Reactions of Phosphine–Monoiodoboranes with 4,4′-Di-*tert*-butylbiphenylide and Electrophiles. Trial of Generation of Tricoordinate Boron Anions and Synthesis of *B*-Functionalized Phosphine–Boranes

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The generation and reactions of tricoordinate boron anions have been investigated using phosphine–boranes. Tricyclohexylphosphine–monoiodoborane was reduced by 2 equiv of lithium 4,4′-di-*tert*-butylbiphenylide (LDBB) in tetrahydrofuran at −78 °C. The generated chemical species reacted with a variety of electrophiles such as water, chlorotrimethylsilane, diphenyl disulfide, methyl trifluoromethanesulfonate, ethylene oxide, benzaldehyde, diethyl carbonate, and carbon dioxide to afford phosphine–boranes possessing a substituent at the boron atom. Reaction of tri-*tert*-butylphosphine–monoiodoborane with LDBB, followed by treatment with water or benzyl bromide, provided di-*tert*-butylphosphine–borane or benzyl(di-*tert*-butyl)phosphine–borane, respectively. These transformations are reasonably interpreted by assuming the existence of tricoordinate boron anions as reactive intermediates.

Introduction

Tricoordinate boron species possessing a dinegative formal charge at the boron atom have an isoelectronic relationship with tricoordinate carbanions. These chemical species are interesting, particularly with respect to whether or not they exhibit reactivities similar to those of carbanions. However, previous investigations on anionic boron species are mostly concerned with tetracoordinate boron-ate complexes,[1] and only a few studies dealing with tricoordinate boron anions have been described in the literature.[2,3] In 1991, Grimes and his coworkers initially reported that metallacarboranes such as $(C_5Me_5)Co(Et_2C_2B_3H_5)$ were subjected to deprotonation with *n*-butyllithium and that the generated boron anion species, upon treatment with alkyl halides or acid chlorides, underwent regioselective *B*-alkylation or *B*-acylation at the middle boron atom.[2] The results apparently demonstrate that the boron anions behave as nucleophiles resembling carbanions. However, the generated boron anions are not simple tricoordinate ones, and hence direct comparison of their reactivities with those of the corresponding carbanions is difficult in these metallacarborane systems.

On the other hand, our interest in simple tricoordinate boron anions led us to carry out *ab initio* RHF/6-31+G** calculations on BH_3^{2-} and CH_3^-. In the minimum energy state, BH_3^{2-} forms a planar triangular structure and CH_3^- forms a pyramidal structure. The energies of the orbitals possessing formal lone pair electrons were calculated to be +0.20748 au and −0.04901 au for BH_3^{2-} and CH_3^- anions, respectively.[4] These calculations indicate that the boron anion is in an extremely high energy state in comparison with the corresponding carbanion, and they also predict that tricoordinate boron anions cannot exist without electronic or steric stabilization factors. On the basis of these theoretical considerations, we planned to generate tricoordinate boron anions using phosphine–boranes.[5] This idea is based on a concept called borane hyperconjugation, i.e., a conjugation between the B–H σ bond and the vacant orbitals at the phosphorus atom, which was previously postulated for the explanation of the stability of phosphine–boranes.[6,7] We considered that an analogous conjugation between structures **A** and **B** might also be conceivable, and that it might stabilize the tricoordinate boron anion to enable its existence as a reactive intermediate, because

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(1) For comprehensive accounts on chemistry of boron ate complexes, see: (a) Brown, H. C. *Organic Synthesis via Boranes*; John Wiley: New York, 1975. (b) Onark, T. *Organoborane Chemistry*; Academic Press: London, 1975. (c) Brown, H. C.; Zaidlewicz, M.; Negishi, E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 45. (d) Negishi, E.; Idacavage, M. J. *Org. React.* **1985**, *33*, 1–246. (e) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988 and references therein.

(2) (a) Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics* **1990**, *9*, 1177–1181. (b) Piepgrass, K. W.; Davis, J. H.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 680–681. (c) Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2397–2403. (d) Piepgrass, K. W.; Stockman, K. E.; Piepgrass, K. W.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404–2413.

(3) Eisch and his co-workers prepared a tricoordinate boron-dianion $[(Ph_5C_4B)^{2-}K^+_2]$ by the reaction of tetraphenylborole with potassium. This anionic species, however, was very stable by virtue of delocalization, and its protolysis required extreme conditions (toluene–acetic acid–6 M HCl, reflux, 20 h). Eisch, J. J.; Galle, J. E.; Kojima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379–385.

(4) Negative charges at the boron and carbon atoms were calculated to be −1.55 and −1.44, respectively.

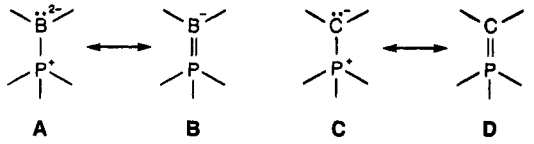
(5) For reviews dealing with phosphine–boranes, see: (a) Schmidbaur, H. *J. Organometal. Chem.* **1980**, *200*, 287–306. (b) Arbusov, B. A.; Nikonov, G. N. *Rev. Heteroatom. Chem.* **1990**, *3*, 1–23. (c) Power, P. P. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 449–460. (d) Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655–660. (e) Imamoto, T. *J. Synth. Org. Chem. Jpn.* **1987**, *45*, 592–602. (f) Imamoto, T. *J. Synth. Org. Chem.* **1993**, *51*, 223–231.

(6) A concept of borane hyperconjugation has been documented. (a) Graham, W. A. G.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1956**, *3*, 164–177. (b) Burg, A. B.; Brendel, G. *J. Am. Chem. Soc.* **1958**, *80*, 3198–3202. (c) Coyle, T. D.; Kaesz, H. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 2989–2994. (d) Cowley, A. H.; Damasco, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 6815–6821. (e) Demuynck, J.; Veillard, A. *J. Chem. Soc., Chem. Commun.* **1970**, 873–874. (f) Hillier, I. H.; Marriott, J. C.; Saunders, V. R.; Ware, M. J.; Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc., Chem. Commun.* **1970**, 1586–1587. (g) Cowley, A. H.; Kemp, R. A.; Lattman, M.; McKee, M. L. *Inorg. Chem.* **1982**, *21*, 85–88.

(7) For discussions on P–B bond nature based on spectroscopic studies, see: (a) Young, D. E.; McAchran, G. E.; Shore, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 4390–4396. (b) Rudolph, R. W.; Schultz, C. W. *J. Am. Chem. Soc.* **1971**, *93*, 6821–6822. (c) Albanese, J. A.; Kreider, D. G.; Schaeffer, C. D., Jr.; Yoder, C. H.; Samples, M. S. *J. Org. Chem.* **1985**, *50*, 2059–2062. (d) Couley, A. H.; Kemp, R. A.; Lattman, M.; McKee, M. L. *Inorg. Chem.* **1982**, *21*, 85–88.

0022-3263/94/1959-6753$04.50/0

this conjugation closely resembles a phosphorus ylide–ylene conjugation between structures **C** and **D**, which has been well documented as the most important factor for stabilizing phosphorus ylides.[8]



Here we report the generation of tricoordinate boron anions using phosphine–boranes and their reactivities with various electrophiles.[9]

Results and Discussion

We initially considered that the expected boron anions might be generated by the direct deprotonation of the boranato hydrogens with strong bases and that they might undergo nucleophilic addition to carbonyl groups. Based on this idea, tricyclohexylphosphine–borane (**1**) was treated successively with *tert*-butyllithium and benzaldehyde in THF at −78 °C. However, no appreciable products were obtained in this case. On the other hand, the use of the potassium *tert*-butoxide-*n*-butyllithium reagent system (a superbase)[10] as the deprotonation agent afforded, after treatment with benzaldehyde, a single product possessing the α-hydroxybenzyl group, in 77% yield.[11] This product, however, was not the expected one, tricyclohexylphosphine-(α-hydroxybenzylborane, but dicyclohexyl[1-(α-hydroxybenzyl)cyclohexyl]phosphine–borane. These results clearly indicate that deprotonation did not occur at the boron atom, but that it preferably occurred at the 1-position of the cyclohexyl group (Scheme 1).

