SYNTHESIS AND PROPERTIES OF NEW FUSED BICYCLIC COMPOUNDS CONTAINING P–B–S LINKAGES

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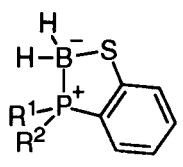
Abstract – New bicyclic compounds, (*P–B*)-12-phenyl-12*H*-dibenzo[*d,g*]-[1,3,6,2]dithiaphosphaborocine (**3a**) and (*P–B*)–12-cyclohexyl-12*H*-dibenzo[*d,g*]-[1,3,6,2]dithiaphosphaborocine (**3b**), were synthesized by the reaction of phenyl- and cyclohexylbis(2-mercaptophenyl)phosphine (**5a** and **5b**) with BH_3–THF. The structures of **3a** and **3b** were definitively determined by X-Ray crystallographic analysis. The reaction of tris(2-mercaptophenyl)phosphine (**5c**) with BH_3–THF gave a bicyclic compound, (*P–B*)-12-{2-[(4-hydroxybutyl)thio]phenyl}-12*H*-dibenzo[*d,g*][1,3,6,2]dithiaphosphaborocine (**8**).

INTRODUCTION

In our continuing study on phosphine–boranes,[1–3] we recently reported synthesis and properties of new five-membered heterocyclic compounds (**1**) containing a P–B–S linkage.[2c] These heterocycles are a heavy element analog of boroxazolidines (**2**), whose structure and reactivities have been studied in detail.[4,5] In addition, this heterocyclic system is expected to exhibit intriguing chemical properties.



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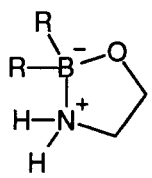

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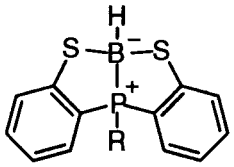
In this paper, we report the syntheses and properties of heterocyclic compounds (**3a**) and (**3b**) containing a new bicyclic system where the two rings having P–B–S linkages are fused on the P–B bond. An attempt for the synthesis of tricyclic compound (**4**) is also described.



3a: R = Ph
3b: R = cyclohexyl

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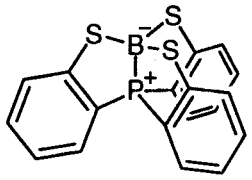

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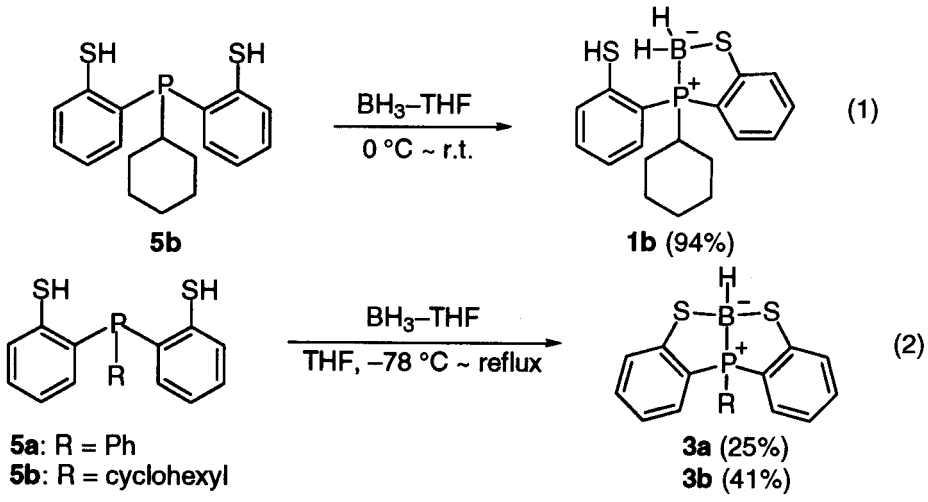
RESULTS AND DISCUSSION

