *1*, 76. [g] Determined by the conversion to (*S*)-4-nonanol; see note f. [h] Determined by ^{1}H NMR spectroscopy of the (−)-MTPA ester by using Eu(fod)$_3$ shift reagent. [i] Absolute configuration was determined by the conversion to (*S*)-1-phenyl-1-butanol; see note f. [j] Optical purities were determined by 200-MHz ^{1}H NMR spectroscopy of the (−)-MTPA ester. We were indebted to Dr. A. Ishihara of Ono Pharmaceutical Co. for these measurements. [k] Determined by GC analysis. Propargyl Grignard reagent gave a 1:1 mixture.



1

Scheme 1



bar and two dropping funnels, was dried and flushed with nitrogen. The flask was charged with 300 mL of dry ether and cooled by stirring in a −78 °C bath. Freshly distilled trimethyl borate (26 mL, 220 mmol) was charged in the funnel. Freshly prepared propargylmagnesium bromide (ca. 1 M in ether, 200 mmol)[5] was pressure-transferred to the other funnel. Two reactants were added to the vigorously stirred reaction mixture at −78 °C alternately in small portions during a period of 1 h. After the addition was complete, the resulting white slurry was stirred at −78 °C for 20 min and 0 °C for 10 min and then hydrolyzed by the addition of water (13 mL) during 5 min and of 2 N sulfuric acid (110 mL) during 10 min. The mixture was transferred to a 1-L separatory funnel, the ether layer was separated, and the aqueous layer was extracted with ether three times. The combined ether layer and extracts were dried (Na_2SO_4) and concentrated in vacuo to give a pale yellow mass, which was dissolved in ether and triturated with hexane. The colorless crystals of allenylboronic acid thus obtained was further purified by repeated recrystallizations (ether–hexane; 30–35% yield).[6,7]

Allenylboronic acid (311 mg, 3.7 mmol) was placed in a 50-mL flask under argon. Dry tetrahydrofuran (THF; 4 mL) and L-(+)-diethyl tartrate (1.53 g, 7.4 mmol) in dry THF (4 mL) were added successively, and the mixture was stirred at 25 °C for 14 h. Concentration of the resulting solution under low pressure (1 mmHg) afforded an oil. Addition of THF and concentration in vacuo were repeated two additional times to remove a trace of water. The residue[8] was dissolved in dry toluene (20 mL), and cyclohexanecarbaldehyde (0.67 ml, 5.6 mmol) was added dropwise at −78 °C under argon. The resulting slightly cloudy mixture was stirred at −78 °C for 9 h and at −20 °C for 12 h, and the product was extracted with ether three times. The combined ether layers were dried over sodium sulfate, concentrated in vacuo, and chromatographed on silica gel to give (*S*)-1-cyclohexyl-3-butyn-1-ol (313 mg, 56% yield) as a colorless oil, $[\alpha]^{25}_D$ + 7.78° (*c* 3.1, methanol). Analysis of this material as the (−)-MTPA ester[9] gave an enantiomeric excess (ee) of 92%.

Notable features of the new process follow: (1) The reaction of cyclohexanecarbaldehyde with the allenylboronic ester derived

(5) Freshly prepared from propargyl bromide and magnesium in ether in the presence of mercuric chloride: Sondheimer, F.; Amiel, V.; Gaoni, V. *J. Am. Chem. Soc.* **1962**, *84*, 270. It is known that propargylmagnesium bromide isomerizes partly to give the organomagnesium from propyne when standing at room temperature.

(6) Mp 150 °C dec; ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 6.5 (br s, OH), 4.85, 4.52 (AB_2, 3 H).

(7) Allenylboronic acid was previously prepared as an intermediate for the preparation of dibutylallenyl boronate; see: Faure, E.; Gaudemar, M. *C. R. Hebd. Acad. Sci., Ser. C* **1966**, *262*, 1332. Allenylboronic acid thus prepared can be stored at −20 °C under argon. In air, it catches fire within several minutes.

(8) Allenic form was confirmed by ^{1}H NMR (CCl_4) analysis: δ 4.92, 4.70 (A_2B, 3 H).