These experimental results led us to search for other approaches for obtaining tricoordinate boron anions. We postulated that the reduction of phosphine–monohaloboranes and related substrates might generate the target chemical species, and we attempted to reduce tricyclohexylphosphine–boranes possessing a good leaving group at the boron atom, using strong reducing agents.[12] After various screenings of the reducing agents and reaction

Scheme 1

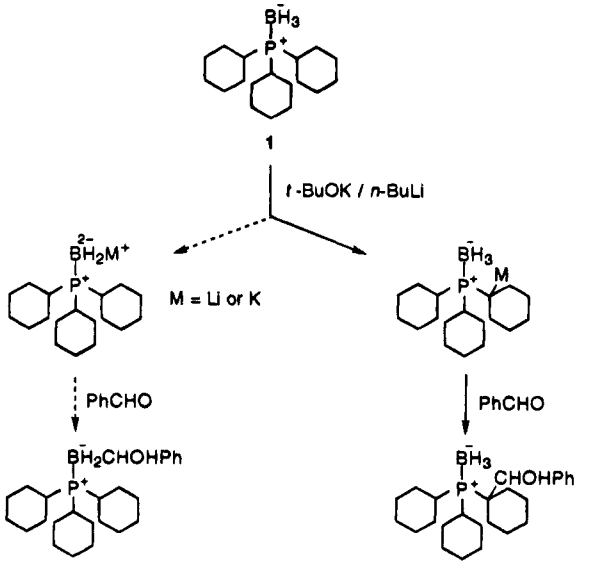
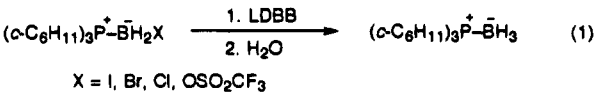


Table 1. Reduction of *B*-Substituted Tricyclohexylphosphine–Boranes with LDBB

entry	X	conditions[a]	yield (%)[b]
1	I	−78 °C, 5 min	89
2	Br	−20 °C, 10 min	83
3	Cl	0 °C, 90 min	80[c]
4	OSO_2CF_3	0 °C, 10 min	93
5	OSO_2CH_3	20 °C, 120 min	*d*

[a] All reactions were carried out in THF. *B*-Substituted phosphine–borane (1 mmol) in THF (2 mL) was added to a solution of LDBB (4 mmol) in THF at −78 °C. [b] Isolated yield of tricyclohexylphosphine–borane. [c] Starting material was recovered in 20% yield. [d] No reaction occurred.

conditions, we found that lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[13,14] was effective in the reduction of these substrates (eq 1 and Table 1). Thus, tricyclohexylphosphine–monoiodoborane (**2**), when treated with more than 2 molar equiv of LDBB at −78 °C, was rapidly reduced to give, after workup with water, tricyclohexylphosphine–borane (**1**) in 89% yield.[15] Monobromo and monochloro derivatives and triflate[16] were also subjected to reduction at the temperatures indicated in Table 1. Methanesulfonate,[17] however, resisted reduction at room temperature.



(1)

(8) For representative reviews, see: (a) Maercker, A. *Org. React.* **1965**, 14, 270–490. (b) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966. (c) Gosney, I.; Powley, A. G. in *Organophosphorus Reagents in Organic Synthesis*, Cadogan, J. I. G., Ed.; Academic Press: London, 1979, pp 17–153. (d) Smith, D. J. H. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, N. D., Sutherland, I. O., Eds.; Pergamon Press: Oxford, 1979; Vol. 2, Chapter 10.6. (e) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927 and references therein.

(9) Preliminary results of this work were reported at the 3rd International Symposium on Heteroatom Chemistry, 1992, Riccione, and the 7th IUPAC Symposium on Organo-Metallic Chemistry Directed towards Organic Synthesis, 1993, Kobe. See also: Imamoto, T. In *Organic Synthesis in Japan: Past, Present, and Future*; Noyori, R., Ed; Tokyo Kagaku-Dojin: Tokyo, 1992; pp 129–134.

(10) (a) Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741–744. (b) Margot, C.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 1035–1038.

(11) The reaction of triphenylphosphine–borane under similar conditions resulted in the formation of many products.

(12) Reductive cleavage of boron–halogen bonds by one-electron reductants has been reported. (a) Auten, R. W.; Kraus, C. A. *J. Am. Chem. Soc.* **1952**, 3398–3401. (b) Brotherton, R. J.; McCloskey, A. L.; Petterson, L. L.; Steinberg, H. *J. Am. Chem. Soc.*, **1960**, *82*, 6242–6245. (c) Köster, R.; Benedikt, G.; Grassberger, M. A. *Ann. Chem.* **1968**, *719*, 187–209. (d) van der Kerk, S. M.; Boersma, J.; van der Kerk, G. J. M. *Tetrahedron Lett.* **1976**, 4765–4766. (e) Herberich, G. E.; Ganter, C.; Wesemann, L.; Boese, R. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 912–913. (f) Herberich, G. E.; Englert, U.; Ganter, C.; Wesemann, L. *Chem. Lett.* **1992**, *125*, 23–29.

(13) (a) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924–1930. (b) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1983**, *48*, 4705–4713.

(14) LDBB is known to be effective for reductive cleavage of carbon–heteroatom bonds. For some representative examples, see: (a) Ireland, R. E.; Smith, M. G. *J. Am. Chem. Soc.* **1988**, *110*, 854–860. (b) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152–161. (c) Cohen, T.; Jeong, I.-H.; Mudryk, B.; Bhupathy, M.; Awad, M. M. A. *J. Org. Chem.* **1990**, *55*, 1528–1536. (d) Cohen, T.; Doubleday, M. D. *J. Org. Chem.* **1990**, *55*, 4784–4786. (e) Mudryk, B.; Cohen, T. *J. Am. Chem. Soc.* **1991**, *113*, 1866–1867. (f) Rawson, D. J.; Meyers, A. I. *Tetrahedron Lett.* **1991**, *32*, 2095–2098.

(15) Tricyclohexylphosphine–monoiodoborane was not reduced in THF at −78 °C by $LiAlH_4$, *tert*-butyllithium, or samarium(II) iodide.

(16) This compound was prepared by the reaction of tricyclohexylphosphine–borane with trifluoromethanesulfonic acid in dichloromethane. Imamoto, T.; Yanagawa, M. Unpublished results.

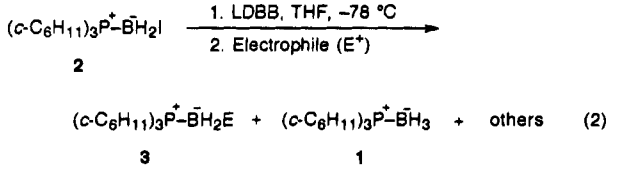
(17) Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2846–2849.