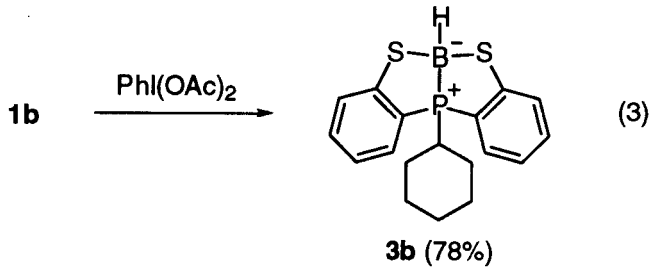
Synthesis of Heterocyclic Compounds (3a) and (3b)

In the previous paper, we synthesized five-membered heterocyclic compounds (**1**) from diaryl- and dialkyl-(2-mercaptophenyl)phosphine by successive reactions with *n*-butyllithium and BH_2Cl–SMe_2.[2c] Based on the results, we attempted the syntheses of heterobicyclic compounds (**3a**) and (**3b**) by treatment of bis(2-mercaptophenyl)phosphines (**5a**) and (**5b**) with 2 equivalents of *n*-butyllithium, followed by addition of $BHCl_2$–SMe_2.

Successive addition of 2 equivalents of *n*-butyllithium and $BHCl_2$–SMe_2 to (**5a**) resulted in the formation of a complex mixture, although a trace amount of the desired compound (**3a**) was obtained. Since it has been known that reaction of an amine–borane[6] or diborane[7] with a thiol affords the corresponding thioborane *via* substitution on the boron atom accompanied by generation of H_2, we tried reaction of **5a** and **5b** with BH_3–THF. When **5b** was allowed to react with one equivalent of BH_3–THF, the corresponding monocyclic compound (**1b**) was produced in 94% yield (Equation 1). On the other hand, no characterizable compound was obtained by the reaction of **5a** under similar conditions. Detailed investigation of the conditions for the reaction of **5a** with BH_3–THF resulted in finding that bicyclic product (**3a**) was obtained in 25% yield by treatment of **5a** with 2 equivalents of BH_3–THF at –78 °C, followed by heating in refluxing THF (Equation 2).



Reaction of **5b** with BH_3–THF under similar conditions gave the corresponding bicyclic compound (**3b**) in 41% yield. The bicyclic compound (**3b**) could be obtained in good yield (78%) by treatment of **1b** with $PhI(OAc)_2$ as well.



Structure of monocyclic compound 1b and bicyclic compounds (3a) and (3b)

The structures of **1b**, **3a**, and **3b** were confirmed by the spectroscopic data together with elemental analyses, and definitively determined by X-Ray crystallographic analysis.[8]

As shown in Figure 1, the five-membered ring of **1b** has envelope conformation. On the other hand, the ORTEP drawings shown in Figures 2 and 3 indicate that the five-membered rings of **3a** and **3b** are nearly planar. This structural difference is reflected in their torsional angles of the five-membered rings (Table 1) and sum of the five interior angles in the rings (Table 2). The torsional angles in **3a** and **3b** are in the range of –16.0° to +16.7°, while the largest deviation in **1b** is –36.3° (Table 1). The sum of the bond angles in **3a** and **3b** is nearly 540°, which is those of planar pentagons, and the value of **1b** is smaller than 540° by 15° (Table 2). The planarity of the five-membered rings of **3a** and **3b** may be explained by the rigid form in the bicyclic system. The P–B bond distances of the bicyclic compounds

3a (1.945 Å) and **3b** (1.928 Å) are almost the same as that of the monocyclic compound (**1b**) (1.916 Å), and these bond lengths are in the ordinary range of those for phosphine–boranes.[1]

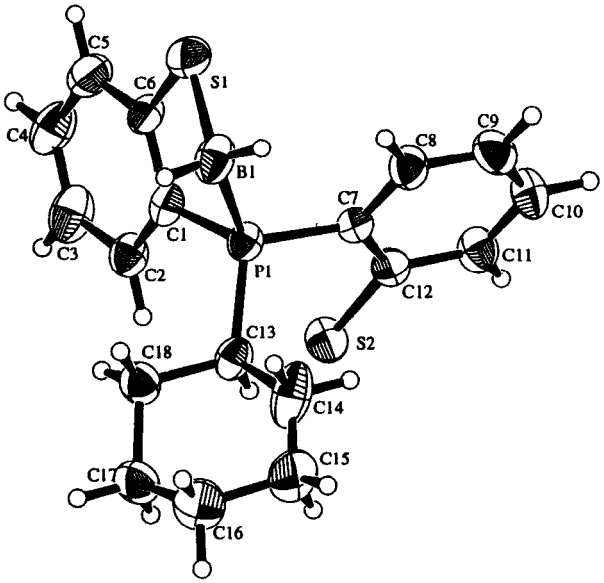


Figure 1. ORTEP drawing of compound (**1b**). Selected bond distances (Å): P(1)–B(1) 1.929(8), B(1)–S(1) 1.951(9), S(1)–C(6) 1.772(7), C(6)–C(1) 1.405(9), C(1)–P(1) 1.815(6).