(9) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

with the molar ratio of tartrate to allenylboronic acid of 1:2 gave 1-cyclohexyl-3-butyn-1-ol with 75% ee. Thus, the optical yield appeared to decrease by the presence of remaining allenylboronic acid, and the ratio of 2:1 was used in subsequent experiments.[10] (2) A single mechanistic feature dominates the chiral tilt since most of the reactions examined so far fit the transition state of **1**. (3) Aromatic and α,β-unsaturated aldehydes gave lower enantioselectivities. It is well-known, however, that benzylic as well as allylic alcohols may be prepared with satisfactory enantioselectivities by the existing techniques.[11] (4) Generally DIPT gave a slightly higher enantiomeric excess than DET.

It seems clear that the methodology described herein has a vast potential in organic synthesis. Acetylenic alcohols may be transformed into other important classes of functionalities including β-hydroxyl ketones and *Z*-homoallylic alcohols.

Acknowledgment. Financial supports from the Ministry of Education, Japanese Government (Grant-in-Aid 57118008) and Asahi Glass Foundation are acknowledged.

Registry No. L(+)-DET, 87-91-2; D-(−)-DET, 13811-71-7; L-(+)-DIPT, 2217-15-4; D-(−)-DIPT, 62961-64-2; cyclohexanecarbaldehyde, 2043-61-0; hexanal, 66-25-1; trimethylacetaldehyde, 630-19-3; benzaldehyde, 100-52-7; *p*-nitrobenzaldehyde, 555-16-8; *p*-methoxybenzaldehyde, 123-11-5; 2-furaldehyde, 98-01-1; *trans*-2-hexenal, 6728-26-3; *trans*-cinnamaldehyde, 14371-10-9; 1-perillaldehyde, 2111-75-3; allenylboronic acid, 83816-41-5; (*S*)-1-cyclohexyl-3-butyn-1-ol, 83816-42-6; (*R*)-1-cyclohexyl-3-butyn-1-ol, 83816-43-7; (*S*)-1-nonyn-4-ol, 81077-12-5; (−)-5,5-dimethyl-1-hexyn-4-ol, 83816-44-8; (*S*)-1-phenyl-3-butyn-1-ol, 83816-45-9; (*R*)-1-phenyl-3-butyn-1-ol, 83816-46-0; (+)-1-*p*-nitrophenyl-3-butyn-1-ol, 83816-47-1; (−)-1-*p*-methoxyphenyl-3-butyn-1-ol, 83816-48-2; (+)-1-(2-furyl)-3-butyn-1-ol, 83816-49-3; (*S*)-*trans*-5-nonen-1-yn-4-ol, 83816-50-6; (+)-*trans*-6-phenyl-5-hexen-1-yn-4-ol, 83816-51-7; 1-(4-(1-methylethenyl)cyclohexen-1-yl)-3-butyn-1-ol, 83816-52-8.

(10) The reaction of allenylboronic acid with aldehydes in THF was slow at −78 °C unless the reaction was warmed to 0 °C. Thus, with the ratio of 1:2, the yield of the reaction drops to 32%.

(11) Recent preparation of optically active benzyl and allyl alcohols: (a) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129. (b) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

Structure of the $[B_2H_7]^-$ Anion

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Ever since it was first synthesized by Brown and co-workers in 1957,[1] the $[B_2H_7]^-$ anion has attracted a considerable amount of attention. As perhaps the only example of a species containing an unsupported[2] B–H–B bond, it provided investigators with the ideal system for probing the details of the three-center two-electron linkage. Various spectroscopic investigations provided support for the single-H-bridged model,[3] $[H_3B(\mu\text{-}H)BH_3]^-$. Ab initio calculations have concluded that the central B–H–B linkage of the $[B_2H_7]^-$ anion is linear,[4] at least in the gas phase, while other calculations on the isoelectronic $[C_2H_7]^+$ cation have predicted that the central C–H–C backbone is bent.[5] Meanwhile, an X-ray structure determination on the closely related $[B_2(C_4H_8)_2H_3]^-$ anion unambiguously showed a bent (140°) B–H–B core.[6] In this paper we report the single-crystal X-ray structural characterization of the $[B_2H_7]^-$ anion in $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$.

