Synthesis and Properties of New Five-Membered Heterocyclic Compounds Containing a P–B–S Linkage

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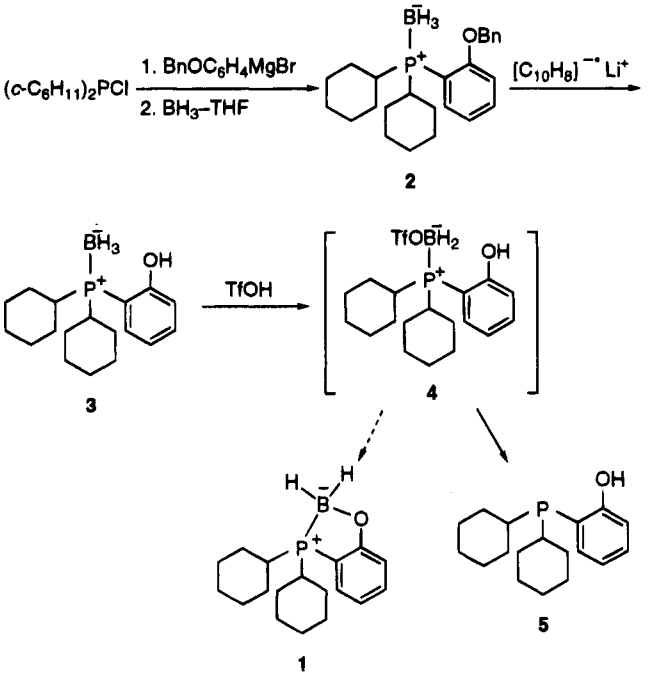
Introduction

In our continuing study on phosphine–boranes,[1] we found that a phosphonium-stabilized tricoordinate boron dianion was generated by the reaction of tricyclohexylphosphine–monoiodoborane with 4,4′-di-*tert*-butylbiphenylide.[2] The boron dianion was trapped by reaction with electrophiles, leading to B-functionalized phosphine–boranes. However, our attempts at isolation or spectroscopic characterization of the anionic species were unsuccessful because it was very unstable even at low temperature.[3] We envisioned that relatively stable anions might be generated from five-membered cyclic phosphine–boranes possessing a B–O or a B–S bond. For this purpose we required five-membered heterocyclic compounds which are fused with the benzene ring. This paper describes the synthesis and properties of this new class of heterocyclic compounds.[4,5]

Results and Discussion

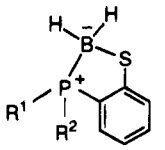
Our initial attempt was undertaken with the preparation of (*P–B*)-(2-(boryloxy)phenyl)dicyclohexylphosphine (**1**), which involves a boron–oxygen bond. Chlorodicyclohexylphosphine was allowed to react with 2-(benzyloxy)phenylmagnesium bromide, followed by treatment with borane–THF, to afford (2-(benzyloxy)phenyl)dicyclohexylphosphine–borane (**2**). The benzyl group of this compound was reductively removed by reaction with lithium naphthalenide to afford dicyclohexyl(2-hydroxyphenyl)phosphine–borane (**3**) in almost quantitative yield.[6] The compound **3** was then treated with trifluoromethanesulfonic acid in CH_2Cl_2 in order to prepare a key intermediate **4**. The reaction was complete within a few minutes at room temperature. However, the isolated compound was not the expected one but dicyclohexyl(2-hydroxyphenyl)phosphine (**5**). The mechanism

Scheme 1



for the formation of compound **5** has not yet been clarified, but we suppose that intermediate **4** or compound **1** is extremely unstable and is rapidly converted to **5** via hydrolysis.[7] One-pot conversion of compound **3** to compound **1** on successive treatments with trifluoromethanesulfonic acid and sodium hydride was also unsuccessful. Furthermore, another route via the reaction of phosphine **5** with butyllithium and monochloroborane–dimethyl sulfide was examined. However, the expected compound **1** was not produced; instead, compound **3** was isolated in 40% yield (Scheme 1).

These experimental results led us to examine the synthesis of sulfur-containing five-membered phosphine–boranes **6a–d**. At first, (2-mercaptophenyl)diphenylphos-



6a: $R^1 = R^2 = Ph$
6b: $R^1 = Ph$, $R^2 = 2\text{-}MeOC_6H_4$
6c: $R^1 = Ph$, $R^2 = 2\text{-}MeSC_6H_4$
6d: $R^1 = R^2 = c\text{-}C_6H_{11}$

phine (**7a**) and (2-mercaptophenyl)(2-methoxyphenyl)phenylphosphine (**7b**) were prepared by the reaction of lithium 2-lithiobenzenethiolate[8] with chlorodiphenylphosphine or chloro(2-methoxyphenyl)phenylphosphine according to the literature procedure.[9,10] They were allowed to react successively with butyllithium and monochloroborane–dimethyl sulfide to give compounds **6a** and **6b**, respectively, in good yields (eq 1). In a similar procedure, compound **6c** was obtained from compound **7c** in 61% yield (eq 2). Compound **6d** was also prepared in a one-pot procedure by the successive reactions of chlorodicyclo-

