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Heterocycles

Synthesis and Structure of a 1-Phospha-2-boraacenaphthene Derivative and Its Chalcogenation Reactions

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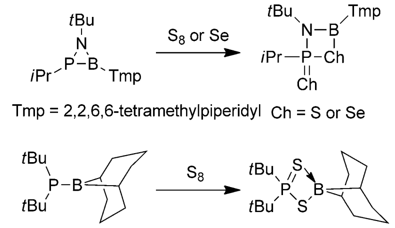
Dedicated to Emeritus Professor Renji Okazaki on the occasion of his 77th birthday

Abstract: The first stable 1-phospha-2-boraacenaphthene **1** was synthesized by the reduction of 1-dimesitylboryl-8-dichlorophosphinonaphthalene (**2a**) with elemental magnesium, and it was fully characterized. The chalcogenation reaction of **1** with elemental sulfur or selenium afforded the unique heterocycles, 2-thia- and 2-selena-1-phospha-3-boraphenalenes **9S** and **9Se**, respectively, through the insertion of the chalcogen atom into a P–B bond of **1**. Further chalcogenation of **9** afforded the corresponding phosphine chalcogenides. These newly obtained chalcogenated compounds have been characterized. The unique dynamic behavior of 2-chalcogena-1-phospha-3-boraphenalene-1-chalcogenides **10** in solution has also been described.

Introduction

There has been broad interest in the chemistry of phosphine borane ($R_3P–BR_3$) bearing a P–B coordinate bond especially from the viewpoint of frustrated Lewis pairs (FLPs) in recent years.[1] In particular, those with a forcedly connected P–B coordinate bond in a rigid linker such as a 1,8-naphthalene skeleton are of great interest because they would be appropriate model compounds for investigating the static nature of the P–B coordinate bonds.[2] On the other hand, there seem to be less examples of investigation of a P–B bond in a phosphinoborane ($R_2P–BR_2$) probably due to the difficulty in the isolation of a stable phosphinoborane,[3] though a phosphinoborane would be a promisingly attractive species as a candidate for unique chemical and physical properties.[3,4] Indeed, kinetic or thermodynamic stabilization should be necessary to isolate monomeric phosphinoborane as a stable compound, since a phosphinoborane undergoes facile oligomerization in a head-to-tail manner with forming intermolecular P–B dative bonds.[3,5] A series of kinetically stabilized phosphinoboranes bearing mesityl, phenyl, trimethylsilyl, and 1-adamantyl groups have been reported by Power et al.,[6] whereas phosphinoboranes thermodynamically stabilized by coordination of a Lewis acid and base, $[(LA)H_2P–BH_2(LB)]$ (LA = Lewis acid, LB = Lewis base), have been reported by Scheer et al.[7] We report here the synthesis and properties of 1-phospha-2-boraacenaphthene **1**, which is a unique heterocyclic compound bearing a P–B bond tethered with a naphthyl unit at the 1,8-positions.[8] On the basis of the previous reports on the chalcogenation reactions of phosphinoborane derivatives shown in Scheme 1,[7c,9] the chalcogenation reaction of **1** would be expected to afford unique heterocyclic compounds containing a P(Ch)–Ch–B (Ch=S, Se) moiety. Thus, we have examined the sulfurization and selenization reactions of **1** in the expectation of synthesis of new heterocyclic compounds containing P, B, and chalcogen atoms.



Scheme 1. Examples of chalcogenation reactions of phosphinoboranes.

Results and Discussion

Diarylboryl-8-dichlorophosphinonaphthalenes **2a,b** were prepared from 1,8-dibromonaphthalene in two steps.[8] The X-ray crystallographic analyses of **2a,b** (Figure 1a and b) showed the longer P–B distance of **2a** (2.892(2), 2.961(2) Å) than that of **2b** (2.108(2) Å), suggesting negligible intramolecular P–B coordination in **2a** due to the steric congestion in contrast to the concrete P–B coordinate bond in **2b**. Thus, it should be noted that the boron atom of **2a** surrounded by mesityl (Mes) groups should be more congested than that of **2b** bearing two 3,5-di-*tert*-butylphenyl (Dtp) groups. In the ^{11}B NMR spec-

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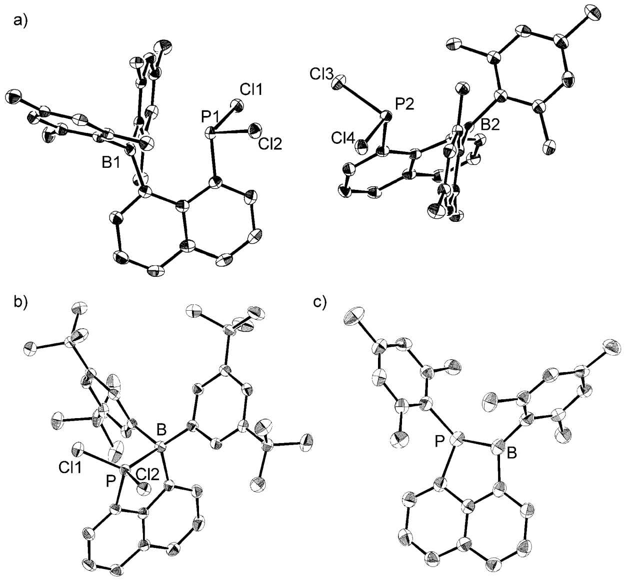
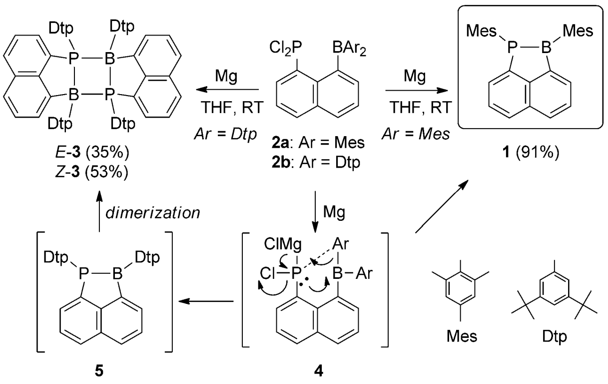


Figure 1. Molecular structures of a) 1-diarylboryl-8-dichlorophosphinonaphthalenes **2a**, b) **2b**, and c) 1-phospha-2-boraacenaphthene **1** (thermal ellipsoids with 50% probability). All hydrogen atoms were omitted for clarity. a) Two independent molecules of **2a** were found in the unit cell. Selected distances [Å]: a) **2a**: P1–B1, 2.892(2), P1–Cl1, 2.0581(7), P1–Cl2, 2.0886(7), P2–B2, 2.961(2), P2–Cl3, 2.1083(7), P2–Cl4, 2.0562(7). b) **2b**: P–B, 2.108(2), P–Cl1, 2.0112(8), P–Cl2, 2.0408(7). c) **1**: P–B, 1.889(3).