Table 2. Reactions of Compound 2 with LDBB and Electrophiles

entry[a]	electrophile	molar ratio of 2/LDBB/TMDA/electrophile	products (%)[b]
1	D_2O	1/4/0/10	(c-C_6H_{11})$_3$PBH$_2$D (**3a**) (89)
2	Me_3SiCl	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$SiMe$_3$ (**3b**) (81), **1** (3)[c]
3	Me_3SiOTf	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$SiMe$_3$ (**3b**) (84), **1** (10)
4	PhSSPh	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$SPh (**3c**) (46), **1** (11)
5	PhSSPh	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$SPh (**3c**) (57), **1** (21)
6	PhSeSePh	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$SePh (**3d**) (80), **1** (5)
7	PhSeSePh	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$SePh (**3d**) (89), **1** (5)
8	MeI	1/4/0/3	(c-C_6H_{11})$_3$PBH$_2$Me (**3e**) (8), **1** (37)
9	MeI	1/4/4/12	(c-C_6H_{11})$_3$PBH$_2$Me (**3e**) (37), **1** (17)
10	MeOTf	1/4/0/3	(c-C_6H_{11})$_3$PBH$_2$Me (**3e**) (62), **1** (28)
11	MeOTf	1/4/4/12	(c-C_6H_{11})$_3$PBH$_2$Me (**3e**) (86), **1** (14)
12	EtOTf	1/4/0/3	(c-C_6H_{11})$_3$PBH$_2$Me (**3f**) (34), **1** (53)
13	CH_2=$CHCH_2Br$	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$CH$_2$CH=CH$_2$ (**3g**) (4), **1** (6)[d]
14	ethylene oxide	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$(CH$_2$)$_2$OH (**3h**) (34), **1** (52)
15	propylene oxide	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$CH$_2$CHOHMe (**3i**) (25), **1** (74)
16	propylene oxide	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$CH$_2$CHOHMe (**3i**) (50), **1** (47)
17	MeCHO	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$CHOHMe (**3j**) (47), **1** (40)
18	MeCHO	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$CHOHMe (**3j**) (53), **1** (47)
19	PhCHO	1/4/0/3	(c-C_6H_{11})$_3$PBH$_2$CHOHPh (**3k**) (55), **1** (40)
20	PhCHO	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$CHOHPh (**3k**) (79), **1** (trace)
21	PhCHO	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$CHOHPh (**3k**) (40), **1** (16), (c-C_6H_{11})$_3$PBH$_2$C$_6$H$_4$CHO-*p* (**3l**) (8)
22	Me_2CO	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$C(OH)Me$_2$ (**3m**) (11), **1** (84)
23	$(CD_3)_2CO$	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$C(OH)(CD$_3$)$_2$ (**3n**) (28), (c-C_6H_{11})$_3$PBH$_2$D (**3a**) (53)
24	PhCOMe	1/4/4/3	**1** (46)[e]
25	Ph_2CO	1/4/0/3	(c-C_6H_{11})$_3$PBH$_2$C$_6$H$_4$COPh-*p* (**3o**) (46), **1** (24)
26	*p*-MeOC$_6$H$_4$COPh	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$C$_6$H$_4$(COC$_6$H$_4$OMe-*p*)-*p* (**3p**) (37), **1** (10)
27	fluorenone	1/4/4/3	tricyclohexylphosphine–[3-(9-oxofluorenyl)]borane complex (**3q**) (20), **1** (18)
28	$PhCO_2Et$	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$COPh (**3r**) (38), **1** (6)
29	$PhCO_2Et$	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$COPh (**3r**) (29), **1** (16)
30	$(EtCO)_2O$	1/2/0/1	(c-C_6H_{11})$_3$PBH$_2$CO$_2$Et (**3s**) (93), **1** (5)
31	$(EtCO)_2O$	1/4/4/3	(c-C_6H_{11})$_3$PBH$_2$CO$_2$Et (**3s**) (98), **1** (trace)
32	CO_2	1/2/0[f]	(c-C_6H_{11})$_3$PBH$_2$CO$_2$H (**3t**) (77), **1** (6)
33	CO_2	1/4/4[f]	(c-C_6H_{11})$_3$PBH$_2$CO$_2$H (**3t**) (90), **1** (10)

[a] All reactions were carried out in THF at −78 °C under argon. [b] Isolated yield based on compound **2**. [c] (c-C_6H_{11})$_3$PBH$_2$Cl was isolated in 3% yield. [d] (c-C_6H_{11})$_3$PBH$_2$Br was detected on TLC. However, this compound decomposed on silica gel during purification procedure. [e] No addition products were isolated. [f] Carbon dioxide was introduced after addition of LDBB.

Encouraged by these results, we next examined the reactivities of the generated intermediates. Compound **2** was chosen as the most suitable precursor, since it reacted readily with LDBB at low temperatures. A variety of electrophiles were tested as trapping agents. Thus, the electrophiles were added to the reaction mixture of compound **2** and LDBB, and the products were isolated and their structures were determined in conventional manner (eq 2). The results are shown in Table 2.



The reaction with D_2O afforded *B*-deuterated compound **3a**. The reactions with chlorotrimethylsilane, trimethylsilyl triflate, diphenyl disulfide, or diphenyl diselenide provided the corresponding *B*-functionalized compounds (**3b**, **3c**, and **3d**) in good to high yields. Surprisingly, *B*-alkylations occurred when strong alkylation agents were employed (entries 8–12).

The reactions with carbonyl compounds are particularly interesting. Acetaldehyde and benzaldehyde were subjected to nucleophilic addition reaction to give compounds **3j** and **3k**, respectively. It should be noted that these reactions closely resemble the carbonyl addition reaction of carbanions. The reaction with acetone, however, provided the addition product **3m** in poor yield; instead, compound **1** was obtained in high yield (entry 22). Use of acetone-d_6 afforded deuterated phosphine–borane **3a**. This result indicates that the generated reactive intermediate possesses high basicity and undergoes proton abstraction from acetone. Use of aromatic ketones as carbonyl components induced another type of reaction. For example, the reaction with benzophenone afforded compound **3o**, whose structure was unequivocally determined by single-crystal X-ray analysis, as shown in Figure 1.[18] Similarly, compounds **3p** and **3q** were isolated in moderate yields from *p*-methoxybenzophenone and fluorenone, respectively. It is noted that in these reactions a considerable amount of a dimerized phosphine–borane, (c-C_6H_{11})$_3$PBH$_2$BH_2P(C$_6$H$_{11}$-c)$_3$ (**4**), was produced.[19] Ethyl benzoate, diethyl carbonate, and carbon dioxide also served as electrophiles, yielding phosphine–borane derivatives possessing carbonyl functionalities at the boron atom (entries 28–33).

These results can be reasonably interpreted by assuming the existence of a boron anion (**5**) as the reactive intermediate. Thus, we consider that the reduction of compound **2** with 2 mol equiv of LDBB generates boron anion **5** and this anion reacts with electrophiles to afford the *B*-functionalized compounds **3** (Scheme 2).[20,21] It is reasonable to consider that the reactions other than that with aromatic ketones proceed through nucleophilic

(18) The authors have deposited atomic coordinate for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(19) Reaction with 4,4′-dimethylbenzophenone or nitrobenzene afforded compound **4** in 79 or 65% yield, respectively.