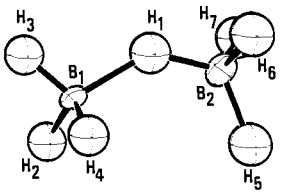

Figure 1. The structure of the $[B_2H_7]^-$ anion.

Table I. Selected Distances (Å) and Angles (deg) in $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$

N-P(1)	1.583 (3)	C-Cl(1)	1.764 (5)
N-P(2)	1.586 (3)	C-Cl(2)	1.752 (5)
P(1)-N-P(2)	138.6 (2)	Cl(1)-C-Cl(2)	112.1 (3)
B(1)···B(2)	2.107 (7)	H(1)-B(1)-H(2)	115 (3)
B(1)-H(1)	1.27 (5)	H(1)-B(1)-H(3)	108 (3)
B(1)-H(2)	1.11 (4)	H(1)-B(1)-H(4)	105 (3)
B(1)-H(3)	0.90 (4)	H(2)-B(1)-H(3)	96 (4)
B(1)-H(4)	0.91 (5)	H(2)-B(1)-H(4)	111 (4)
B(2)-H(1)	1.00 (5)	H(3)-B(1)-H(4)	122 (4)
B(2)-H(5)	1.09 (5)	H(1)-B(2)-H(5)	123 (4)
B(2)-H(6)	1.11 (5)	H(1)-B(2)-H(6)	98 (3)
B(2)-H(7)	1.07 (5)	H(1)-B(2)-H(7)	103 (3)
		H(5)-B(2)-H(6)	107 (3)
B(1)-H(1)-B(2)	136 (4)°	H(5)-B(2)-H(7)	108 (3)
		H(6)-B(2)-H(7)	118 (3)
	Average Values		
$B\text{-}H_t$	1.03	$H_t\text{-}B\text{-}H_t$	110
$B\text{-}H_b$	1.14	$H_t\text{-}B\text{-}H_b$	109

The title compound was prepared according to the following reaction sequence, which employed procedures similar to those described previously in the preparation of $[B_2H_7]^-$ salts:[3d,7]

$$[(Ph_3P)_2N]^+Cl^- + LiBH_4 \xrightarrow[\text{room temp}]{CH_2Cl_2/Et_2O} [(Ph_3P)_2N]^+[BH_4]^- + LiCl\downarrow \quad (1)$$

$$[(Ph_3P)_2N]^+[BH_4]^- + {}^1/_2B_2H_6 \xrightarrow[-78\ °C]{CH_2Cl_2} [(Ph_3P)_2N]^+[B_2H_7]^- \quad (2)$$

Crystals of $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ were grown at room temperature from a CH_2Cl_2 solution into which $(C_2H_5)_2O$ was allowed to diffuse slowly. The clear, colorless crystals showed a tendency to become opaque when removed from the mother liquor. Therefore, they were rapidly loaded into thin-walled capillaries at −78 °C immediately after removal from the solution in which they were grown.

$[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.589$ (10) Å, $b = 10.578$ (9) Å, $c = 17.014$ (18) Å, $\alpha = 90.61$ (8)°, $\beta = 93.58$ (9)°, $\gamma = 93.86$ (8)°. X-ray diffraction data were collected at low temperature (−96 °C) on a Syntex $P2_1$ diffractometer. The positions of all non-hydrogen atoms were revealed in a single E map generated by direct methods,[8] and these were refined anisotropically to yield an initial

(1) (a) Brown, H. C.; Stehle, P. F.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020. (b) Brown, H. C.; Tierny, P. A. *J. Am. Chem. Soc.* **1958**, *80*, 1552.

(2) We define a molecule having an unsupported X–H–X bond as one that is held together solely by that one unique bond. Thus, a molecule such as B_2H_6, which has two B–H–B bridge bonds, is excluded by this definition.

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