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(1) Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655. Imamoto, T.; Oshiki, T.; Kusumoto, T.; Sato, T. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Oshiki, T.; Imamoto, T. *J. Am. Chem. Soc.* **1992**, *114*, 3975. Imamoto, T.; Oshiki, T.; Onozawa, T.; Matsuo, M.; Hikosaka, T.; Yanagawa, M. *Heteroatom Chem.* **1992**, *3*, 563. Imamoto, T.; Matsuo, M.; Nonomura, T.; Kishikawa, K.; Yanagawa, M. *Heteroatom Chem.* **1993**, *4*, 475.

(2) Imamoto, T.; Hikosaka, T. *J. Org. Chem.* **1994**, *59*, 6753.

(3) Recently, the existence of a tricoordinate boron dianion, $BH3^{2-}$, was proved by ^{11}B NMR spectroscopy. Godfroid, R. A.; Hill, T. G.; Onak, T. P.; Shore, S. G. *J. Am. Chem. Soc.* **1994**, *116*, 12107.

(4) Acyclic phosphine–boranes possessing a P–B–S bond linkage have been reported. Vahrenkamp, H. *J. Organomet. Chem.* **1971**, *28*, 167. Schmidbaur, H.; Weiss, E.; Graf, W. *Organometallics* **1985** *4*, 1233.

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(6) A conventional hydrogenolysis in methanol using 10% Pd/C as a catalyst was not effective in this case even under rather drastic conditions (50 °C and 50 atm of hydrogen pressure), probably because the phosphine–borane substrate poisoned the catalyst.

(7) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.

(8) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654. Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

(9) Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327.

(10) Masson, S.; Saint-Clair, J.-F.; Saquet, M. *Synthesis* **1993**, 485.

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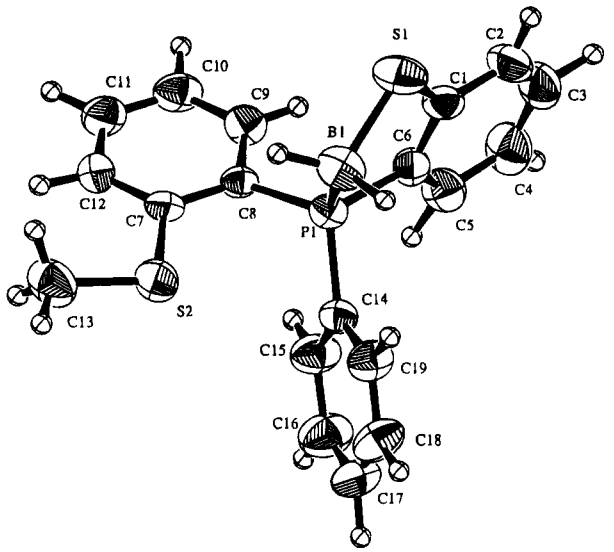
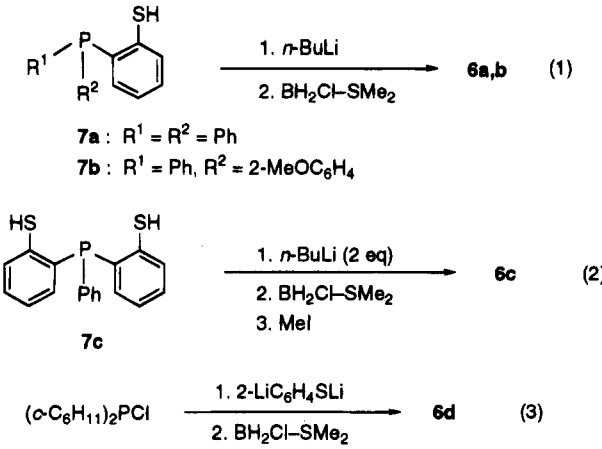


Figure 1. ORTEP drawing of compound **6c**.

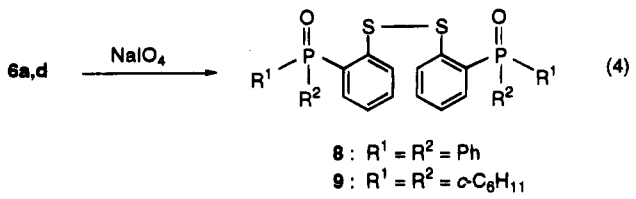
hexylphosphine with lithium 2-lithiobenzenethiolate and monochloroborane–dimethyl sulfide (eq 3).