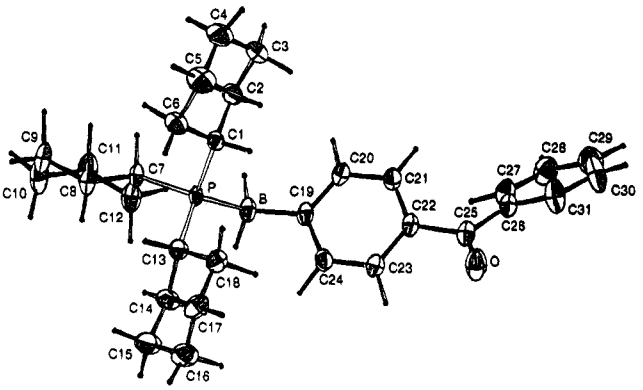
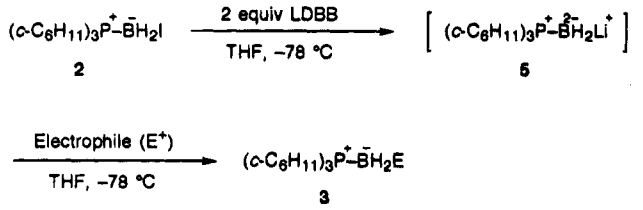
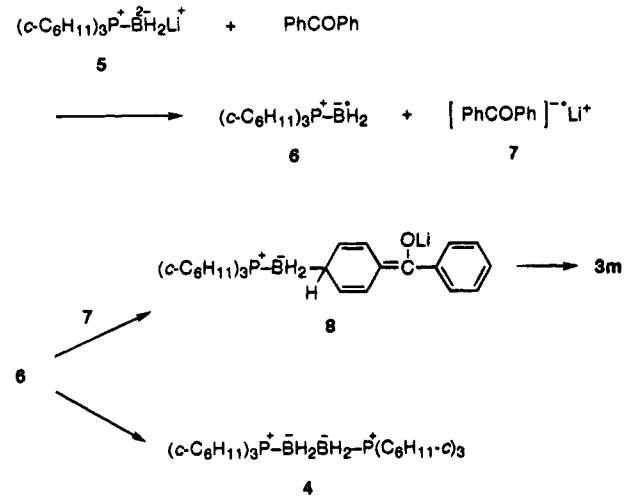


Figure 1. ORTEP drawing of $(c\text{-}C_6H_{11})_3PBH_2C_6H_4COC_6H_5$ (**3o**).

Scheme 2



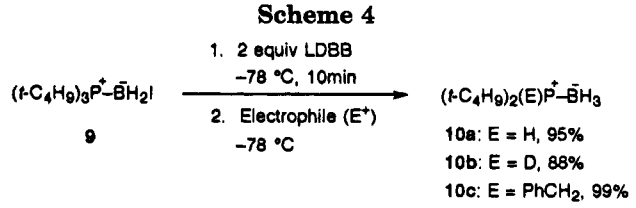
Scheme 3



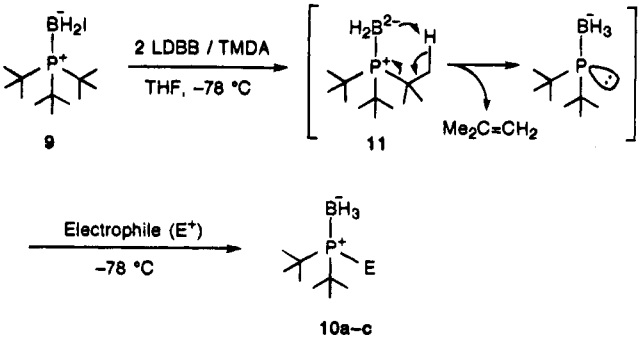
substitution or addition in a manner similar to the reaction patterns of carbanions.

The reaction with aromatic ketones is not yet fully understood, but we assume that the reaction involves a single-electron transfer process. A presumed reaction pathway is illustrated in Scheme 3 for the reaction with benzophenone. Thus, one electron is transferred from the boron anion **5** to benzophenone to generate a boranyl radical **6** and benzophenone ketyl radical **7**.[22] These radical species are coupled in the 1,6-addition manner to give **8**, which after workup is converted to compound **3m** via oxidation in air. The dimerized phosphine–borane **4** is formed by homo-coupling of the boranyl radical **6**.

Scheme 4



Scheme 5



It is worth mentioning that these reaction sequences provide a new method for functionalization of the boranato group of phosphine–boranes. The phosphine–borane derivatives obtained by these reactions are not readily synthesized by the use of previously existing methods,[17,23] and hence, we believe our method is useful for synthesis.

Next, tri-*tert*-butylphosphine–monoiodoborane (**9**) was allowed to react with LDBB, followed by treatment with H_2O. In sharp contrast to the reaction of **2**, di-*tert*-butylphosphine–borane **10a** was produced in excellent yield.[24] Quenching with D_2O afforded compound **10b**, and use of benzyl bromide as an electrophile provided benzyl(di-*tert*-butyl)phosphine–borane **10c** (Scheme 4). 2-Methylpropene was detected in the reaction mixture by GC analysis. It is apparent from these results that the phosphorus–carbon bond was cleaved, and reactions with electrophiles occurred at the phosphorus atom, not at the boron atom.

We considered that these reactions proceed through the pathway depicted in Scheme 5. Thus, the initially formed boron anion **11** undergoes an intramolecular pericyclic reaction to give a tricoordinate phosphorus species which subsequently reacts with electrophiles to afford compounds **10a–c**.

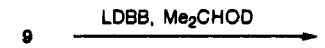
In order to trap intermediate **11**, the reaction was carried out in the presence of 2-propan-*d*-ol. The result is described in eq 3. The formation of a significant amount of *B*-deuterated tri-*tert*-butylphosphine–borane **12** strongly supports the existence of intermediate **11**.

(20) One might consider the possibility that the products are formed by the substitution reaction of compound **2** with nucleophiles generated by the reduction of the added electrophiles with LDBB. In order to exclude this possibility, we examined the reactions of compound **2** with lithium hydride, lithium phenylthiolate, and methylithium at −78 °C, and found that no or only traces of the substitution reactions occurred under these conditions.

(21) We attempted to measure ^{11}B NMR in order to observe the boron anion. Unfortunately, however, only broad signals indicating no definite chemical shifts were observed at −78 °C in THF–THF-d_8. Some decomposition occurred with the elevation of temperature, and at 20 °C a triplet at −54.2 ppm (J = 100 Hz) was observed.

(22) Boranyl radicals derived from phosphine–boranes and related substrates have been described in the literature. (a) Köster, R.; Benedikt, G.; Schrötter, H. W. *Angew. Chem.* **1964**, 649–450. (b) Berclaz, par T.; Geoffroy, M. *Mol. Phys.* **1976**, *32*, 815–821. (c) Baban, J. A.; Roberts, B. P. *J. Chem. Soc. Chem. Commun.* **1983**, 1224–1226. (d) Barban, Z. A.; Roberts, B. P.; *J. Chem. Soc. Perkin Trans. 2* **1984**, 1717–1772. (e) Dang, H.-S.; Roberts, B. P. *Tetrahedron Lett.* **1992**, *33*, 6169–6172.

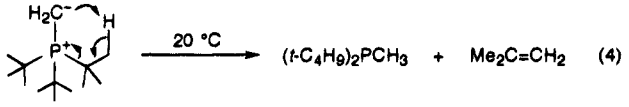
(23) (a) Köster, R.; Rickborn, B. J. *Am. Chem. Soc.* **1967**, *89*, 2782–2784. (b) Wisian-Neilson, P.; Wilkins, M. A.; Weigel, F. C.; Foret, C. J.; Martin, D. R. J. *Inorg. Nucl. Chem.* **1981**, *43*, 457–458. (c) Bestmann, H. J.; Röder, T. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 782–783. (d) Schmidbaur, H.; Weiss, E.; Graf, W. *Organometallics* **1985**, *4*, 1233–1237. (e) Bestmann, H. J.; Röder, T.; Sühs, K. *Chem. Ber.* **1988**, *121*, 1509–1517.



$$(t\text{-}C_4H_9)_2(H)P^+\text{–}\bar{B}H_3 \quad + \quad (t\text{-}C_4H_9)_3\overset{+}{P}\text{–}\bar{B}H_2D \qquad (3)$$

10a 32% 12 42%

This pericyclic reaction is compared with the reaction of tri-*tert*-butylphosphonium methylide (eq 4), which was previously reported by Schmidbaur and his co-workers.[26] It is apparent from the reaction temperature that the boron anion is more reactive than the corresponding carbanion.



$$\xrightarrow{20\ ^\circ C} (t\text{-}C_4H_9)_2PCH_3 + Me_2C{=}CH_2 \qquad (4)$$

In summary, we have examined the reactions of phosphine–monoiodoboranes with LDBB to generate tricoordinate boron anion species. The reactive intermediates generated resemble carbanions in their reactivities; they undergo nucleophilic substitution, carbonyl addition, and intramolecular electrocyclic reaction.