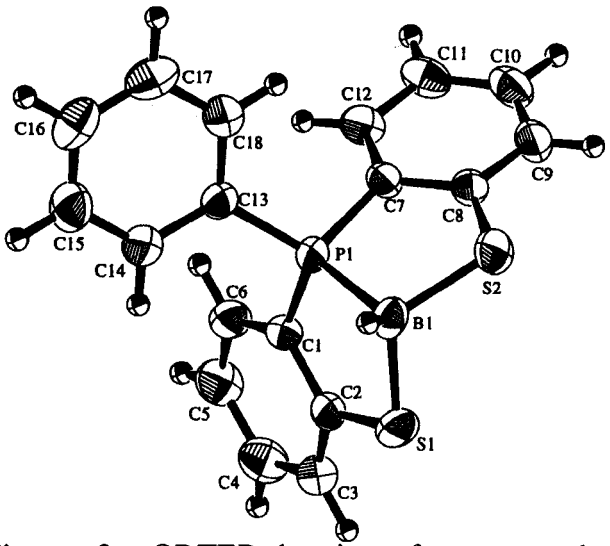


Figure 2. ORTEP drawing of compound (**3a**). Selected bond distances (Å): P(1)–B(1) 1.945(5), B(1)–S(1) 1.923(5), S(1)–C(2) 1.752(4), C(2)–C(1) 1.405(5), C(1)–P(1) 1.781(4), B(1)–S(2) 1.911(5), S(2)–C(8) 1.760(4), C(8)–C(7) 1.396(6), C(7)–P(1) 1.789(4).

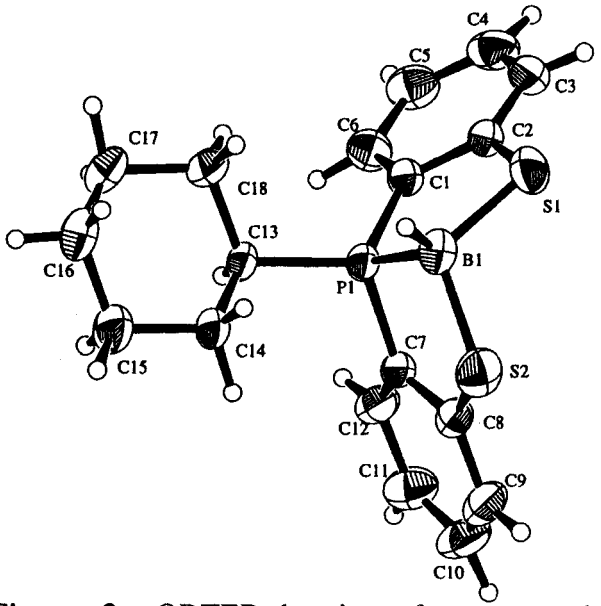


Figure 3. ORTEP drawing of compound (**3b**). Selected bond distances (Å): P(1)–B(1) 1.928(6), B(1)–S(1) 1.922(6), S(1)–C(2) 1.745(5), C(2)–C(1) 1.408(6), C(1)–P(1) 1.774(4), B(1)–S(2) 1.916(6), S(2)–C(8) 1.741(5), C(8)–C(7) 1.415(6), C(7)–P(1) 1.788(4).