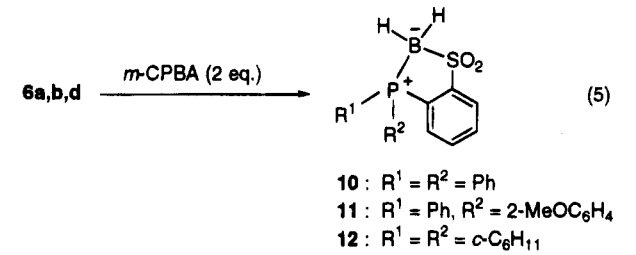
The structures of these compounds **6a–d** were determined by spectroscopic data together with elemental analyses. In their IR spectra, two sharp peaks appeared at around 2400 cm^{-1}, indicating the presence of the BH_2 group. In the FAB-mass spectra, significant, large molecular ion peaks were observed for all of these compounds. The ^{31}P NMR signals of compounds **6c** and **6d** appeared at 29.9 and 45.1 ppm, respectively, as broad peaks. The broadening of the peaks is caused by the boron quadrupolar field and the coupling of the phosphorus nucleus with ^{11}B and ^{10}B nuclei.[11]

The structure of compound **6c** was unequivocally determined by X-ray crystallographic analysis. The ORTEP drawing, which clearly indicates the five-membered structure involving a P–B–S bond linkage, is shown in Figure 1.[12] The bond length (1.943(7) Å) between the phosphorus and the boron atoms is not unusual compared with reported P–B bond lengths.[13] Of the three bond angles of boron–phosphorus–carbon, the angle (100.2(3)°) of B1–P1–C6 is the smallest. This is probably due to fusion of the five-membered ring with the benzene ring.

The reactivities of compounds **6a–d** were examined. Compound **6a**, on heating in methanol containing acetic acid, rapidly decomposed to afford compound **7a** in almost quantitative yield. Compounds **6a–d** were readily oxidized by $NaIO_4$ or *m*-chloroperbenzoic acid (*m*-CPBA). Thus, the oxidation of **6a** and **6d** with two equiv of $NaIO_4$ occurred in aqueous THF at room temperature. The isolated products were assigned by their IR and FAB-mass spectra as bis-phosphine oxides **8** and **9** which involved a disulfide moiety (eq 4). On the other hand,



the reactions of compounds **6a,b,d** with 2 equiv of *m*-CPBA provided colorless crystalline compounds whose structures were assigned as the sulfone analogs **11** and **12**, respectively, by spectroscopic data and elemental analyses (eq 5).[14–16] Compound **12** was subjected to X-ray



crystallographic analysis in order to confirm its structure. The ORTEP drawing is shown in Figure 2.[12]

It is noted that the boranato functionality remained unchanged in these *m*-CPBA oxidations. Attempts to prepare sulfoxide analogs using 1 equiv of *m*-CPBA were unsuccessful. Thus, these reactions provided the sulfone analogs as the major products along with considerable amounts of the starting materials. This reactivity is responsible for the facile disproportionation reaction of the initially formed sulfoxides into sulfone and sulfide analos under the reaction conditions.[5]

Experimental Section

General. All glassware was dried at 120 °C, assembled hot, and cooled under argon. THF was distilled from sodium benzophenone ketyl under argon prior to use. 1,1,2,2-Tetram-

(11) Cowley, A. H.; Damasco, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 6815. Rudolph, R. W.; Schultz, C. W. *J. Am. Chem. Soc.* **1971**, *93*, 6821. Kameda, M.; Shimoi, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3705. Burg, A. B. *Inorg. Chem.* **1985**, *24*, 3342. Power, W. P. *J. Am. Chem. Soc.* **1995**, *117*, 1800.

(12) The authors have deposited the atomic coordinates for the structures of **6c** and **12** 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.

(13) Iijima, K.; Hakamata, Y.; Nishikawa, T.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3033. Bhattacharyya, A.; Sarkar, S. B.; Das, M. K.; Talapatra, S. K. *Acta Crystallogr. C* **1988**, *44*, 701. Bradley, D. C.; Hursthouse, M. B.; Motevalli, M.; Dao-Hong, Z. *J. Chem. Soc., Chem. Commun.* **1991**, 7. Schmidbaur, H.; Wimmer, T.; J. Lachmann, J.; Müller, G. *Chem. Ber.* **1991**, *124*, 275. Schmidbaur, H.; Stützer, A.; Bissinger, P.; Schier, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1519.

(14) The reaction of compound **6d** with *m*-CPBA (2 equiv) afforded many products.