Further investigations on the isolation and characterization of more stabilized tricoordinate boron anions are underway in our laboratory.

Experimental Section

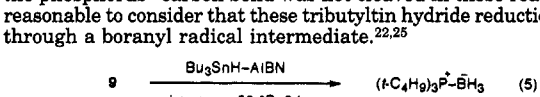
General. All glassware was dried at 120 °C, assembled hot, and cooled under argon. THF and ether were distilled from sodium benzophenone ketyl under argon prior to use. Benzene and TMEDA were distilled from CaH_2 and stored under argon atmosphere. All reactions were carried out under argon atmosphere. Products were isolated by column chromatography on silica gel (Wakogel C-200 or C-300) or preparative TLC on silica gel (Wakogel B-5F). ^{11}B and ^{31}P NMR spectra were recorded (at 28.7 or 36.2 MHz). Chemical shifts are reported from TMS (^1H and ^{13}C), trimethyl borate (^{11}B), and phosphoric acid (^{31}P) in δ units.

Reaction of Tricyclohexylphosphine–Borane with a Superbase and Benzaldehyde. A mixture of tricyclohexylphosphine–borane (294 mg, 1.00 mmol), potassium *tert*-butoxide (336 mg, 3.00 mmol), and THF (5 mL) was cooled to −78 °C. *n*-Butyllithium (2.0 mL of 1.55 M hexane solution, 3.1 mmol) was added to the mixture, and stirring was continued for 6 h. Benzaldehyde (300 μL, 3.0 mmol) was added, and after 1 h the reaction was quenched with water. The reaction mixture was extracted with ether and the combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was washed twice with hexane to obtain the crude product (346 mg), which was purified by preparative TLC (silica gel, CH_2Cl_2, $R_f = 0.53$) to afford pure dicyclohexyl-[1-(α-hydroxybenzyl)cyclohexyl]phosphine–borane (308 mg, 0.769 mmol, 77%): mp 164–165 °C; IR (KBr) 3380, 2895, 2850, 2350, 1440, 1060, 770, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.5 (m, 35H), 3.8 (d, 1H, OH), 5.3 (dd, 1H, CHPh), 7.2–7.4 (m, 3H), 7.5–7.6 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.87 (d, $J = 8.6$ Hz), 21.90 (d, $J = 6.4$), 25.12 (s), 25.89 (s), 26.16 (s), 27.31 (d, $^2J_{CP} = 12.8$ Hz), 27.56 (d, $^2J_{CP} = 8.6$ Hz), 27.75 (d, $^3J_{CP} = 4.3$ Hz), 27.84 (d, $^3J_{CP} = 4.3$ Hz), 28.28 (s), 29.41 (s), 29.58 (d, $^3J_{CP} = 4.3$ Hz), 30.01 (d, $^3J_{CP} = 4.3$ Hz), 32.98 (d, $^1J_{CP} = 25.8$ Hz), 35.87 (d, $^1J_{CP} = 25.8$ Hz), 45.92 (d, $^1J_{CP} = 21.4$ Hz), 127.55 (s), 127.86 (s), 142.06 (d, $^3J_{CP} = 4.3$ Hz); HRMS (FAB) calcd for $C_{25}H_{41}BOP$ 399.2988 (M − H), found 399.2997.

Tricyclohexylphosphine–Monoiodoborane (2). This compound was prepared by the general procedure for the preparation of phosphine–monoiodoboranes.[27] Iodine (2.02 g, 7.95 mmol) was added to a solution of tricyclohexylphosphine–borane (4.41 g, 15 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at room temperature until the starting material disappeared on TLC. The solvent was evaporated and the brown solid residue was dissolved in CH_2Cl_2 (25 mL). Ethyl acetate (50 mL) was added to this solution, and the mixture was left to stand at room temperature for 2 h. The precipitated solid was collected by filtration and washed with CH_2Cl_2–ethyl acetate (1:2) to give colorless needles (3.82 g, 61%): mp 155.0–155.5 °C; IR (KBr) 2865, 2825, 2390 (ν (B–H)), 1430, 1120, 945, 885 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.05 (m, 2H), 1.24–1.96 (m, 30H), 2.06–2.16 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.99, 27.21 (d, $^2J_{CP} = 10.8$ Hz), 28.03, 30.97 (d, $^1J_{CP} = 32.2$ Hz); ^{11}B NMR ($CDCl_3$) δ −56.1; ^{31}P NMR ($CDCl_3$) δ 4.98. Anal. Calcd for $C_{18}H_{35}BIP$: C, 51.46; H, 8.40. Found: C, 51.48; H, 8.47.

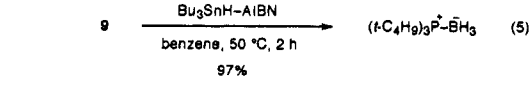
Reactions of Tricyclohexylphosphine–Monoiodoborane (2) with LDBB and Electrophiles. A typical procedure is described for the reaction with benzaldehyde. A solution of compound **2** (420 mg, 1.00 mmol) in THF (4 mL) was added to a solution of LDBB[28] (10 mL, 0.40 M, 4.0 mmol) containing TMEDA (610 μL, 4.0 mmol) at −78 °C. After stirring for 10 min, benzaldehyde (330 μL, 3.2 mmol) was added and stirring was continued for another 10 min. Water (10 mL) was added and the mixture was extracted with ether. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was passed through a short column of silica gel using hexane and dichloromethane to remove 4,4′-di-*tert*-butylbiphenyl. The crude product obtained was purified by preparative TLC on silica gel using ether–hexane (1:4) to give **3k** (316 mg, 79%) and **3l** (31.7 mg, 8%). **3k, $(c\text{-}C_6H_{11})_3PBH_2CH(OH)Ph$:** mp 122–123 °C; IR (KBr) 3400 (br), 2880, 2825, 2300, 1435, 1030, 1000, 750, 700 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 1.04–1.97 (m, 35H), 1.22 (br s, 1H), 4.87–4.90 (m, 1H), 7.12–7.14 (m, 1H), 7.33–7.36 (m, 2H), 7.70–7.71 (m, 2H); ^{13}C NMR (C_6D_6) δ 26.52, 27.67 (d, $^2J_{CP} = 10.8$ Hz), 28.54, 31.43 (d, $^1J_{CP} = 28.0$ Hz), 72, 124.75, 125.84, 128.32, 154.29; HRMS (FAB) calcd for $C_{25}H_{41}BOP$ 399.2988 (M − H), found 399.2998. Anal. Calcd for $C_{25}H_{42}BOP$: C, 75.00; H, 10.57. Found: C, 74.95; H, 10.83. **3l, $(c\text{-}C_6H_{11})_3PBH_2C_6H_4CHO\text{-}p$:** mp 124–126 °C; IR (KBr) 2925, 2870, 2290, 1675, 1580, 1435, 1215, 1165, 1000, 825 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 0.7–3.0 (m, 2H), 0.8–1.9 (m, 33H), 7.76–7.81 (m, 4H), 9.88 (s, 1H, CHO); ^{13}C NMR (C_6D_6) δ 26.38, 27.23, 27.46 (d, $^2J_{CP} = 9.8$ Hz), 28.19 (d, $^3J_{CP} = 2.0$ Hz), 31.14 (d, $^1J_{CP} = 27.4$ Hz), 31.39, 35.76, 42.73, 43.73, 75.23, 123.36,

(24) In order to compare these reactions, reduction of **9** with tributyltin hydride was carried out in the presence of a catalytic amount of AIBN. The reaction proceeded in benzene at 50 °C to give tri-*tert*-butylphosphine–borane in 97% yield (eq 5). Under similar conditions, reaction with tributyltin deuteride provided *B*-deuterated tri-*tert*-butylphosphine–borane in 92% yield (eq 6). It is noted that the phosphorus–carbon bond was not cleaved in these reactions. It is reasonable to consider that these tributyltin hydride reductions proceed through a boranyl radical intermediate.[22,25]



$$\xrightarrow[\text{benzene, 50 °C, 2 h}]{Bu_3SnH\text{–}AIBN} (t\text{-}C_4H_9)_3\overset{+}{P}\text{–}\bar{B}H_3 \qquad (5)$$

97%



$$\xrightarrow[\text{benzene, 50 °C, 5 h}]{Bu_3SnD\text{–}AIBN} (t\text{-}C_4H_9)_3\overset{+}{P}\text{–}\bar{B}H_2D \qquad (6)$$

92%

(25) (a) Wardell, J. L. In *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: New York, 1989; pp 315–358. (b) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

(26) Schmidbaur, H.; Blaschke, G.; Köhler, F. H. *Z. Naturforsch. B* **1977**, *32*, 757–761.