tra in C_6D_6, the contrastive signals of **2a** and **2b** were observed as a highly broadened signal ($\Delta\nu_{1/2} = 1570$ Hz) at $\delta = 63.9$ ppm of **2a** and a relatively sharp signal ($\Delta\nu_{1/2} = 750$ Hz) at $\delta = 10.1$ ppm of **2b**, suggesting that their structural features in solution are similar to those observed in the crystalline state. Reduction of less hindered phosphineborane **2b** with magnesium metal in THF solution at room temperature gave a mixture of two isomers, (*E*)-**3** and (*Z*)-**3**, dimers of the corresponding 1-phospha-2-boraacenaphthene **5**, isolated in 35 and 53% yields, respectively (Scheme 2).[10] Therefore, the introduction of Dtp groups should not be suitable for the isolation of a 1-phospha-2-boraacenaphthene as a monomeric form. On the other hand, reduction of **2a** with magnesium metal under the same conditions afforded 1-phospha-2-boraacenaphthene **1** as orange crystals isolated in 91% yield.[8] Thus, sterically demanding substituents on the P–B moiety should be of importance in the stability of the 1-phospha-2-boraacenaphthene. The formation of **1** by the reduction of dichlorophosphine **2a** is most likely interpreted in terms of the intermediacy of phosphinidenoid **4**, which would undergo facile isomerization giving **1** through the intramolecular aryl migration from boron to phosphorus (Scheme 2). Thus, it would be expected that this synthetic approach should be generally applicable toward synthesis of a 1-phospha-2-boraacenaphthene from a 1-diarylboryl-8-dichlorophosphinonaphthalene when the boron atom has two sterically demanding aryl groups.

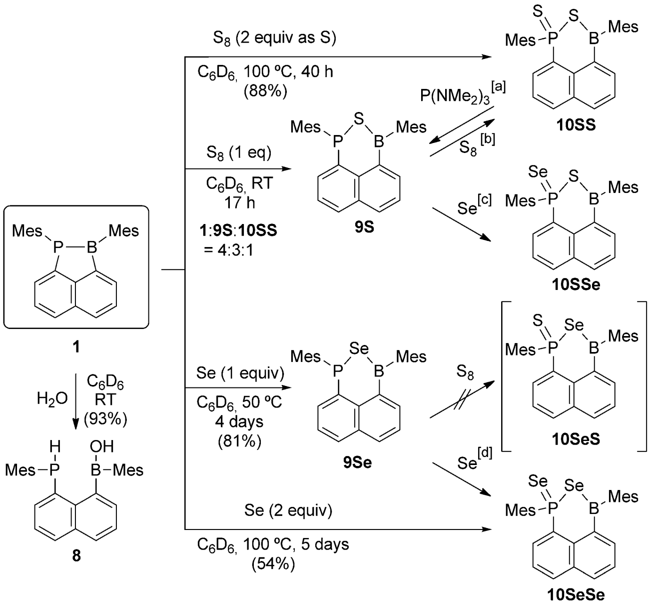


Scheme 2. Synthesis of 1-phospha-2-boraacenaphthene **1**.

The monomeric molecular structure of **1** was definitively determined by using X-ray crystallographic analysis (Figure 1c).[8] Although the boron atom is located on the same plane of the naphthalene skeleton, the phosphorus atom deviates from the plane by about 0.36 Å, in which the boron and phosphorus atoms exhibit the planar and pyramidal geometries, respectively. The P–B bond length of **1** is 1.889(3) Å, which is slightly longer than those in Mes_2PBMes_2 (**6**; 1.839(8) Å) and Ph_2PBMes_2 (**7**; 1.859(3) Å),[6] but apparently shorter than those of **2a,b**, suggesting the existence of a considerably strong P–B σ-bond in **1**. Combined consideration of the P–B bond length and the pyramidalization of the P atom in **1** suggests its negligible $>P^{(+)}{=}B^{(-)}<$ double-bond character. In the ^{11}B NMR spectrum of the C_6D_6 solution of **1**, a broad signal was observed at $\delta_B = 77.9$ ppm ($\Delta\nu_{1/2} = 1400$ Hz), which is similar to those of **6** ($\delta_B = 82.4$ ppm) and **7** ($\delta_B = 70.9$ ppm),[6] suggesting the trigonal-planar geometry around the boron atom in solution. In the ^{31}P NMR spectrum, the C_6D_6 solution of **1** exhibit the relatively upper-field-shifted signal at $\delta_P = -28.2$ ppm as compared with those of **6** ($\delta_P = 27.4$ ppm) and **7** ($\delta_P = 26.7$ ppm),[6] probably because of its different geometry of the phosphorus atom due to steric reasons.

Phosphaboraacenaphthene **1** was stable under inert conditions even on heating of the C_6D_6 solution in a sealed tube at 100 °C for 24 h. However, addition of degassed water into the C_6D_6 solution of **1** afforded 1-hydroxy(mesityl)boryl-8-mesitylphosphinonaphthalene (**8**) in 93% yield (Scheme 3), suggesting that the P–B bond exhibits enough reactivity towards small molecules. On the other hand, theoretical calculations of **1** revealed the highest occupied molecular orbital (HOMO) of **1** exhibited a dominant contribution of lone-pair n-orbital of the phosphorus atom, indicating that the lone-pair n-orbital of the phosphorus atom can be reactive. Finally, as shown in Scheme 1, the previous reports on the chalcogenation reactions of stable phosphinoboranes resulting in the formation of the corresponding phosphine-chalcogenides incorporated with a heterocyclic system prompted us to examine the chalcogenation reactions of the obtained 1-phospha-2-boraacenaphthene **1**.

Chalcogenation reactions of 1-phospha-2-boraacenaphthene **1** are summarized in Scheme 3. All chalcogenation reactions described below have been performed in a degassed and sealed tube. Sulfurization reaction of **1** with S_8 (2 equiv as S) in C_6D_6 at 100 °C for 40 h resulted in the formation of 2-thia-1-phospha-3-boraphenalene-1-sulfide **10SS** in 88% yield. Thus,



Scheme 3. Reactions of 1-phospha-2-boraacenaphthene **1**. [a] $P(NMe_2)_3$ (2.5 equiv), C_6D_6, 60 °C, 3 h, 87 %. [b] S_8 (1 equiv as S), C_6D_6, 100 °C, 9 h, quant. [c] Se (1.5 equiv), C_6D_6, 100 °C, 24 h, 82 %. [d] Se (1.5 equiv), C_6D_6, 100 °C, 3.5 days, 80 %.

the sulfurization of **1** was found to afford the new heterocyclic compound of **10 SS** bearing a P(*S*)–S–B moiety as expected. At this stage, we wonder which sulfur atom would firstly be introduced onto the 1-phospha-2-boraacenaphthene skeleton. Treatment of **1** with 1 equiv of elemental sulfur (S_8) in C_6D_6 at RT for 17 h gave a mixture of **1**, 2-thia-1-phospha-3-boraphenalene **9 S**, and 2-thia-1-phospha-3-boraphenalene-1-sulfide **10 SS** in a ratio of 4:3:1 as judged by the ^{1}H and ^{31}P NMR spectra, indicating the intermediacy of **9 S** in the sulfurization of **1** giving **10 SS**. It was difficult to purify the reaction mixture of **1**, **9 S**, and **10 SS** by using general methods of purification such as column chromatography or GPC due to their instability under these purification conditions. Finally, it was found that the desulfurization reaction of **10 SS** by $P(NMe_2)_3$ exclusively gave **9 S**, which could be purified by recrystallization from toluene/hexane and isolated in 87 % yield. Treatment of S_8 (1 equiv as S) in C_6D_6 at 100 °C for 9 h was found to afford **10 SS** quantitatively.