Table 1. Torsion Angles (deg) of the Five-membered Heterocycles

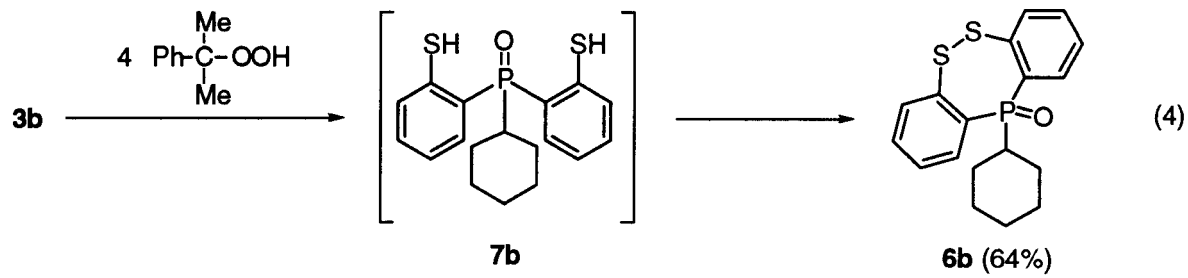
	1b	3a		3b	
P–B	–36.3(4)	2.9(3)	9.8(3)	–10.1(3)	–16.0(3)
B–S	33.4(4)	–0.7(3)	–14.0(3)	8.3(3)	16.5(3)
S–C	–19.4(5)	–2.5(4)	16.7(4)	–3.8(4)	–12.9(4)
C–C	–6.0(6)	4.9(5)	–10.9(4)	–3.5(5)	2.0(5)
C–P	28.6(5)	–4.7(4)	–0.6(4)	9.0(4)	9.9(4)

Table 2. Bond Angles (deg) of the Five-membered Heterocycles

	1b	3a		3b	
P–B–S	99.2(4)	101.7(2)	102.6(2)	101.5(3)	102.5(3)
B–S–C	97.3(3)	101.2(2)	99.7(2)	101.2(2)	99.7(2)
S–C–C	118.2(4)	120.6(3)	119.9(3)	120.0(4)	120.2(4)
C–C–P	112.2(4)	113.0(3)	113.7(3)	113.2(4)	113.2(4)
C–P–B	97.7(3)	103.2(2)	101.5(2)	103.1(2)	101.3(2)
sum of the interior angles	524.6	539.7	537.4	539.0	536.9

Oxidation of 3b

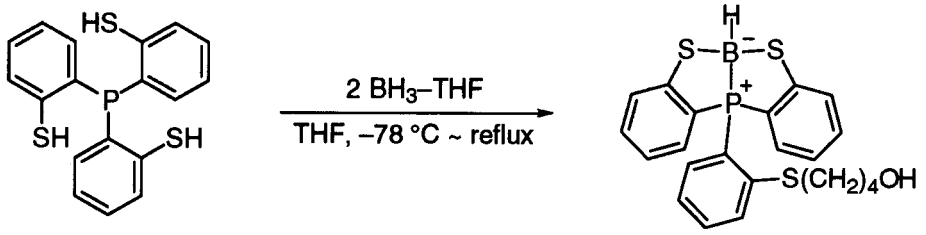
We have so far reported that oxidation of five-membered heterocycles (**1**) with 2 equivalents of *m*-CPBA gave the corresponding sulfone in good yield.[2c] We attempted the oxidation of the bicyclic compound (**3b**) with 4 equivalents of *m*-CPBA, however this reaction resulted in the formation of a complex mixture. On the other hand, treatment of **3b** with 4 equivalents of cumene hydroperoxide gave cyclic disulfide (**6b**) (64%) (Equation 4). Since it has been known that oxidation of a phosphine–borane gives the corresponding phosphine oxide[9] and that oxidation of bis(mercaptophenyl)phenylphosphine oxide affords the corresponding cyclic disulfide,[10] this reaction probably proceeds *via* phosphine oxide (**7b**).



7b **6b** (64%) (4)

Attempted Synthesis of Tricyclic Compound (4)