(15) Use of a large excess of *m*-CPBA provided highly polar substrates whose structures were not determined.

(16) Simple phosphine–boranes were oxidized by a 4 molar excess of *m*-CPBA to afford the corresponding phosphine oxides in excellent yields. Imamoto, T.; Hirose, K.; Amano, H.; Seki, H. To be published.

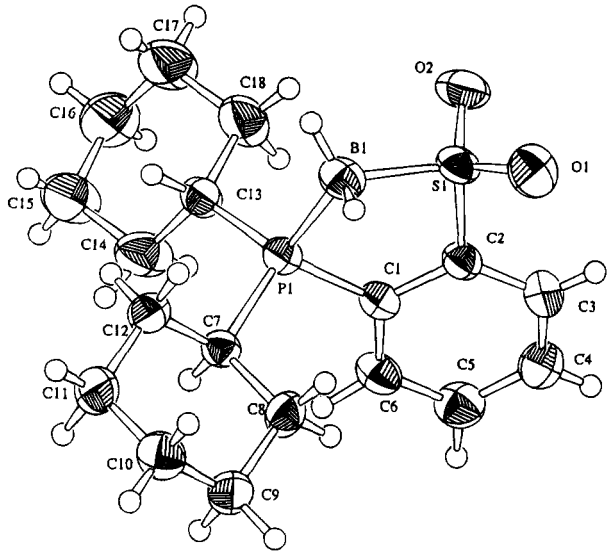


Figure 2. ORTEP drawing of compound **12**.

ethylethylenediamine (TMEDA) was distilled from CaH_2 and stored under argon atmosphere. Monochloroborane–dimethyl sulfide complex was purchased from Aldrich. Products were isolated by column chromatography on silica gel or preparative TLC on silica gel. Chemical shifts are reported from TMS (^1H and ^{13}C), phosphoric acid (^{31}P), and trimethyl borate (^{11}B) in δ units.

(2-(Benzyloxy)phenyl)dicyclohexylphosphine–Borane (2). To a solution of chlorodicyclohexylphosphine (22.7 g, 97.6 mmol) in dry THF (50 mL) was added with mechanical stirring a solution of (2-(benzyloxy)phenyl)magnesium bromide prepared by the reaction of 2-(benzyloxy)bromobenzene (24.1 g, 91.4 mmol) and magnesium (3.0 g, 0.12 mol) in dry THF (60 mL) at −78 °C under argon. The mixture was allowed to warm to rt with stirring, and borane–THF (100 mL of 1 M THF solution) was added. The mixture was carefully added to ice-cold 1 M HCl (200 mL) with vigorous stirring. The precipitated solid was collected and washed with water to give a white powder (14.8 g, 41%): mp 157.5–158.5 °C (hexane/1,2-dichloroethane = 7/2); ^1H NMR ($CDCl_3$) δ 7.95–7.88 (m, 1H), 7.55–7.35 (m, 1H), 7.43 (s, 5H), 7.07–6.94 (m, 2H), 5.09 (s, 2H), 2.40–2.20 (m, 2H), 1.85–1.00 (20H); ^{13}C NMR (126 MHz) ($CDCl_3$) δ 160.3 (d, J_{P-C} = 4.3 Hz), 138.4 (d, J_{P-C} = 12.9 Hz), 135.9, 132.9, 128.7, 128.6, 128.3, 121.1 (d, J_{P-C} = 10.8 Hz), 114.6 (d, J_{P-C} = 45.1 Hz), 110.7 (d, J_{P-C} = 4.3 Hz), 70.6, 32.4 (d, J_{P-C} = 34.4 Hz), 28.0, 27.5, 27.0, 26.9, 26.8, 25.9; IR (KBr) 2280 cm^{-1}; MS(EI) 380 (M − BH_3, 100), 298 (43), 192 (37), 91 (48); HRMS (FAB) calcd for $C_{25}H_{36}BOP$ 394.2597, found 394.2558. Anal. Calcd for $C_{25}H_{36}BOP$: C, 76.15; H, 9.20. Found: C, 76.20; H, 9.18.