In contrast to the case of the sulfurization reaction described above, heating of C_6D_6 solution of **1** with elemental selenium at 50 °C for four days afforded 2-selena-1-phospha-3-boraphenalene **9 Se** isolated exclusively in 81 % yield. It should be noted that compounds **9 S** and **9 Se** are the first examples of the new heterocycles with phosphorus, boron, and chalcogen atoms in the phenalene backbone.[11] A further selenization reaction of **9 Se** with 1.5 equiv of Se in C_6D_6 at 100 °C for 3.5 days resulted in the formation of 2-selena-1-phospha-3-boraphenalene-1-selenide **10 SeSe** in 80 % yield. Alternatively, long-term heating of C_6D_6 solution of **1** with elemental selenium at 100 °C for five days directly gave **10 SeSe** isolated in 54 % yield.

Interestingly, selenization reaction of the P–S–B compound (**9 S**) with 1.5 equiv of Se in C_6D_6 at 100 °C for 24 h resulted in the formation of a mixed-chalcogen system of 2-thia-1-phospha-3-boraphenalene-1-selenide **10 SSe** in 82 % yield. Thus, isolation of the mono-sulfurized compound of **9 S** gave us an opportunity to synthesize such unique mixed-chalcogen systems. However, sulfurization of the P–Se–B compound (**9 Se**) with S_8 afforded no expected compound of 2-selena-1-phospha-3-boraphenalene-1-sulfide **10 SeS**. When **9 Se** was treated with S_8 (1 equiv as S) in C_6D_6 at 80 °C for 19 h and then at 100 °C for 5 days, the ^{1}H NMR spectrum of the reaction mixture showed that all of the starting material had been consumed and **10 SS**, **10 SeSe**, and **10 SSe** were unexpectedly formed in the ratio of 3:2:10 in the ^{1}H NMR spectrum. At the initial stage of the sulfurization reaction of **9 Se**, signals for **9 S** and **10 SeSe** were observed along with those for the starting material (**9 Se**) as judged by the ^{1}H NMR spectra, indicating the facile chalcogen-exchange reaction of **9 Se** giving **9 S** under these conditions (Figure 2).

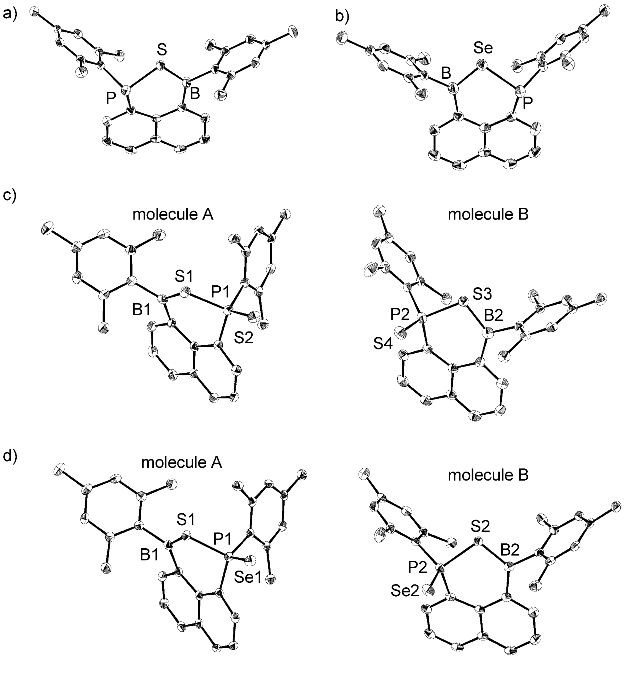
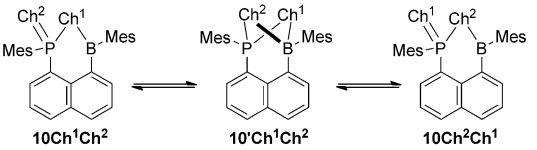


Figure 2. Molecular structures of a) **9 S**, b) **9 Se**, c) **10 SS**, and d) **10 SSe** (thermal ellipsoids with 50 % probability). All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: a) **9 S**: P–S, 2.1204(11), S–B, 1.802(4), P-S-B, 105.64(12); b) **9 Se**: P–Se, 2.2607(10), Se–B, 1.938(4), P-Se-B, 101.52(13); c) **10 SS**: Two independent molecules were found in the unit cell: P1–S1, 2.1125(10), S1–B1, 1.814(3), P1–S2, 1.9524(9), P1-S1-B1, 102.51(11), P2–S3, 2.0948(10), S3–B2, 1.808(3), P2–S4, 1.9514(10), P2-S3-B2, 103.49(11). d) **10 SSe**: Two independent molecules were found in the unit cell: P1–S1, 2.1112(8), S1–B1, 1.817(3), P1–Se1, 2.1056(6), P1-S1-B1, 102.15(9), P2–S2, 2.0970(8), S2–B2, 1.799(3), P2–Se2, 2.1051(6), P2-S2-B2, 103.00(9).

The molecular structures of all of the newly obtained compounds, **9 S**, **9 Se**, **10 SS**, **10 SSe**, and **10 SeSe**, have been unambiguously determined by X-ray crystallographic analyses. All results of the analyses supported their structures with reasonable structural parameters. During the investigation on the molecular structure of **10 SeSe**, interesting phenomena were found. In particular, the two different kinds of crystals of **10 SeSe** were obtained depending on the conditions of the crystal growth. The single crystals obtained by the recrystallization from its toluene/hexane solution at RT was found to exhibit the molecular structure as **10 SeSe** with the P(Se)–Se–B moiety as expected. On the other hand, unexpectedly, the recrystallization from its toluene solution at RT afforded the single crystals exhibiting the structure of **10′ SeSe** with the P(μ-Se_2)B moiety. Unfortunately, the detailed structural parameters could not be discussed with appropriate accuracy, because of the inevitable severe 1:1 disorder with a pseudo-C_2 axis. However, the theoretically optimized structural parameters for **10′ SeSe** at B3PW91/6-311+G(3d)[6-31G(d) for C,H] level were in good agreement with those experimentally observed, supporting the reasonable solution of the X-ray data.[12] Anyway, there should be no concrete chemical bond between the P and B atoms in **10′ SeSe** because the observed distance (ca. 2.7 Å) between the P and B atoms was longer than those in the previously reported phosphine boranes. Theoretical calculations on **10 SeSe** and **10′ SeSe** suggested the relative energy of **10′ SeSe** would be only $+2.9\ \text{kcal mol}^{-1}$ (self-consistent field (SCF), at B3PW91/6-311+G(3d)[6-31G(d) for C,H]) as compared with **10 SeSe**, indicating that the difference of the structures in the crystalline state would be simply due to the crystal packing force (Figure 3).