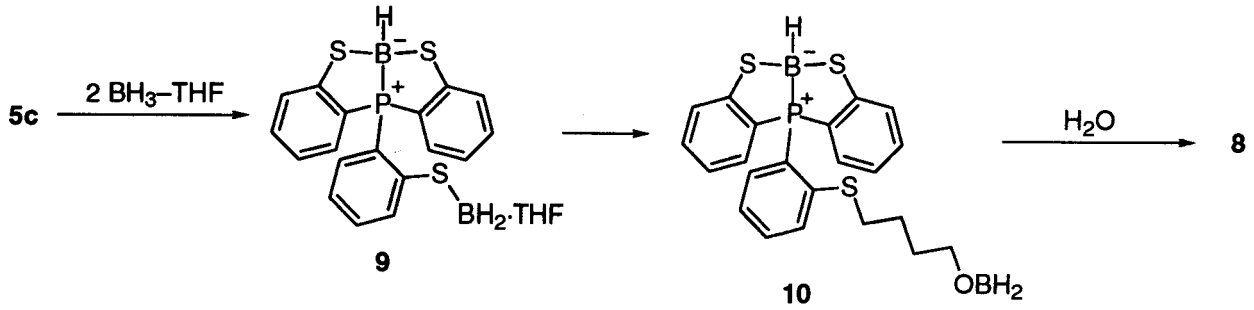
For the purpose of the synthesis of compound (**4**) containing a tricyclic system, tris(2-mercaptophenyl)phosphine (**5c**) was allowed to react with 2 equivalents of BH_3–THF. Unexpectedly, this reaction gave compound (**8**) (Equation 5) instead of compound (**4**).



5c **8** (94%) (5)

The formation of **8** can be explained by a mechanism described below (Scheme 1). Reaction of **5c** with 2 equivalents of BH_3–THF gives compound (**9**) containing two boron atoms. The coordinated THF, which is activated by the coordination to the thioborane, undergoes ring opening reaction. The resulting compound (**10**) is hydrolyzed to compound (**8**).

Scheme 1



EXPERIMENTAL

General: All glassware was dried at 120 °C, assembled while it is hot, and cooled under argon. THF was distilled from sodium benzophenone ketyl under argon before use. Chloroform and toluene were distilled and stored over molecular sieves 4A. 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). The ^1H (400 MHz), ^{13}C (100 MHz), ^{11}B (128 or 160 MHz), and ^{31}P (162 or 202 MHz) NMR spectra were recorded on JEOL JNM-GSX-400. Chemical

shifts are reported from TMS (^{1}H and ^{13}C), trimethyl borate (^{11}B), and phosphoric acid (^{31}P) in δ units.

Synthesis of (cyclohexyl)bis(2-mercaptophenyl)phosphine (5b)

To a THF solution (50 mL) of trichlorophosphine (5.8 mL, 67 mmol) was added dropwise at –78 °C a 0.82M THF solution of cyclohexyl magnesium chloride (84 mL, 69 mmol). After gradual warming to rt, the reaction mixture was heated at reflux for 2 h and cooled to 0 °C. A solution of lithium 2-lithiobenzenethiolate,[11] which was prepared from thiophenol (15.4 mL, 150 mmol), a 1.63 M hexane solution of *n*-butyllithium (190 mL, 310 mmol), and *N,N,N',N'*-tetramethylethylenediamine (47.5 mL, 315 mmol) in cyclohexane (400 mL), was added dropwise over 20 min to the mixture. The solution was refluxed for 3 h and treated with water. The mixture was extracted with ether three times and the combined extracts were evaporated under reduced pressure. The separation of the resulting dark green oil by chromatography (SiO_2, hexane/$CHCl_3$ = 3/1) gave phosphine **5b** (13.0 g, 58%). The further purification was performed by recrystallization from hexane. **5b**: white powder; mp 97–102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22–1.48 (m, 6H), 1.64–1.85 (m, 4H), 2.19–2.30 (m, 1H), 4.44 (s, 2H), 7.08–7.19 (m, 4H), 7.25–7.29 (m, 4H); IR (KBr) 2930, 2475, 1570, 1450, 745 cm^{-1}.