Dicyclohexyl(2-hydroxyphenyl)phosphine–Borane (3). A solution of lithium naphthalenide (30 mmol) in THF (100mL) was added to a solution of compound **2** (3.94 g, 10 mmol) in THF (30 mL) at 0 °C. The mixture was gradually warmed to ambient temperature, and stirring was continued for about 4 h until the starting material had disappeared. The reaction mixture was treated with 1 M HCl (100 mL) and extracted with ether, and the combined extracts were dried over $MgSO_4$. After evaporation of the solvent, the residual solid was washed with hexane to leave a crude product (2.12 g, 70%), which was recrystallized from hexane–1,2-dichloroethane (10/1) to afford colorless needles: mp 163.0–163.5 °C; ^1H NMR ($CDCl_3$) δ 7.94 (br s, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.28 (td, J = 8.2, 1.7 Hz), 6.98–6.91 (m, 2H), 1.57–1.20 (m, 22H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 162.2 (d, J_{P-C} = 7.4 Hz), 133.2, 132.1, 119.9 (d, J_{P-C} = 7.3 Hz), 118.2 (d, J_{P-C} = 5.9 Hz), 107.5 (d, J_{P-C} = 48.5 Hz), 32.1 (d, J_{P-C} = 35.2 Hz), 26.7, 26.6 (d, J_{P-C} = 4.4 Hz), 26.3, 26.1 (d, J_{P-C} = 3.0 Hz), 25.8; IR (KBr) 2270 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{29}BOP$ 303.2049, found 303.2047. Anal. Calcd for $C_{18}H_{30}BOP$: C, 71.07; H, 9.94. Found: C, 71.21; H, 10.06.

Dicyclohexyl(2-hydroxyphenyl)phosphine (5): mp 51.0–52.5 °C (hexane); ^1H NMR ($CDCl_3$) δ 7.29–7.23 (m, 2H), 7.05 (br s, 1H), 6.92–6.87 (m, 2H), 2.05–0.95 (m, 22H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 161.2 (d, J_{P-C} = 19.1 Hz), 132.9, 130.9, 119.8, 114.8, 32.3 (d, J_{P-C} = 7.3 Hz), 30.2 (d, J_{P-C} = 19.1 Hz), 28.5 (d, J_{P-C} = 5.9 Hz), 27.1, 26.9, 26.82, 26.75, 26.2; IR (KBr) 3280 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{27}OP$ 290.1800, found 290.1807. Anal. Calcd for $C_{18}H_{27}OP$: C, 74.45; H, 9.37. Found: C, 73.90; H, 9.43.

***(P–B)*-(2-(Borylthio)phenyl)diphenylphosphine (6a).** To a mixture of (2-mercaptophenyl)diphenylphosphine[9] (5.89 g, 20 mmol), 2,2′-dipyridyl (1 mg), and dry THF (40 mL) was added butyllithium (12.3 mL of 1.7 M hexane solution) at 0 °C until the color of the solution turned red. Monochloroborane–dimethyl sulfide (2.3 mL, 22 mmol) was added, and the mixture was kept at ambient temperature overnight. The reaction mixture was treated with 1 M HCl solution and extracted with dichloromethane. Evaporation of the solvent left a pasty mass, which was triturated with hexane–ethyl acetate (1/3) (ca. 20 mL). The precipitated solid (3.12 g) was collected on a Buchner funnel. The filtrate was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel using hexane–ethyl acetate (5/1) as the eluent to give another crop (1.60 g, 26%). The combined products were recrystallized from dichloromethane–methanol (1/10) to give colorless crystals: mp 127–129 °C; ^1H NMR (270 MHz) ($CDCl_3$) δ 7.6–7.2 (m, 13H), 7.1–7.0 (m, 1H); ^{13}C NMR (100MHz) ($CDCl_3$) δ 155.7 (d, J_{P-C} = 36.6 Hz), 133.1 (d, J_{P-C} = 10.3 Hz), 132.5 (d, J_{P-C} = 2.9 Hz), 132.0 (d, J_{P-C} = 2.9 Hz), 131.3 (d, J_{P-C} = 4.4 Hz), 129.1 (d, J_{P-C} = 10.3 Hz), 128.1 (d, J_{P-C} = 8.8 Hz), 126.1 (d, J_{P-C} = 79.2 Hz), 125.6 (d, J_{P-C} = 60.2 Hz), 123.4 (d, J_{P-C} = 7.3 Hz); IR (KBr) 2425, 2340 cm^{-1}; MS (FAB) m/z 305 (M^+, 100). Anal. Calcd for $C_{18}H_{16}BPS$: C, 70.61; H, 5.27. Found: C, 70.15; H, 5.15.

(2-Mercaptophenyl)diphenylphosphine–Borane. This compound was obtained as a byproduct in the preparation of compound **6a**: mp 119–120 °C; ^1H NMR (CDCl) δ 7.7–7.1 (m, 14H), 4.28 (s, 1H); IR (KBr) 2500, 2350 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{17}BPS$ 307.0883, found 307.0883. Anal. Calcd for $C_{18}H_{18}BPS$: C, 70.15; H, 5.89. Found: C, 69.88; H, 5.81.