Scheme 4. Intramolecular chalcogen exchange in **10 ChCh**.

Table 1. NMR spectral data for **1**, **9 S**, **9 Se**, **10 SS**, **10 SSe**, and **10 SeSe**.[a]

Compound	1	9 S	9 Se	10 SS	10 SSe	10 SeSe
δ_B [ppm]	77.9	65.1	70.6	65.6	65.9	68.6
$\Delta\nu_{1/2}(\delta_B)$ [Hz]	1400	1110	1050	1190	1130	1100
δ_P [ppm]	−28.2	−4.2	−18.1	37.5	19.7	2.0
δ_{Se} [ppm]	–		150.0	–	−16.6	226.2[b]
J_{PSe} [Hz]	–		178	–	779	539

[a] In C_6D_6 at RT. [b] Measured at 60 °C.

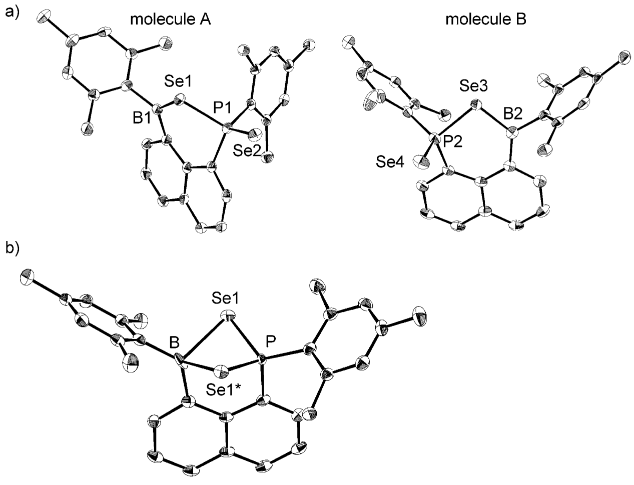


Figure 3. Molecular structures of a) **10 SeSe** and b) **10′ SeSe** (thermal ellipsoids with 50 % probability). All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: a) **10 SeSe**: Two independent molecules were found in the unit cell: P1–Se1, 2.2526(8), Se1–B1, 1.943(3), P1–Se2, 2.1084(8), P1-Se1-B1, 98.05(10), P2–Se3, 2.2314(8), Se3–B2, 1.922(3), P2–Se4, 2.1071(8), P2-Se3-B2, 99.72(11). b) **10′SeSe**: Crystallographic pseudo-C_2 axis passes through the center of the molecule: Definitive structural parameters could not be obtained due to the severe disorder with pseudo-C_2 symmetry. Obtained structural parameters: P–Se1, 2.139(6), Se1–B, 2.30(3), P–Se1*, 2.117(6), Se1*–B, 2.33(3) Å; P-Se1-B, 75.9(7), P-Se1*-B, 75.6(7), Se1-B-Se1*, 87.9(10), Se1-P-Se1*, 98.2(2)°.

The isolation of crystals of **10′ SeSe** naturally induced us to consider the dynamic behavior of compound **10** in solution as shown in Scheme 4. The NMR spectral data for **9** and **10** were summarized in Table 1. Although one can think that **10 SeSe** has two independent selenium atoms, the ^{77}Se NMR spectrum of **10 SeSe** in C_6D_6 shows only a broadened signal at RT and one doublet signal coupled with the neighboring phosphorus atom at 60 °C. The observed $|^1J_{PSe}|$ coupling constant (539 Hz) is considerably larger than that of **9 Se** (150 Hz) and similar to that of [Ph_2PSe_2Li·THF·TMEDA] ($^1J_{PSe}=578$ Hz; TMEDA = tetramethylethylenediamine),[13] in which the π-electrons would be delocalized on the PSe_2 moiety as a P(μ-Se_2)Li species. Therefore, **10 SeSe** could be considered to exhibit the structure as **10′ SeSe** with a P(μ-Se_2)B moiety in solution, in which signals for two selenium nuclei appeared equivalently in the ^{77}Se NMR spectrum. However, the structure of **10′ SeSe** cannot explain its 1) broadened ^{11}B NMR signal ($\delta_B=68.6$ ppm, $\Delta\nu_{1/2}=1100$ Hz) indicating the three-coordinated boron atom, 2) relatively upper-field ^{31}P chemical shift ($\delta_P=2.0$ ppm), and 3) considerably lower-field ^{77}Se NMR chemical shift ($\delta_{Se}=226$ ppm). As compared with the δ_B, δ_P, and δ_{Se} chemical shifts of **9 Se** ($\delta_B=70.6$, $\delta_P=-18.1$, and $\delta_{Se}=150.0$ ppm), those of **10 SeSe** are similar in δ_B, and lower field in δ_P and δ_{Se}, suggesting electron deficiency in the P and Se atoms in **10 SeSe**. Thus, it can be concluded that the facile exchange of the two selenium atoms would occur in solution, exhibiting the dynamic behavior between **10 SeSe** and **10′SeSe**, in which the structure as **10 SeSe** bearing P(Se)–Se–B moiety should be the dominant contributor of the dynamic behavior along with the smaller contribution of **10′SeSe** bearing the P(μ-Se_2)B moiety. The dynamic behavior could not be perturbed even at −60 °C on the basis of NMR spectra in toluene. It should be noted that the IR spectrum of the single crystal of **10 SeSe** (KBr pellet), not those of **10′ SeSe**, was almost identical that of the CCl_4 solution of **10 SeSe**, suggesting the dominant contribution of **10 SeSe** in solution, whereas the theoretically simulated IR spectra of **10 SeSe** and **10′ SeSe** seem to be somewhat different and that of **10 SeSe** (calculated) is in good agreement with that observed. The ^{1}H NMR spectra also suggested such facile chalcogen exchange in **10 SeSe** in solution. In both cases of **9 S** and **9 Se**, the six methyl groups of the two mesityl groups were observed independently at room temperature in ^{1}H NMR spectrum in C_6D_6, suggesting the restricted rotation of the P–Mes and B–Mes bonds. However, the *ortho*-methyl groups of each Mes group of **10 SeSe** were observed equivalently in the ^{1}H NMR spectrum, suggesting an averaged **10′ SeSe** structure in solution through fast exchange of the two selenium atoms.

Similar to the case of **10 SeSe**, the *ortho*-methyl groups of each Mes group of **10 SS** also gave an equivalent signal, indicating a dynamic behavior similar to that of **10 SeSe**. In the case of **10 SSe**, its *ortho*-methyl groups of each Mes group were independently observed, but this gives no information on the facile exchange of S and Se, because even its averaged structure of **10′ SSe** would afford the independent signals for the *ortho*-methyl groups. Although the ^{31}P NMR chemical shift of **10 SS** ($\delta_P = 37.5$ ppm) and **10 SSe** ($\delta_P = 19.7$ ppm) would be somewhat shifted to lower field than that of **10 SeSe**, we believe facile chalcogen exchange would occur in all cases of **10 SS**, **10 SSe**, and **10 SeSe**. The IR spectra of **10 SS**, **10 SSe**, and **10 SeSe** are similar to each other and those theoretically simulated as expected. Thus, the observed dynamic behavior of **10 ChCh** species would be specific feature in the P(Ch)–ChB skeleton.