(27) (a) Smith, G. L.; Kelly, H. C. *Inorg. Chem.* **1968**, 2000–2004. (b) Myers, W. H.; Ryschkewitsch, G. E. *Phosphorus* **1975**, *5*, 97–99. (c) Denniston, M. L.; Chiusano, M.; Brown, J.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 379–382. (d) Sisler, H. H.; Mathur, M. A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1745–1750. (e) Pennington, B. T.; Chiusano, M. A.; Dye, D. J.; Martin, E. D.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 389–394.

(28) LDBB was prepared according to a procedure described in the literature.[13] The concentration was determined by titration; the solution was added using a syringe to a solution of accurately weighed *l*-menthol in dry THF under argon.

125.54, 125.60, 127.25, 128.22, 128.50, 129.15, 134.55, 134.61, 137.35, 137.45, 191.79; HRMS (FAB) calcd for $C_{25}H_{41}BOP$ 399.2988 (M + H), found 399.2988.

In a similar manner, following compounds were prepared and characterized.

Compound 3a, (c-C_6H_{11})$_3$PBH$_2$D: mp 175–177 °C; IR (KBr) 2880, 2825, 2320, 1740 (ν(B–D)), 1440, 995, 890, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.1–0.7 (m, 2H), 1.19–1.90 (m, 33H); ^{13}C NMR ($CDCl_3$) δ 26.18 (s), 27.29 (d, $^2J_{CP}$ = 9.8 Hz), 27.88 (s), 30.92 (d, $^1J_{CP}$ = 30.3 Hz); HRMS (FAB) calcd for $C_{18}H_{32}DBP$ 292.2476 (M − 3H), found 292.2480. Anal. Calcd for $C_{18}H_{35}DBP$: C, 73.22; H, 12.29. Found: C, 73.18; H, 12.17.

Compound 3b, (c-C_6H_{11})$_3$PBH$_2$SiMe$_3$: mp 158–160 °C; IR (KBr) 2880, 2830, 2300, 1440, 1235, 840, 820, 755, 670 cm^{-1}; ^{1}H NMR (C_6D_6) δ −0.5–1.5 (m, 2H), 0.54 (s, 9H), 1.1–2.0 (m, 33H); ^{13}C NMR (C_6D_6) δ 4.54 (d, J = 4.3 Hz), 26.42 (s), 27.53 (d, $^2J_{CP}$ = 8.6 Hz), 28.45 (s), 32.45 (d, $^1J_{CP}$ = 30.1 Hz); ^{31}P NMR ($CDCl_3$) δ 31.3; ^{11}B NMR ($CDCl_3$) δ −62.6 (br d, J_{BP} = *ca.* 70 Hz); HRMS (FAB) calcd for $C_{21}H_{43}BPSi$ 365.2965 (M − H), found 365.2964. Anal. Calcd for $C_{21}H_{44}BPSi$: C, 68.83; H, 12.10. Found: C, 68.72; H, 11.73. Recently, Schmidbaur *et al.* reported the crystal and molecular structure of this compound.[29]

Compound 3c, (c-C_6H_{11})$_3$PBH$_2$SPh: mp 101–103 °C; IR (KBr) 2880, 2825, 2340, 1570, 1435, 995, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.8 (m, 2H), 1.20–2.08 (m, 33H), 6.97 (t, J = 7.3, 1H), 7.12–7.16 (m, 2H), 7.50 (dd, J = 1.1 Hz; 6.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.02, 27.26 (d, $^2J_{CP}$ = 9.8 Hz), 27.99 (d, $^2J_{CP}$ = 2.0 Hz), 30.49 (d, $^1J_{CP}$ = 30.3 Hz), 122.99, 127.96 (s), 130.05 (s), 142.41 (d, J = 6.8); ^{31}P NMR ($CDCl_3$) δ 13.7 (br s); HRMS (FAB) calcd for $C_{24}H_{39}BPS$ 401.2603 (M − H), found 401.2605. Anal. Calcd for $C_{24}H_{40}PBS$: C, 71.63; H, 10.02. Found: C, 71.82; H, 9.73.

Compound 3d, (c-C_6H_{11})$_3$PBH$_2$SePh: mp 119–121 °C; IR (KBr) 2880, 2830, 2330, 1570, 1435, 970, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.8 (m, 2H), 1.11–2.08 (m, 33H), 7.02–7.13 (m, 3H), 7.63 (dd, J = 1.3 Hz; 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.00 (s), 27.23 (d, $^2J_{CP}$ = 10.8 Hz), 28.08 (d, $^3J_{CP}$ = 2.0 Hz), 30.75 (d, $^1J_{CP}$ = 30.3 Hz), 124.09 (s), 128.13 (s), 132.72 (s), 134.42 (d, J = 3.9); ^{31}P NMR ($CDCl_3$) δ 14.0 (br s); ^{11}B NMR ($CDCl_3$) δ −48.6 (br s); HRMS (FAB) calcd for $C_{24}H_{40}BP^{80}Se$ 450.2126, found 450.2119. Anal. Calcd for $C_{24}H_{40}PBSe$: C, 64.15; H, 8.97. Found: C, 64.05; H, 8.75.

Compound 3e, (c-C_6H_{11})$_3$PBH$_2$Me: mp 115–116 °C; IR (KBr) 2880, 2825, 2285, 2250, 1435, 1055, 1040, 1005, 890, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.17 (m, 3H), 0.70–2.10 (m, 2H), 1.14–1.93 (m, 33H); ^{13}C NMR ($CDCl_3$) δ −4.2 (br s), 26.31, 27.49 (d, $^2J_{CP}$ = 9.8 Hz), 28.12 (d, $^3J_{CP}$ = 2.0 Hz), 30.81 (d, $^1J_{CP}$ = 27.4 Hz); ^{31}P NMR ($CDCl_3$) δ 19.1; ^{11}B NMR ($CDCl_3$) δ −50.9 (br d, J_{BP} = *ca.* 60 Hz); HRMS (FAB) calcd for $C_{19}H_{37}$-BP 307.2726 (M − H), found 307.2712. Anal. Calcd for $C_{19}H_{38}$-PB: C, 74.02; H, 12.42. Found: C, 74.31; H, 12.57.

Compound 3f, (c-C_6H_{11})$_3$PBH$_2$Et: mp 106–107 °C; IR (KBr) 2880, 2825, 2280, 1435, 1265, 1060, 1000, 980, 885, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30–0.43 (m, 2H,), 0.96 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HP}$ = 2.4 Hz, 3H), 1.15–1.95 (m, 35H); HRMS (FAB) calcd for $C_{20}H_{39}BP$ 321.2883 (M − H), found 321.2882.