(2-Mercaptophenyl)(2-methoxyphenyl)phenylphosphine. (2-Methoxyphenyl)magnesium bromide (39 mL of 0.46 M THF solution) was slowly added at −78 °C with vigorous stirring to a solution of dichlorophenylphosphine (2.4 mL, 18 mmol) in dry THF (25 mL). The cooling bath was removed, and the temperature was allowed to elevate to room temperature. Then, a solution of lithium 2-lithiobenzenethiolate[8] (18 mmol) was slowly added, and the mixture was refluxed for 1 h. The reaction mixture was diluted with water (50 mL), and the pH of the mixture was adjusted at 4.0 by adding 1 M HCl. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. The resulting pasty oil was triturated with methanol to give a crystalline solid, which was collected on a Buchner funnel and washed with methanol. This crude material (2.67 g, 46%) was recrystallized from ethyl acetate–methanol (1/1) to give colorless crystals: mp 130–131 °C; ^1H NMR ($CDCl_3$) δ 7.39–7.25 (m, 7H), 7.22–7.17 (t, 1H), 7.06–7.01 (t, 1H), 6.93–6.85 (m, 2H), 6.80–6.77 (q, 1H), 6.69–6.64 (m, 1H), 4.18 (s, 1H), 3.75 (s, 3H); IR (KBr) 2450 cm^{-1}.

***(P–B)*-(2-(Borylthio)phenyl)(2-methoxyphenyl)phenylphosphine (6b).** This compound was prepared in 49% yield from (2-mercaptophenyl)(2-methoxyphenyl)phenylphosphine by the same procedure for the preparation of compound **6a**: mp 157–158 °C (ethyl acetate/hexane = 1/2); ^1H NMR (270 MHz) ($CDCl_3$) δ 7.65–7.25 (m, 10H), 7.20–6.90 (m, 3H), 3.67 (3H, s); IR (KBr) 2400, 2350 cm^{-1}; MS (FAB) m/z 335 (M^+). Anal. Calcd for $C_{19}H_{18}BOPS$: C, 67.88; H, 5.40. Found: C, 67.76; H, 5.24.

***(P–B)*-(2-(Borylthio)phenyl)(2-(methylthio)phenyl)phenylphosphine (6c).** Butyllithium (11.8 mL of 1.69 M hexane solution) was added to a solution of compound **7c**[9] in dry THF (25 mL) at 0 °C. To this solution was added monochloroborane–dimethyl sulfide(1.04 mL, 10 mmol) at the same temperature, and the mixture was stirred for 4 h at ambient temperature. To this mixture was added iodomethane (0.62 mL, 10 mmol) at 0 °C. After being stirred at room temperature, the mixture was poured into water, and the product was extracted with ethyl acetate. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residual oil was dissolved in dichloromethane.

The solution was passed through a short column of silica gel using dichloromethane as the eluent. After evaporation of the solvent, the residual solid was recrystallized from ethyl acetate–hexane (1/3) to give colorless cubes (1.05 g, 30%). From the mother solution, another crop (1.1 g, 31%) was obtained. An analytical sample was prepared by further recrystallization from ethyl acetate–hexane (1/3): mp 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 7.7–7.0 (m, 13H), 2.34 (s, 3H); ^{13}C NMR (100 MHz) ($CDCl_3$) (selected peaks) δ 156.2 (d, J_{P-C} = 88.4 Hz), 143.2 (d, J_{P-C} = 11.8 Hz), 134.1 (d, J_{P-C} = 7.4 Hz), 123.2 (d, J_{P-C} = 7.4 Hz), 19.4; ^{31}P NMR (162 MHz) ($CDCl_3$) δ 29.9; ^{11}B NMR ($CDCl_3$) −41.4 (br s); IR (KBr) 2425, 2350 cm^{-1}; MS (FAB) m/z 352 (M^+, 54). Anal. Calcd for $C_{18}H_{28}BPS$: C, 64.78; H, 5.15. Found: C, 64.60; H, 5.01.

X-ray Crystallographic Analysis of Compound 6c. A well-shaped prismatic crystal of compound **6c** was obtained by recrystallization from hexane–ethyl acetate (3/1): $C_{19}H_{18}S_2PB$; space group $P1$ (#2); Z = 2; D = 1.30 g cm^{-3}; cell constants a = 9.055(1) Å, b = 14.600(3) Å, c = 7.394(1) Å, α = 92.39(1)°, β = 105.62(1)°, γ = 105.26(1)°; V = 901.4(3) Å^3. Lattice constants and intensity data for **6c** were measured using graphite-monochromated Cu Kα radiation on a Rigaku AFC5S diffractometer. The data were collected at a temperature of 23 ± 1 °C using the $\omega - 2\theta$ scan technique at a speed of 32.0°/min to a maximum 2θ value of 135.2°. Of the 3445 reflections which were collected, 3224 were unique (R_{int} = 0.104). The data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods and expanded using Fourier techniques. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2471 observed reflections ($I > 3.00\sigma(I)$) and 280 variable parameters and converged with unweighed and weighed agreement factors of R = 0.056 and Rw = 0.066. Selected bond distances (Å) and angles (deg): P(1)–B(1) 1.943(7), B(1)–S(1) 1.918(7), S(1)–C(1) 1.746(6), C(1)–C(6) 1.399(7), P(1)–C(6) 1.794(5), P(1)–C(8) 1.800(5), P(1)–C(14) 1.805(5), P(1)–B(1)–S(1) 100.5(3), B(1)–S(1)–C(1) 99.6(3), S(1)–C(1)–C(6) 119.3(4), B(1)–P(1)–C(6) 100.2(3), P(1)–C(6)–C(1) 113.4(4).