Conclusion

1-Phospha-2-boraacenaphthene **1** has been successfully synthesized by the unique reaction of the reduction of **2 a** with elemental magnesium, and its structural features have been revealed. Chalcogenation reactions of **1** gave the unique heterocycles, 2-chalcogena-1-phospha-3-boraphenalenes **9 S** and **9 Se**, which have a P–Ch–B moiety tethered to the naphthalene skeleton. Further chalcogenation reaction of **9** gave the corresponding phosphine chalcogenides **10**. Compounds **9** and **10** are the first examples of the new heterocycles with phosphorus, boron, and chalcogen atoms in the phenalene backbone. These compounds are fully characterized by spectroscopic and X-ray crystallographic analyses. In particular, the dynamic behavior of **10 SeSe** was found in solution, in which the two selenium atoms underwent facile exchange with each other through the intermediate of **10′ SeSe** bearing a P(μ-Se_2)B four-membered ring system. Interestingly, two kinds of single crystals of **10 SeSe** and **10′ SeSe** were isolated depending on the recrystallization conditions. Thus, it can be conceivable that the related compounds, **10 ChCh**, would undergo similar facile chalcogenation-exchange. These fundamental studies on the chalcogenation reactions of **1** will be helpful for the understanding of the chalcogenation of phosphinoborane and the creation of the unique heterocyclic systems containing several heteroatoms by utilizing a P–B bond.

Experimental Section

General

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by an Ultimate Solvent System (Glass Contour Company).[14] Solvents used in the spectroscopy were dried by using a potassium mirror (for [D$_6$]benzene) or phosphorus pentoxide (for CCl_4), respectively. The ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were measured in C_6D_6 with a BRUKER AVANCE III-600 spectrometer. Signals due to C_6D_5H ($\delta = 7.15$ ppm) in ^{1}H NMR and those due to C_6D_6 ($\delta = 128.0$ ppm) in ^{13}C NMR were used as internal references, respectively. The ^{31}P NMR (121 MHz), ^{11}B NMR (95 MHz), and ^{77}Se NMR (57 MHz) spectra were measured in C_6D_6 with a JEOL AL-300 spectrometer using 85 % H_3PO_4 in water (0 ppm), $BF_3{\cdot}OEt_2$ (0 ppm), and Ph_2Se_2 (460 ppm) as an external standard, respectively. Multiplicity of signals in ^{13}C NMR was determined by DEPT, HSQC, and HMBC techniques. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer (EI and FAB). Infrared spectra were recorded as KBr pellets using a JASCO FT/IR-460 Plus spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

Reagents

Elemental selenium (Wako chemical) was used as received. Hexamethylphosphosrus triamide were distilled from molecular sieve 4 A prior to use. Elemental sulfur was recrystallized from benzene in the dark. 1,2-Dimesityl-1-phoapha-2-boraacenaphthene (**1**) was prepared according to the reported procedure.[8]

Syntheses

Treatment of 1 with elemental sulfur (2 equiv): A solution of **1** (122 mg, 0.300 mmol) in C_6D_6 (1 mL) and elemental sulfur (19.2 mg, 0.600 mmol as S) was charged into an NMR tube with J-Young valve. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After heating at 100 °C for 40 h, the solvent was removed under reduced pressure. The residue was recrystallized from its toluene/hexane solution at −40 °C to afford 1,3-dihydro-1,3-dimesityl-2-thia-1-phospha-3-boraphenalene-1-sulfide (**10 SS**, 124 mg, 0.263 mmol, 88 %) as yellow crystals. **10 SS**: yellow crystals. M.p. 197 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, RT): $\delta = 1.89$ (s, 3 H, Mes^{P}-*p*-Me), 2.04 (s, 6 H, Mes^{B}-*o*-Me), 2.18 (s, 3 H, Mes^{B}-*p*-Me), 2.40 (br s, 6 H, Mes^{P}-*o*-Me), 6.47 (d, $^{4}J_{HP} = 4.6$ Hz, 2 H, Mes^{P}-*m*-arom-CH), 6.74 (s, 2 H, Mes^{B}-*m*-arom-CH), 6.95 (dd, $^{3}J_{HH} = 8.2$, 7.0 Hz, 1 H, Phen-5), 7.10 (ddd, $^{3}J_{HH} = 8.1$, 7.3 Hz, $^{4}J_{HP} = 2.5$ Hz, 1 H, Phen-8), 7.48 (ddd, $^{3}J_{HH} = 8.1$ Hz, $^{4}J_{HH} = 1.3$ Hz, $^{4}J_{HP} = 1.3$ Hz, 1 H, Phen-7), 7.55 (ddd, $^{3}J_{HH} = 8.2$ Hz, $^{4}J_{HH} = 1.5$ Hz, $^{4}J_{HP} = 1.5$ Hz, 1 H, Phen-6), 7.91 (dd, $^{3}J_{HH} = 7.0$ Hz, $^{4}J_{HH} = 1.5$ Hz, 1 H, Phen-4), 8.65 ppm (ddd, $^{3}J_{HP} = 18.7$ Hz, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.3$ Hz, 1 H, Phen-9); ^{13}C NMR (150 MHz, C_6D_6, RT): $\delta = 20.59$ (d, $^{5}J_{CP} = 1.3$ Hz, Mes^{P}-*p*-CH_3), 21.23 (Mes^{B}-*p*-CH_3), 22.25 (Mes^{B}-*o*-CH_3), 24.42 (d, $^{3}J_{CP} = 5.2$ Hz, Mes^{P}-*o*-CH_3), 126.15 (d, $^{3}J_{CP} = 15.7$ Hz, Phen-8), 126.22 (Phen-5), 127.98 (Mes^{B}-*m*-arom-CH), 130.40 (br, Phen-3a), 131.14 (d, $^{1}J_{CP} = 82.7$ Hz, Mes^{P}-*ipso*-arom-CH), 132.11 (d, $^{3}J_{CP} = 12.3$ Hz, Mes^{P}-*m*-arom-CH), 133.29 (d, $^{4}J_{CP} = 3.4$ Hz, Phen-7), 133.57 (d, $^{3}J_{CP} = 8.9$ Hz, Phen-6a), 134.05 (d, $^{1}J_{CP} = 80.0$ Hz, Phen-9a), 134.12 (d, $^{2}J_{CP} = 7.3$ Hz, Phen-9b), 135.39 (d, $^{2}J_{CP} = 12.9$ Hz, Phen-9), 136.35 (d, $^{4}J_{CP} = 1.2$ Hz, Phen-6), 138.28 (Mes^{B}-*p*-arom), 138.42 (Mes^{B}-*o*-arom), 138.76 (br, Mes^{B}-*ipso*-arom), 141.10 (d, $^{4}J_{CP} = 3.0$ Hz, Mes^{P}-*p*-arom), 141.59 (Phen-4), 142.30 ppm (d, $^{2}J_{CP} = 11.6$ Hz, Mes^{P}-*o*-arom); ^{11}B NMR (95 MHz, C_6D_6, RT): $\delta = 65.6$ ppm ($\Delta v_{1/2} = 1190$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta = 37.5$ ppm (d, $^{3}J_{PH} = 18.6$ Hz); HRMS (FAB) *m/z*: 470.1466 [*M*]$^{+}$; elemental analysis calcd (%) for $C_{28}H_{28}{}^{11}BPS_2$ (470.1463): C 71.49, H 6.00; found: C 71.47, H 6.16.