Compound 3g, (c-C_6H_{11})$_3$PBH$_2$CH$_2$CH=CH$_2$: mp 80–81 °C; IR (KBr) 2880, 2850, 2250, 1610, 1435, 1185, 1000, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.5–2.2 (m, 37H), 4.63–4.66 (m, 1H), 4.80 (d, J = 16.7), 6.00–6.10 (m, 1H); HRMS (FAB) calcd for $C_{21}H_{39}PB$ 333.2882 (M − H), found 333.2883.

Compound 3h, (c-C_6H_{11})$_3$PBH$_2$(CH$_2$)$_2$OH: mp 100–101 °C dec; IR (KBr) 3300 (br), 2880, 2830, 2275, 1435, 1030, 960, 890, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–0.9 (m, 2H), 1.0–2.2 (m, 36H), 3.64 (t, $^3J_{HH}$ = 9 Hz, 2H); ^{13}C NMR (C_6D_6) δ 26.37 (s), 27.48 (d, $^2J_{CP}$ = 8.8 Hz), 28.33 (s), 31.08 (d, $^1J_{CP}$ = 27.9 Hz), 67.15 (d, $^3J_{CP}$ = 25.0 Hz); HRMS (FAB) calcd for $C_{20}H_{37}$-BOP 335.2676 (M − 3H), found 335.2668. Anal. Calcd for $C_{20}H_{40}BOP$: C, 71.00; H, 11.92. Found: C, 71.20; H, 11.70.

Compound 3i, (c-C_6H_{11})$_3$PBH$_2$CH$_2$CHOHMe: mp 108–109 °C dec; IR (KBr) 3300 (br), 2880, 2825, 2260, 1435, 995, 890, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.5–0.8 (m, 2H), 1.0–2.1 (m, 38H), 2.2 (s, 1H, OH), 3.65–3.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.12 (s), 26.17 (s), 27.37 (d, $^2J_{CP}$ = 10.3 Hz), 28.04 (s), 30.75 (d, $^1J_{CP}$ = 26.3 Hz), 71.10 (d, $^3J_{CP}$ = 22.0 Hz); HRMS (FAB) calcd for $C_{21}H_{41}BOP$ 351.2988 (M − H), found 351.2984.

Compound 3j, (c-C_6H_{11})$_3$PBH$_2$CHOHMe: mp 108.0–108.5 °C; IR (KBr) 3400 (br), 2880, 2825, 2260, 1435, 1060, 1000, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.62 (br s, 1H), 1.05–1.99 (m, 35H), , 1.74–1.76 (m, 3H), 3.94–3.95 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 26.55 (s), 27.6, 28.5, 29.66 (d, J = 21.5 Hz), 31.45 (d, $^1J_{CP}$ = 27.4 Hz), 64 (br s); ^{31}P NMR ($CDCl_3$) δ 16.7; ^{11}B NMR ($CDCl_3$) δ −45.6 (br d, J_{BP} = *ca.* 50 Hz); HRMS (FAB) calcd for $C_{20}H_{39}BOP$ 337.2832 (M − H), found 337.2833. Anal. Calcd for $C_{20}H_{40}BOP$: C, 71.00; H, 11.92. Found: C, 70.82; H, 12.22.

Compound 3m, (c-C_6H_{11})$_3$PBH$_2$C(OH)Me$_2$: mp 75–76 °C dec; IR (KBr) 3350 (br), 2900, 2850, 2280, 1440, 1120, 1035, 1000, 885 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{41}BOP$ 351.2989 (M − H), found 351.2986.

Compound 3n, (c-C_6H_{11})$_3$PBH$_2$C(OH)(CD$_3$)$_2$: mp 81–82 °C dec; IR (KBr) 3350 (br), 2920, 2860, 2300, 2220, 1435, 1040, 890 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{35}D_6BOP$ 357.3365 (M − H), found 357.3368.

Compound 3o, (c-C_6H_{11})$_3$PBH$_2$C$_6$H$_4$COPh-*p*: mp 143–144 °C; IR (KBr) 2900, 2840, 2280, 1635, 1580, 1435, 1300, 1275, 1000, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–3.0 (m, 2H), 1.00 (m, 9H), 1.27 (m, 6H), 1.4–1.7 (m, 9H), 1.80 (m, 9H), 7.05–7.14 (m, 3H), 7.82–7.84 (m, 4H), 7.95–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.42 (s), 27.50 (d, $^2J_{CP}$ = 8.6 Hz), 28.25 (s), 31.11 (d, $^1J_{CP}$ = 28.0 Hz), 127.94 (s), 128.16 (s), 128.32 (s), 129.34 (s), 130.20 (s),131.38 (s), 136.93 (d, J = 6.5 Hz), 139.54 (s), 196.33 (s); ^{31}P NMR ($CDCl_3$) δ 15.6 (br s); ^{11}B NMR ($CDCl_3$) δ −46.9 (br s). Anal. Calcd for $C_{31}H_{44}BOP$: C, 78.47; H, 9.35. Found: C, 78.37; H, 9.43.

X-ray Crystallographic Analysis of 3o. A well-shaped monoclinic crystal of **3o** was obtained by recrystallization from hexane: $C_{31}H_{44}BOP$; space group $P2_1/n$; Z = 4; D = 1.123 g cm^{-3}; cell constants a = 15.670(6), b = 13.735(3), c = 13.191(4), β = 96.845(26); V = 2818.8. Lattice constants and intensity data for **3o** were measured using graphite-monochromated Cu K$_\alpha$ radiation on a Rigaku AFC-5 diffractometer. A total of 3799 unique reflections with $F_0 > 3\sigma(F_0)$ were obtained using the ω–2θ scanning method with a 2θ scan speed of 4°/min to 120°. The structure was solved by the UNICS-III system (Computer Library of University of Tokyo) based on direct methods. Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilizing anisotropic thermal parameters for all nonhydrogen atoms resulted in R = 0.065.

Compound 3p: mp 126–128 °C; IR (KBr) 2875, 2825, 2290, 1630, 1580, 1435, 1250, 1165, 1000, 925, 850, 840, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (m, 35H), 3.88 (s, 3H), 6.93–6.96 (m, 2H), 7.51–7.53 (m, 2H), 7.57–7.59 (m, 2H), 7.80–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.15 (s), 27.34 (d, $^2J_{CP}$ = 10.3 Hz), 27.92 (d, $^3J_{CP}$ = 3.0 Hz), 30.74 (d, $^1J_{CP}$ = 27.8 Hz), 55.41 (s), 113.26 (s), 128.65 (d, J = 2.9 Hz), 131.12 (s), 132.37 (s),134.26 (d, J = 2.9), 136.04 (s), 136.11 (s), 162.66 (s), 196.51 (s); HRMS (FAB) calcd for $C_{32}H_{47}BO_2P$ 505.3407 (M + H), found 505.3407. Anal. Calcd for $C_{32}H_{46}BO_2P$: C, 76.18; H, 9.19. Found: C, 75.95; H, 9.12.

Compound 3q: mp 157–159 °C; IR (KBr) 2890, 2840, 2300, 1695, 1580, 1420, 1290, 1005, 920, 770, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.4 (m, 35H), 7.20–7.62 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 26.23 (s), 27.43 (d, $^2J_{CP}$ = 9.3 Hz), 28.04 (d, $^1J_{CP}$ = 2.9 Hz), 30.94 (d, $^1J_{CP}$ = 28.4 Hz), 119.54 (s), 122.87 (d, J = 2.9 Hz), 123.93 (s), 124.34 (s), 127.94 (d, J = 5.9 Hz), 128.23 (s), 131.26 (d, J = 3.9 Hz), 134.02 (s), 135.24 (s), 137.08 (d, J = 6.9 Hz), 142.93 (d, J = 2.9 Hz), 145.83 (s), 194.78 (s); HRMS (FAB) calcd for $C_{31}H_{43}BOP$ 473.3145 (M + H), found 473.3146.