Synthesis of (P–B)-[2-(borylthio)phenyl](cyclohexyl)(2-mercaptophenyl)phosphine (1b)

Borane–THF (2.0 mL of 1.0 M solution in THF, 2.0 mmol) was added at 0 °C to a THF solution (2.0 mL) of **5b** (665 mg, 2.0 mmol). Gradual warming to rt gave white precipitates. The reaction mixture was treated with water and extracted with $CHCl_3$ three times. The combined extracts were dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel using hexane–ethyl acetate (5/1) as the eluent to give white solids of **1b** (648 mg, 94%). The pure product was obtained by recrystallization from hexane/ethyl acetate = 5/1. **1b**: colorless prism crystals; mp 126–127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09–1.81 (m, 9H), 2.04–2.10 (m, 1H), 2.12–3.03 (br m, 2H), 3.06–3.14 (m, 1H), 4.19 (s, 1H), 7.07–7.12 (m, 1H), 7.20–7.27 (m, 1H), 7.30–7.38 (m, 2H), 7.41–7.58 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ

25.8, 26.7 (d, J_{CP} = 14.9 Hz), 26.89 (d, J_{CP} = 3.3 Hz), 26.94 (d, J_{CP} = 7.4 Hz), 27.2 (d, J_{CP} = 5.0 Hz), 34.3 (d, J_{CP} = 33.9 Hz), 121.5 (d, J_{CP} = 72.8 Hz), 122.5 (d, J_{CP} = 6.6 Hz), 126.0, 126.6 (d, J_{CP} = 9.1 Hz), 128.3 (d, J_{CP} = 9.1 Hz), 131.7 (d, J_{CP} = 2.5 Hz), 132.4 (d, J_{CP} = 2.5 Hz), 132.6 (d, J_{CP} = 3.3 Hz), 134.0 (d, J_{CP} = 5.8 Hz), 134.2 (d, J_{CP} = 7.4 Hz), 135.2 (d, J_{CP} = 9.9 Hz), 158.2 (d, J_{CP} = 36.4 Hz); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz) δ –47.0 (br s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 42.2; IR (KBr) 2380, 2455 cm^{-1}; MS (FAB) *m/z* 343 (M^+). Anal. Calcd for $C_{18}H_{22}BPS_2$: C, 62.80; H, 6.44. Found: C, 62.92; H, 6.45.

Synthesis of (P–B)-12-phenyl-12H-dibenzo[d,g][1,3,6,2]dithiaphosphaborocine (3a)

Borane–THF (2.0 mL of 1.0 M solution in THF, 2.0 mmol) was added at –78 °C to a THF solution (4 mL) of **5a** (326 mg, 1.0 mmol). After gradual warming to rt the mixture was heated at reflux for 8 h. The reaction mixture was treated with water and extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After evaporation under reduced pressure, the residue was purified by preparative TLC (SiO_2, hexane/ethyl acetate = 3/1) to give a white solid of **3a** (85 mg, 25%). The pure product was obtained by recrystallization from hexane/ethyl acetate = 5/1. **3a**: white crystals; mp 161–162 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.41–4.64 (br m, 1H), 7.07–7.12 (m, 2H), 7.31–7.37 (m, 2H), 7.40–7.45 (m, 2H), 7.48–7.56 (m, 6H), 7.57–7.63 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 123.1 (d, J_{CP} = 63.1 Hz), 123.5 (d, J_{CP} = 82.0 Hz), 124.1 (d, J_{CP} = 8.2 Hz), 127.7 (d, J_{CP} = 9.0 Hz), 129.5 (d, J_{CP} = 12.3 Hz), 131.0 (d, J_{CP} = 5.7 Hz), 132.6 (d, J_{CP} = 10.7 Hz), 132.7 (d, J_{CP} = 2.5 Hz), 132.9 (d, J_{CP} = 2.5 Hz), 156.1 (d, J_{CP} = 35.3 Hz); $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz) δ –33.7 (d, J_{BP} = 85.1 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 49.8; IR (KBr) 2445 cm^{-1}; MS (FAB) *m/z* 336 (M^+). Anal. Calcd for $C_{18}H_{14}BPS_2$: C, 64.30; H, 4.20. Found: C, 64.24; H, 4.13.

Synthesis of (P–B)-12-cyclohexyl-12H-dibenzo[d,g][1,3,6,2]dithiaphosphaborocine (3b) by reaction of 5b with BH_3–THF

Borane–THF (1.0 mL of 1.0 M solution in THF, 1.0 mmol) was added at –78 °C to a THF solution (2 mL) of **5b** (166 mg, 0.5 mmol). After gradual warming to rt, the mixture was heated at reflux for 8 h.