Treatment of 10 SS with hexamethylphosphosrus triamide: A C_6D_6 solution (0.8 mL) of **10 SS** (94.1 mg, 0.200 mmol) and $P(NMe_2)_3$ (91 µL, 0.50 mmol) was degassed and sealed in an NMR tube. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After heating at 60 °C for 3 h, the volatile of the reaction mixture was removed under reduced pressure. The residue was washed with hexane, followed by recrystallization from its toluene/hexane solution to afford 1,3-dihydro-1,3-dimesityl-2-thia-1-phospha-3-boraphenalene (**9S**, 76.2 mg, 0.173 mmol, 87 %) as yellow crystals. **9S**: M.p. 218 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, RT): $\delta = 2.04$ (s, 3H, Mes$^{\mathrm{P}}$-*p*-Me), 2.16 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 2.22 (s, 3H, Mes$^{\mathrm{B}}$-*p*-Me), 2.47 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 2.58 (br s, 6H, Mes$^{\mathrm{P}}$-*o*-Me), 6.72–6.73 (m, 2H, Mes$^{\mathrm{P}}$-*m*-arom CH), 6.78–6.79 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.86–6.87 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.93 (ddd, $^{3}J_{HH} = 8.0$, 7.3 Hz, $^{4}J_{HP} = 2.3$ Hz, 1H, Phen-8), 7.00 (dd, $^{3}J_{HH} = 8.3$, 7.0 Hz, 1H, Phen-5), 7.36–7.40 (m, 2H, Phen-7 and Phen-9), 7.57 (dd, $^{3}J_{HH} = 8.3$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H, Phen-6), 7.86 ppm (ddd, $^{3}J_{HH} = 7.0$ Hz, $^{4}J_{HH} = 1.4$ Hz, $^{5}J_{HP} = 1.4$ Hz, 1H, Phen-4); ^{13}C NMR (150 MHz, C_6D_6, 25 °C): $\delta = 21.03$ (Mes$^{\mathrm{P}}$-*p*-CH_3), 21.27 (Mes$^{\mathrm{B}}$-*p*-CH_3), 22.33 (Mes$^{\mathrm{B}}$-*o*-CH_3), 22.54 (Mes$^{\mathrm{B}}$-*o*-CH_3), 23.27 (br, Mes$^{\mathrm{P}}$-*o*-CH_3), 125.48 (d, $^{3}J_{CP} = 4.9$ Hz, Phen-8-CH), 126.22 (d, $^{5}J_{CP} = 1.1$ Hz, Phen-5-CH), 127.84 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 128.20 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 129.17 (d, $^{4}J_{CP} = 3.5$ Hz, Phen-7-CH), 129.45 (d, $^{2}J_{CP} = 30.5$ Hz, Phen-9-CH), 129.5 (br, Mes$^{\mathrm{P}}$-*m*-arom-CH), 131.8 (br, Mes$^{\mathrm{P}}$-*m*-arom-CH), 131.92 (d, $^{1}J_{CP} = 40.0$ Hz, Mes$^{\mathrm{P}}$-*ipso*-arom), 132.74 (br, Phen-3a), 134.80 (Phen-6a), 135.43 (d, $^{2}J_{CP} = 8.9$ Hz, Phen-9b), 135.97 (d, $^{4}J_{CP} = 2.0$ Hz, Phen-6-CH), 135.98 (d, $^{1}J_{CP} = 40.0$ Hz, Phen-9a), 137.59 (Mes$^{\mathrm{B}}$-*p*-arom), 137.81 (Mes$^{\mathrm{B}}$-*o*-arom), 138.77 (d, $^{4}J_{CP} = 2.6$ Hz, Phen-4-CH), 139.12 (Mes$^{\mathrm{B}}$-*o*-arom), 140.56 (br, Mes$^{\mathrm{B}}$-*ipso*-arom), 141.02 (d, $^{4}J_{CP} = 1.0$ Hz, Mes$^{\mathrm{P}}$-*p*-arom), 145.72 ppm (Mes$^{\mathrm{P}}$-*o*-arom); ^{11}B NMR (95 MHz, C_6D_6, RT): $\delta = 65.1$ ppm ($\Delta\nu_{1/2} = 1110$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta = -4.2$ ppm (d, $J_{PH} = 8.4$ Hz); HRMS (FAB) *m/z*: 438.1753 $[M]^{+}$; elemental analysis calcd (%) for $C_{28}H_{28}{}^{11}BPS$ (438.1742): C 76.72, H 6.44; found: C 76.66, H 6.45.