***(P–B)*-(2-(Borylthio)phenyl)dicyclohexylphosphine (6d).** Chlorodicyclohexylphosphine (5.0 g, 21.5 mmol) was added slowly to a solution of lithium 2-lithiobenzenethiolate[8] (21.5 mmol) at 0 °C, and the mixture was gradually heated to reflux. After being refluxed for 2 h, the mixture was cooled to room temperature and was allowed to react with monochloroborane–dimethyl sulfide (8.0 mL, 77 mmol) for 5 h. The reaction mixture was poured into 1 M HCl (200 mL) with stirring. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The resulting solid was washed with methanol to give a crude product (4.6 g, 67%). The pure product was obtained by recrystallization from hexane–ethyl acetate (1/1): mp 179.0–180.0 °C; ^{1}H NMR (270 MHz) ($CDCl_3$) δ 7.44 (dd, J = 8.6, 2.1 Hz, 1H), 7.29–7.23 (m, 2H), 7.00 (br t, J = 7.3 Hz, 1H), 2.1–1.2 (m, 22H); ^{13}C NMR (126MHz) ($CDCl_3$) δ 158.0 (d, J_{P-C} = 32.2 Hz), 132.5, 130.7 (d, J_{P-C} = 4.3 Hz), 127.8 (d, J_{P-C} = 8.5 Hz), 122.2 (d, J_{P-C} = 6.4 Hz), 121.6, 31.5 (d, J_{P-C} = 34.4 Hz), 26.5 (d, J_{P-C} = 12.8 Hz), 26.2 (d, J_{P-C} = 6.5 Hz), 25.7; ^{31}P NMR (121 MHz) ($CDCl_3$) δ 45.1; IR (KBr) 2390, 2360 cm^{-1}; MS (FAB) m/z 317 (M^+, 100). Anal. Calcd for $C_{18}H_{28}BPS$: C, 67.93; H, 8.87. Found: C, 67.86; H, 8.77.

Bis(2-(diphenylphosphinoyl)phenyl) Disulfide (8). A solution of compound **6a** (306 mg, 1 mmol) in THF (6 mL) was added to a solution of $NaIO_4$ (426 mg, 2 mmol) in water (3 mL). The mixture was stirred at room temperature for 15 h, whereupon its color turned from white to yellow and finally to brown. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined extracts were washed with sodium hydrogensulfite solution and brine. After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel to give the disulfide (251 mg, 81%). The product was recrystallized from AcOEt–MeOH (2/1): mp > 250 °C; R_f = 0.17 (silica gel, AcOEt); ^{1}H NMR ($CDCl_3$) δ 7.75–7.00 (m, 28H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 142.6 (d, J_{P-C} = 5.8 Hz), 133.7 (d, J_{P-C} = 11.7 Hz), 132.6–130.0 (m), 128.6 (d, J_{P-C} = 11.8 Hz), 127.3 (d, J_{P-C} = 8.8 Hz), 125.4 (d, J_{P-C} = 21.7 Hz); IR (KBr) 1425, 1175, 1110 cm^{-1}; MS (EI) m/z 618 (M^+, 3), 310 (100); MS (FAB) m/z 619 (M + 1, 91), 309 (100). Anal. Calcd for $C_{36}H_{28}O_2P_2S_2$: C, 69.89; H, 4.56. Found: C, 69.73; H, 4.40.

Bis(2-(dicyclohexylphosphinoyl)phenyl) Disulfide (9). This compound was obtained by the oxidation of compound **6d** with $NaIO_4$. The product was recrystallized from AcOEt–MeOH (2/1): mp > 250 °C; ^{1}H NMR ($CDCl_3$) δ 7.89–7.74 (m, 4H), 7.44–7.27 (m, 4H), 2.4–1.1 (m, 44H); ^{13}C NMR (100 MHz) (CDCl3) δ 140 (br s), 134.3, 131.9, 128.3 (d, J_{P-C} = 7.3 Hz), 126.8 (d, J_{P-C} = 10.3 Hz), 37.7 (d, J_{P-C} = 67.5 Hz), 26.7–25.4 (m); IR (KBr) 1440, 1170, 1110 cm^{-1}; MS (FAB) m/z 643 (M + 1, 59), 321 (100).