The reaction mixture was treated with water and extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over Na_2SO_4. After evaporation under reduced pressure, the residue was purified by preparative TLC (SiO_2, hexane/ethyl acetate = 3/1) to give a white solid of **3b** (70 mg, 41%). The pure product was obtained by recrystallization from hexane/ethyl acetate = 5/1. **3b**: colorless prismatic crystals; mp 174–176 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21–1.38 (m, 3H), 1.42–1.58 (m, 2H), 1.70–1.90 (m, 5H), 2.60–2.75 (m, 1H), 3.4–4.6 (br m, 1H), 7.04–7.10 (m, 2H), 7.24–7.31 (m, 2H), 7.40–7.49 (m, 4H); ^{11}B{^{1}H} NMR ($CDCl_3$, 160 MHz) δ –33.8 (d, $^1J_{BP}$ = 84.4 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 57.0 (m); IR (KBr) 2440, 2455 cm^{-1}. Anal. Calcd for $C_{18}H_{20}BPS_2$: C, 63.17; H, 5.89. Found: C, 63.21; H, 5.82.

Synthesis of 3b by reaction of 1b with PhI(OCOCH$_3$)$_2$

To a solution of **1b** (688 mg, 2.0 mmol) in $CHCl_3$ (6 mL) was added iodobenzene diacetate (648 mg, 2.0 mmol) at –78 °C. The mixture was stirred at rt for 3 h. After removal of the solvent under reduced pressure, the residue was purified by chromatography on silica gel using $CHCl_3$–hexane (1/2) as the eluent to give 538 mg of **3b** (78%). The pure product (mp 174–176 °C) was obtained by recrystallization from ethyl acetate.

X-Ray Crystallographic Analysis of Compound (1b)

A colorless prism crystal of **1b** suitable for X-Ray crystallographic analysis was obtained by recrystallization from ethyl acetate: $C_{18}H_{22}BPS_2$; crystal system monoclinic; space group $P2_1/c$; $Z = 4$; Dcalcd = 1.267 g cm^{-3}; cell constants a = 9.033(5) Å, b = 9.688(2) Å, c = 20.616(3) Å, β = 90.47(4); V = 1804.1(8) Å^3; μ(MoKα) = 3.77 cm^{-1}; Reflection Collected 1914. All measurements were made on a Rigaku RAXIS II imaging plate area detector with graphite monochromated MoKα radiation. The data collected at a temperature of 15 ± 1 °C to a maximum 2θ value of 44.0°. A total of 156.00° oscillation images were collected, each being exposed for 4.0 minutes. The crystal-to-detector distance was 100.00 mm. The structure was solved by direct methods[12] and expanded using Fourier techniques.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 1771 observed

reflections ($I>3.00\sigma(I)$) and 199 variable parameters and converged (largest parameter shift was 0.04 times its esd) with unweighted and weighted agreement factors of $R = 0.090$, $R_W = 0.105$, GOF = 3.00.

X-Ray Crystallographic Analysis of Compound (3a)

A yellow crystal of **3a** suitable for X-Ray crystallographic analysis was obtained by recrystallization from ethyl acetate–hexane: $C_{18}H_{14}BPS_2$; crystal system monoclinic; space group $P2_1/n$; $Z = 4$; Dcalcd = 1.348 g cm^{-3}; cell constants $a = 10.035(2)$ Å, $b = 12.531(2)$ Å, $c = 13.532(1)$ Å, $\beta = 103.30(1)°$; $V = 1656.0(4)$ Å^3; μ(CuKα) = 37.41 cm^{-1}. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Cu-Kα radiation. Cell constant and orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range $39.29<2\theta<43.95°$ corresponded to a primitive monoclinic cell. The data were collected at a temperature of 23 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 135.1. Of the 3825 reflections which were collected, 3102 were unique ($R_{int} = 0.030$). The data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods[12] and expanded using Fourier techniques.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 2039 observed reflections ($I>1.00\sigma(I)$) and 199 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R = 0.053$, $R_W = 0.057$, GOF = 1.34.