Treatment of 1 with elemental selenium (1 equiv): A C_6D_6 solution (0.8 mL) of **1** (32.5 mg, 80.0 μmol) and elemental selenium (6.3 mg, 80 μmol) was charged into an NMR tube with J-Young valve. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After heating at 50 °C for 4 days, the reaction mixture was filtered with benzene. The solvent of the filtrate was removed under reduced pressure. The residue was washed with benzene to afford 1,3-dihydro-1,3-dimesityl-2-selena-1-phospha-3-boraphenalene (**9Se**, 31.3 mg, 64.5 μmol, 81 %) as yellow crystals. **9Se**: yellow crystals. M.p. 212 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, RT): $\delta = 2.05$ (s, 3H, Mes$^{\mathrm{P}}$-*p*-Me), 2.15 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 2.22 (s, 3H, Mes$^{\mathrm{B}}$-*p*-Me), 2.46 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 2.58 (br s, 6H, Mes$^{\mathrm{P}}$-*o*-Me), 6.73–6.74 (m, 2H, Mes$^{\mathrm{P}}$-*m*-arom CH), 6.77–6.78 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.85–6.86 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.90 (ddd, $^{3}J_{HH} = 7.9$, 7.3 Hz, $^{4}J_{HP} = 2.2$ Hz, 1H, Phen-8), 6.95 (dd, $^{3}J_{HH} = 8.3$, 7.0 Hz, 1H, Phen-5), 7.36 (dm, $^{3}J_{HH} = 7.9$ Hz, 1H, Phen-7), 7.52 (ddd, $^{3}J_{HP} = 9.5$ Hz, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H, Phen-9), 7.59 (dd, $^{3}J_{HH} = 8.3$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H, Phen-6), 7.95 ppm (ddd, $^{3}J_{HH} = 7.0$ Hz, $^{4}J_{HH} = 1.4$ Hz, $^{5}J_{HP} = 1.4$ Hz, 1H, Phen-4); ^{13}C NMR (150 MHz, C_6D_6, 25 °C): $\delta = 21.01$ (Mes$^{\mathrm{P}}$-*p*-CH_3), 21.25 (Mes$^{\mathrm{B}}$-*o*-CH_3), 22.29 (Mes$^{\mathrm{B}}$-*p*-CH_3), 22.63 (Mes$^{\mathrm{B}}$-*o*-CH_3), 23.55 (br, Mes$^{\mathrm{P}}$-*o*-CH_3), 23.68 (Mes$^{\mathrm{P}}$-*o*-CH_3), 125.42 (d, $^{3}J_{CP} = 4.4$ Hz, Phen-8-CH), 126.07 (d, $^{5}J_{CP} = 1.2$ Hz, Phen-5-CH), 127.94 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 128.28 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 129.3 (br, Mes$^{\mathrm{P}}$-*m*-arom-CH), 129.50 (d, $^{4}J_{CP} = 3.6$ Hz, Phen-7-CH), 130.0 (br, Mes$^{\mathrm{P}}$-*m*-arom-CH), 130.48 (d, $^{2}J_{CP} = 30.5$ Hz, Phen-9-CH), 132.13 (d, $^{1}J_{CP} = 44.0$ Hz, Mes$^{\mathrm{P}}$-*ipso*-arom), 134.20 (br, Phen-3a), 135.32 (Phen-6a), 135.68 (d, $^{1}J_{CP} = 45.9$ Hz, Phen-9a), 135.87 (d, $^{2}J_{CP} = 9.9$ Hz, Phen-9b), 136.57 (d, $^{4}J_{CP} = 2.0$ Hz, Phen-6-CH), 136.97 (Mes$^{\mathrm{B}}$-*o*-arom), 137.63 (Mes$^{\mathrm{B}}$-*p*-arom), 138.48 (Mes$^{\mathrm{B}}$-*o*-arom), 138.63 (d, $^{4}J_{CP} = 2.3$ Hz, Phen-4-CH), 140.72 (d, $^{4}J_{CP} = 1.2$ Hz, Mes$^{\mathrm{P}}$-*p*-arom), 141.78 (br, Mes$^{\mathrm{B}}$-*ipso*-arom), 145.56 (Mes$^{\mathrm{P}}$-*o*-arom), 145.68 ppm (br, Mes$^{\mathrm{P}}$-*o*-arom); ^{11}B NMR (95 MHz, C_6D_6, RT) $\delta = 70.6$ ppm ($\Delta\nu_{1/2} = 1050$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta = -18.1$ ppm (d, $^{1}J_{PSe} = 179$ Hz); ^{77}Se NMR (57 MHz, C_6D_6, RT): $\delta = 150.0$ ppm (d, $^{1}J_{PSe} = 178$ Hz); HRMS (FAB) *m/z*: 486.1204 $[M]^{+}$; elemental analysis calcd (%) for $C_{28}H_{28}{}^{11}BP^{80}Se$ (486.1187): C 69.30, H 5.82; found: C 69.08, H 5.96.

Treatment of 1 with elemental selenium (2.0 equiv): A C_6D_6 solution (0.8 mL) of **1** (32.5 mg, 80.0 μmol) and elemental selenium (12.6 mg, 160 μmol) was charged into an NMR tube with J-Young valve. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After heating at 100 °C for 5 days, compounds **10SeSe** and **9Se** were obtained in the ratio of 9:2 as judged by the ^{1}H NMR spectra. The reaction mixture was filtered with benzene and then the solvent of the filtrate was removed under reduced pressure. The residue was reprecipitated from its benzene/hexane solution to afford 1,3-dihydro-1,3-dimesityl-2-selena-1-phospha-3-boraphenalene-1-selenide (**10SeSe**, 24.6 mg, 43.6 μmol, 54 %) as a sole product. **10SeSe**: yellow crystals. M.p. 205 °C (decomp.); ^{1}H NMR (600 MHz, C_6D_6, RT): $\delta = 1.85$ (s, 3H, Mes$^{\mathrm{P}}$-*p*-Me), 1.90 (s, 6H, Mes$^{\mathrm{B}}$-*o*-Me), 2.17 (s, 3H, Mes$^{\mathrm{B}}$-*p*-Me), 2.24 (s, 6H, Mes$^{\mathrm{P}}$-*o*-Me), 6.35 (d, $^{4}J_{HP} = 4.7$ Hz, 2H, Mes$^{\mathrm{P}}$-*m*-arom CH), 6.72 (s, 2H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.89 (dd, $^{3}J_{HH} = 8.0$, 7.0 Hz, 1H, Phen-5), 7.13–7.16 (m, 1H, Phen-8), 7.46 (ddd, $^{3}J_{HH} = 8.1$ Hz, $^{4}J_{HH} = 1.6$ Hz, $^{4}J_{HP} = 1.6$ Hz, 1H, Phen-7), 7.54 (ddd, $^{3}J_{HH} = 8.0$ Hz, $^{4}J_{HH} = 1.6$ Hz, $^{4}J_{HP} = 1.6$ Hz, 1H, Phen-6), 7.86 (dd, $^{3}J_{HH} = 7.0$ Hz, $^{4}J_{HH} = 1.5$ Hz, 1H, Phen-4), 9.21 ppm (dd, $^{3}J_{HP} = 20.0$ Hz, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.3$ Hz, 1H, Phen-9); ^{13}C NMR (150 MHz, C_6D_6, RT): $\delta = 20.45$ (d, $^{5}J_{CP} = 1.5$ Hz, Mes$^{\mathrm{P}}$-*p*-CH_3), 21.18 (Mes$^{\mathrm{B}}$-*p*-CH_3), 22.25 (Mes$^{\mathrm{B}}$-*o*-CH_3), 23.95 (d, $^{3}J_{CP} = 5.8$ Hz, Mes$^{\mathrm{P}}$-*o*-CH_3), 126.028 (Phen-5), 126.035 (d, $^{3}J_{CP} = 15.8$ Hz, Phen-8), 128.08 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 131.13 (d, $^{1}J_{CP} = 66.5$ Hz, Mes$^{\mathrm{P}}$-*ipso*-arom-CH), 131.15 (d, $^{1}J_{CP} = 61.1$ Hz, Phen-9a), 131.72 (d, $^{3}J_{CP} = 11.8$ Hz, Mes$^{\mathrm{P}}$-*m*-arom-CH), 132.73 (br, Phen-3a), 133.80 (d, $^{3}J_{CP} = 8.5$ Hz, Phen-6a), 133.85 (d, $^{4}J_{CP} = 3.5$ Hz, Phen-7), 134.90 (d, $^{2}J_{CP} = 7.3$ Hz, Phen-9b), 136.33 (d, Phen-6), 137.84 (Mes$^{\mathrm{B}}$-*o*-arom), 138.23 (Mes$^{\mathrm{B}}$-*p*-arom), 138.50 (d, $^{2}J_{CP} = 14.4$ Hz, Phen-9), 139.22 (br, Mes$^{\mathrm{B}}$-*ipso*-arom), 140.59 (d, $^{4}J_{CP} = 3.1$ Hz, Mes$^{\mathrm{P}}$-*p*-arom), 140.77 (Phen-4), 141.40 (d, $^{2}J_{CP} = 11.2$ Hz, Mes$^{\mathrm{P}}$-*o*-arom); ^{11}B NMR (95 MHz, C_6D_6, RT): $\delta = 68.7$ ppm ($\Delta\nu_{1/2} = 1100$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta = 2.0$ ppm (d, $^{3}J_{PH} = 19.8$ Hz, $^{1}J_{PSe} = 539$ Hz); ^{77}Se NMR (57 MHz, C_6D_6, 60 °C): $\delta = 226.2$ ppm (br d, $^{1}J_{PSe} = 508$ Hz); HRMS (FAB) *m/z*: found: 566.0635 $[M]^{+}$; elemental analysis calcd (%) for $C_{28}H_{28}{}^{11}BP^{80}Se_2$ (566.0362): C 59.60, H 5.00; found: C 59.61, H 5.10.