***(P–B)*-(2-(Borylsulfonyl)phenyl)diphenylphosphine (10).** This compound was obtained in 86% yield by the treatment of compound **6a** (1 mmol) with *m*-CPBA (2 mmol) in dichloromethane (5 mL) at room temperature: mp 152–153 °C (2-propanol); R_f = 0.86 (MeOH/AcOEt = 1/9); ^{1}H NMR (270 MHz) ($CDCl_3$) δ 8.15–8.05 (m, 1H), 7.85–7.50 (m, 13H); IR (KBr) 2470, 2390 cm^{-1}; MS (FAB) m/z 339 (M + 1, 94), 309 (100), 289 (53). Anal. Calcd for $C_{18}H_{16}BO_2PS$: C, 63.93; H, 4.77. Found: C, 63.45; H, 4.64.

***(P–B)*-(2-(Borylsulfonyl)phenyl)(2-methoxyphenyl)phenylphosphine (11).** This compound was obtained in 92% yield by the oxidation of compound **6b** (0.3 mmol) with *m*-CPBA (0.6 mmol) in dichloromethane (5 mL) at room temperature: mp 187–188 °C dec (methanol); R_f = 0.30 (ethyl acetate–hexane = 3/1); ^{1}H NMR ($CDCl_3$) δ 8.11–8.00 (m, 1H), 7.82–7.76 (m, 1H), 7.67–7.42 (m, 9H), 7.15–7.08 (m, 1H), 7.05–7.00 (m, 1H), 3.72 (3H, s); IR 2500, 2400 cm^{-1}. Anal. Calcd for $C_{19}H_{18}BO_3PS$: C, 61.98; H, 4.93. Found: C, 61.90; H, 4.85.

***(P–B)*-(2-(Borylsulfonyl)phenyl)dicyclohexylphosphine (12).** This compound was obtained in 74% yield by oxidation of compound **6d** (0.4 mmol) with *m*-CPBA (0.8 mmol) in dichloromethane (3 mL) at room temperature: mp 191–192 °C (AcOEt/CH_2Cl_2 = 5/1); R_f = 0.63 (AcOEt/MeOH = 9/1); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.82–7.78 (m, 1H), 7.70–7.65 (m, 1H), 7.60 (t, J = 7.5 Hz, 1H), 2.42–2.33 (m, 2H), 2.1–1.1 (m, 20H); ^{13}C NMR (126 MHz) ($CDCl_3$) δ 157.5, 156.2 (d, J_{P-C} = 12.9 Hz), 134.5, 131.8 (d, J_{P-C} = 6.5 Hz), 130.4, 123.4 (d, J_{P-C} = 10.8 Hz), 117.7 (d, J_{P-C} = 51.6 Hz), 30.9 (d, J_{P-C} = 36.5 Hz), 26.4 (d, J_{P-C} = 4.3 Hz), 26.3, 25.4; ^{31}P NMR ($CDCl_3$) δ 22.3 (br d); ^{11}B NMR ($CDCl_3$) δ −44.4 (br s); IR (KBr) 2470, 2420 cm^{-1}. Anal. Calcd for $C_{18}H_{28}BO_2PS$: C, 61.72; H, 8.06. Found: C, 61.50; H, 8.07.

X-ray Crystallographic Analysis of Compound 12. A well-shaped monoclinic crystal of **12** was obtained by recrystallization from ethyl acetate: $C_{18}H_{28}BO_2PS$; space group $P2_1/n$ (#14); Z = 4; D = 1.243 g cm^{-1}; cell constants a = 11.101(1) Å, b = 14.028(2) Å, c = 12.1001(1) Å, β = 96.645(8)°; V = 1871.5(3) Å^3; temperature of data collection 293 K; 2748 unique reflections ($I > 3.00\sigma(I)$); R = 0.050 and Rw = 0.076. Selected bond distances (Å) and angles (deg): P(1)–B(1) 1.929(4), B(1)–S(1) 1.899(4), S(1)–C(2) 1.793(3), C(1)–C(2) 1.395(4), P(1)–C(1) 1.810(3), P(1)–C(7) 1.822(3), P(1)–C(13) 1.832(3), P(1)–B(1)–S(1) 101.7(2), B(1)–S(1)–C(2) 100.7(1), S(1)–C(2)–C(1) 116.6-(2), P(1)–C(1)–C(2) 114.8(2), B(1)–P(1)–C(1) 101.1(1).

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