X-Ray Crystallographic Analysis of Compound (3b)

A colorless prismatic crystal of **3b** suitable for X-Ray crystallographic analysis was obtained by recrystallization from ethyl acetate: $C_{18}H_{20}BPS_2$; crystal system orthorhombic; space group Pnma; $Z = 12$; Dcalcd = 1.250 g cm^{-3}; cell constants $a = 11.202(2)$ Å, $b = 41.645(2)$ Å, $c = 11.693(2)$ Å; $V = 5455.0(9)$ Å^3; μ(CuKα) = 34.08 cm^{-1}. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Cu-Kα radiation. Cell constant and orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered

reflections in the range $43.83<2\theta<46.56°$ corresponded to a primitive orthorhombic cell. The data were collected at a temperature of 23 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 135.2. Of the 5327 reflections which were collected, 5326 were unique (R_{int} = 0.507). The data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods[12] and expanded using Fourier techniques.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic all. The final cycle of full-matrix least-squares refinement was based on 3002 observed reflections ($I>2.00\sigma(I)$) and 429 variable parameters and converged (largest parameter shift was 0.20 times its esd) with unweighted and weighted agreement factors of R = 0.056, R_W = 0.047, GOF = 2.19.

Reaction of 3b with cumene hydroperoxide

To a toluene solution (3 mL) of **3b** (103 mg, 0.3 mmol) was slowly added cumene hydroperoxide (0.177 mL, 1.2 mmol) at –78 °C. The reaction mixture was warmed to rt and heated at 60 °C for 2 h. After removal of the solvent under reduced pressure, the residue was separated by preparative TLC (SiO_2, hexane/ethyl acetate = 5/1) to give (*P*–*B*)-11-cyclohexyl-11*H*-dibenzo[*c*,*f*][1,2,5]dithiaphosphepine-11-oxide (**6b**) (67 mg, 64%). **6b**: white powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05–1.30 (m, 4H), 1.40–1.58 (m, 4H), 1.70–1.80 (m, 2H), 2.82–2.95 (m, 1H), 7.42–7.57 (m, 6H), 8.35–8.40 (m, 2H); 2930, 2850, 1575, 1450, 1180 cm^{-1}; MS (FAB) *m/z* (relative intensity) 347 (100, M+H$^+$).

Reaction of 5c with BH_3–THF

To a THF solution (2.5 mL) of **5c** (179 mg, 0.50 mmol) was added Borane–THF (1.0 mL of 1.0 M solution in THF, 1.0 mmol) at –78 °C. The solution was gradually warmed to rt, and heated to reflux. After refluxing for 5 h, the mixture was treated with water and extracted by ether three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was separated by preparative TLC (SiO_2, hexane/ethyl acetate = 1/3) to afford (*P*–*B*)-12-{2-[(4-hydroxybutyl)thio]phenyl}-12*H*-dibenzo[*d*,*g*][1,3,6,2]dithiaphospha-borocine (**8**) (206 mg, 94%). The pure product was obtained by recrystallization from hexane/ethyl acetate = 5/1.

8: white powder; mp 133–134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 1H), 1.49–1.63 (m, 4H), 2.86 (t, J = 7 Hz, 2H), 3.57 (t, J = 6 Hz, 2H), 7.03–7.09 (m, 2H), 7.25–7.38 (m, 5H), 7.41–7.50 (m, 3H), 7.54–7.64 (m, 2H), B–H proton was not clearly observed in ^{1}H-NMR; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 25.1, 31.5, 36.6, 62.2, 123.7 (d, J_{CP} = 8.2 Hz), 124.9 (d, J_{CP} = 82.9 Hz), 125.0 (d, J_{CP} = 67.3 Hz), 126.9 (d, J_{CP} = 10.7 Hz), 127.7 (d, J_{CP} = 9.0 Hz), 130.5 (d, J_{CP} = 4.9 Hz), 132.1 (d, J_{CP} = 2.5 Hz), 133.1 (d, J_{CP} = 8.2 Hz), 133.2 (d, J_{CP} = 2.5 Hz), 134.6 (d, J_{CP} = 8.2 Hz), 143.4 (d, J_{CP} = 11.5 Hz), 155.2 (d, J_{CP} = 36.1 Hz); ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz) δ –33.7 (br s); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 45.3; IR (KBr) 3470, 2470 cm^{-1}; MS (FAB) *m/z* 441 ($M+H^+$). Anal. Calcd for $C_{22}H_{22}OBPS_3$: C, 60.00; H, 5.04. Found: C, 60.01; H, 5.08.

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