Treatment of 9S with elemental selenium: A C_6D_6 solution (0.8 mL) of **9S** (43.8 mg, 0.100 mmol) and elemental selenium (11.8 mg, 0.150 mmol) was charged into an NMR tube with J-Young valve. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After heating at 100 °C for 24 h, the reaction mixture was filtered with benzene, and then the solvent of the filtrate was removed under reduced pressure. The residue was reprecipitated from its toluene/hexane solution to afford 1,3-dihydro-1,3-dimesityl-2-thia-1-phospha-3-boraphenalene-1-selenide **10SSe** (42.5 mg, 82.0 μmol, 82 %). **10SSe**: yellow crystals. M.p. 224 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, RT) $\delta = 1.85$ (s, 3H, Mes$^{\mathrm{P}}$-*p*-Me), 1.91 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 1.96 (s, 3H, Mes$^{\mathrm{B}}$-*o*-Me), 2.16 (s, 3H, Mes$^{\mathrm{B}}$-*p*-Me), 2.29 (s, 6H, Mes$^{\mathrm{P}}$-*o*-Me), 6.38 (d, $^{4}J_{HP} = 4.6$ Hz, 2H, Mes$^{\mathrm{P}}$-*m*-arom CH), 6.66–6.67 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.76–6.77 (m, 1H, Mes$^{\mathrm{B}}$-*m*-arom CH), 6.91 (dd, $^{3}J_{HH} = 8.1$, 7.0 Hz, 1H, Phen-5), 7.14 (ddd, $^{3}J_{HH} = 8.1$, 7.3 Hz, $^{4}J_{HP} = 2.5$ Hz, 1H, Phen-8), 7.46 (ddd, $^{3}J_{HH} = 8.1$ Hz, $^{4}J_{HH} = 1.4$ Hz, $^{4}J_{HP} = 1.4$ Hz, 1H, Phen-7), 7.52 (ddd, $^{3}J_{HH} = 8.1$ Hz, $^{4}J_{HH} = 1.5$ Hz, $^{4}J_{HP} = 1.5$ Hz, 1H, Phen-6), 7.82 (dd, $^{3}J_{HH} = 7.0$ Hz, $^{4}J_{HH} = 1.5$ Hz, 1H, Phen-4), 9.08 ppm (ddd, $^{3}J_{HP} = 19.9$ Hz, $^{3}J_{HH} = 7.3$ Hz, $^{4}J_{HH} = 1.4$ Hz, 1H, Phen-9); ^{13}C NMR (150 MHz, C_6D_6, RT): $\delta = 20.49$ (d, $^{5}J_{CP} = 1.4$ Hz, Mes$^{\mathrm{P}}$-*p*-CH_3), 21.21 (Mes$^{\mathrm{B}}$-*p*-CH_3), 22.08 (Mes$^{\mathrm{B}}$-*o*-CH_3), 22.18 (Mes$^{\mathrm{B}}$-*o*-CH_3), 24.18 (br d, $^{3}J_{CP} = 5.1$ Hz, Mes$^{\mathrm{P}}$-*o*-CH_3), 126.17 (d, $^{3}J_{CP} = 16.1$ Hz, Phen-8-CH), 126.20 (Phen-5-CH), 127.79 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 128.13 (Mes$^{\mathrm{B}}$-*m*-arom-CH), 130.89 (br, Phen-3a), 131.37 (d, $^{1}J_{CP}=72.0$ Hz, Mes^{P}-*ipso*-arom), 131.58 (d, $^{1}J_{CP}=69.0$ Hz, Phen-9a), 131.93 (d, $^{3}J_{CP}=12.0$ Hz, Mes^{P}-*m*-arom-CH), 133.30 (d, $^{3}J_{CP}=8.7$ Hz, Phen-6a), 133.62 (d, $^{4}J_{CP}=3.5$ Hz, Phen-7-CH), 134.31 (d, $^{2}J_{CP}=6.0$ Hz, Phen-9b), 136.24 (Phen-6-CH), 137.96 (Mes^{B}-*o*-arom), 138.23 (br, Mes^{B}-*ipso*-arom), 138.33 (Mes^{B}-*p*-arom), 138.40 (d, $^{2}J_{CP}=15.0$ Hz, Phen-9-CH), 138.73 (Mes^{B}-*o*-arom), 140.72 (d, $^{4}J_{CP}=3.0$ Hz, Mes^{P}-*p*-arom), 141.53 (Phen-4-CH), 141.68 ppm (br, Mes^{P}-*o*-arom); ^{11}B NMR (95 MHz, C_6D_6, RT) $\delta=65.9$ ppm ($\Delta\nu_{1/2}=1130$ Hz); ^{31}P NMR (121 MHz, C_6D_6, RT): $\delta=19.7$ ppm (d, $^{3}J_{PH}=19.9$ Hz, $^{1}J_{PSe}=779$ Hz); ^{77}Se NMR (57 MHz, C_6D_6, RT): $\delta=-16.6$ ppm (br d, $^{1}J_{SeP}=779$ Hz); HRMS (FAB) *m/z*: 519.0990 $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{29}{}^{11}BPS^{80}Se$ (519.0986): C 65.01, H 5.46; found: C 65.15, H, 5.45.

X-ray crystallographic analysis of 9S, 9Se, 10SS, 10SeSe, and 10SSe

Single crystals of **9S, 9Se, 10SS, 10SeSe**, and **10SSe** were grown by slow recrystallization of their solution (THF/toluene at −40 °C for **9S** and **9SS**, toluene/hexane at room temperature for **9Se** and **10SeSe**, toluene at room temperature for **10′SeSe** and **10SSe**) in a glovebox filled with argon. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71070$ Å). The structure was solved by direct method (SHELXS-97)[15] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[15] All hydrogen atoms were placed using AFIX instructions, whereas all the other atoms were refined anisotropically. Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as CCDC-973010 (**9S**), CCDC-973011 (**9Se**), CCDC-973014 (**10SS**), CCDC-973013 (**10SeSe**), CCDC-973012 (**10′SeSe**), and CCDC-973015 (**10SSe**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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