Compound 3r, (c-C_6H_{11})$_3$PBH$_2$COPh: mp 128–130 °C; IR (KBr) 2900, 2845, 2340, 1705, 1605, 1570, 1445, 1270, 905, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17–2.50 (m, 32H), 2.11–2.18 (m, 3H), 7.36–7.43 (m, 3H), 8.05–8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.15 (s), 27.36 (d, $^2J_{CP}$ = 10.8 Hz), 28.35 (d, $^3J_{CP}$ = 2.0 Hz), 31.02 (d, $^1J_{CP}$ = 30.3 Hz), 127.61 (s), 127.81 (s), 130.88

(29) Blumenthal, A.; Bissinger, P.; Schmidbaur, H. *J. Organometal Chem.* **1993**, *462*, 107–110.

(s), 136.30 (d, J = 6.9); ^{11}B NMR ($CDCl_3$) δ −49.4 (br d, J_{BP} = *ca.* 70 Hz); HRMS (FAB) calcd for $C_{25}H_{41}BOP$ 399.2988 (M + H), found 399.2987. Anal. Calcd for $C_{25}H_{40}BOP$: C, 75.37; H, 10.12. Found: C, 75.78; H, 10.16.

Compound 3s, (c-C_6H_{11})$_3$PBH$_2$CO$_2$Et: mp 83–86 °C; IR (KBr) 2900, 2850, 2320, 1670, 1440, 1130, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–2.13 (m, 38H), 4.01 (q, J = 7.1, 2H); ^{13}C NMR ($CDCl_3$) δ 14.82, 26.12, 27.34 (d, $^1J_{CP}$ = 10.8 Hz), 28.03 (d, $^3J_{CP}$ = 2.9 Hz), 30.74 (d, $^1J_{CP}$ = 31.3 Hz), 56.59; HRMS (FAB) calcd for $C_{21}H_{41}BO_2P$ 367.2937 (M + H), found 367.2940. This compound was gradually subjected to hydrolysis to give compound **5r** on prolonged contact with moisture.

Compound 3t, (c-C_6H_{11})$_3$PBH$_2$CO$_2$H: mp 136–137 °C dec [lit.[30] mp 132–134 ° C]; IR (KBr) 3035 (br), 2895, 2825, 2350, 1625, 1440, 1230, 1130, 1000, 890, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–2.10 (m, 35H), 8.25 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.08 (s), 27.30 (d, $^2J_{CP}$ = 0.7 Hz), 28.01 (s), 30.85 (d, $^1J_{CP}$ = 19.3 Hz), 197 (br s); ^{31}P NMR ($CDCl_3$) δ 17.6; ^{11}B NMR ($CDCl_3$) δ −53.5 (br d, J_{BP} = *ca.* 70 Hz); HRMS (FAB) calcd for $C_{19}H_{37}BO_2P$ 339.2625 (M + H), found 339.2635. Anal. Calcd for $C_{19}H_{36}BO_2P$: C, 67.46; H, 10.73. Found: C, 67.60; H, 10.48.

Tri-*tert*-butylphosphine–Monoiodoborane (9). This compound was prepared from tri-*tert*-butylphosphine–borane by the usual manner:[27] mp 196–197 °C dec; IR (KBr) 2950, 2890, 2460, 2420, 1475, 1180, 980, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.5–2.9 (m, 2H), 1.57 (d, $^3J_{HP}$ = 12.1 Hz, 27H); ^{13}C NMR ($CDCl_3$) δ 30.68, 38.22 (d, $^1J_{CP}$ = 22.5 Hz); HRMS (FAB) calcd for $C_{12}H_{28}BIP$ 341.1067 (M − H), found 341.1069. Anal. Calcd for $C_{12}H_{29}BIP$: C, 42.14; H, 8.55. Found: C, 42.18; H, 8.32.

Reaction of Tri-*tert*-butylphosphine–Monoiodoborane (9) with LDBB and Benzyl Bromide. A solution of tri-*tert*-butylphosphine–monoiodoborane (**9**) (205 mg, 0.60 mmol) in THF (10 mL) was cooled to −78 °C under argon atmosphere, and to this solution, one portion of cold (−78 °C) LDBB solution (6 mL, 2.4 mmol) was added. After stirring for 10 min, benzyl bromide (850 μL, 7.1 mmol) was added, and the resulting solution was slowly warmed to room temperature before quenching with water. The mixture was worked up in a similar manner as described above, and the crude product obtained was purified by preparative TLC on silica gel using ethyl acetate–hexane (1:8) to afford compound **10c** (148 mg, 99%). Further purification by preparative TLC on silica gel using ether–hexane (1:12) as the eluent afforded a pure product: mp 74–75 °C; IR (KBr) 2900, 2350, 1455, 1365, 1065, 790, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.1–1.0 (m, 3H), 1.26 (d, $^3J_{HP}$ = 12.3 Hz, 18H), 3.15 (d, $^2J_{HP}$ = 12.3 Hz, 2H), 7.21–7.29 (m, 3H), 7.44–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.08 (d, $^1J_{CP}$ = 25.8 Hz), 28.28 (s), 32.81 (d, $^1J_{CP}$ = 25.8 Hz), 126.61 (s), 128.09 (s), 130.68 (s), 134.67 (s). Anal. Calcd for $C_{15}H_{28}BP$: C, 72.02; H, 11.28. Found: C, 72.23; H, 11.54.

Compound 10a (t-C_4H_9)$_2$P(H)BH$_3$: mp 62–63 °C; IR (KBr) 2925, 2310, 1455, 1360, 1060, 1020, 895, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.1–0.9 (m, 3H), 1.32 (d, $^3J_{HP}$ = 13.4 Hz, 18H), 4.11 (dq, $^1J_{HP}$ = 351 Hz, J = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.93, 30.51 (d, $^1J_{CP}$ = 27.4 Hz); HRMS (EI) calcd for $C_8H_{19}P$ 146.1224 (M − BH_3), found 146.1220. Anal. Calcd for $C_8H_{22}BP$: C, 60.04; H, 13.85. Found: C, 59.94; H, 13.74.

Compound 10b (t-C_4H_9)$_2$P(D)BH$_3$: mp 61–63 °C; IR (KBr) 2925, 2310, 1455, 1360, 1065, 1020, 820, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.1–0.9 (m, 3H), 1.32 (d, $^3J_{HP}$ = 13.6 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 28.93, 30.38 (d, $^1J_{CP}$ = 27.4 Hz); HRMS (EI) calcd for $C_8H_{18}DP$ 147.1288 (M − BH_3), found 147.1280. Anal. Calcd for $C_8H_{21}DBP$: C, 59.66; H, 13.77. Found: C, 59.69; H, 13.45.

Reaction of Tri-*tert*-butylphosphine–Monoiodoborane with Bu_3SnH in the Presence of AIBN. A mixture of compound **9** (102.6 mg, 0.30 mmol), Bu_3SnH (245 μL, 0.90 mmol), AIBN (14.8 mg, 0.090 mmol), and benzene (1 mL) was warmed under argon atmosphere at 50 °C for 2 h. The reaction mixture was cooled to room temperature and partitioned between water (5 mL) and ether (5 mL). The organic layer was separated and washed with diluted HCl, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short column of silica gel using hexane and dichloromethane to remove Bu_3SnH. The crude product was purified by preparative TLC on silica gel using AcOEt–hexane (1:5) to give t-Bu_3PBH_3 (62.9 mg, 97%). The reaction of **9** with Bu_3SnD under similar conditions (in benzene, 50 °C, 5 h) afforded t-Bu_3PBH_2D in 92% yield.

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(30) Das, M. K.; Maiti, P. K.; Roy, S.; Mittakanti, M.; Morse, K. W.; Hall, I. H. *Arch. Pharm. (Weinheim, Ger.)* **1992**, *325*, 267–272.