An Isolable Phosphaborene Stabilized by an Intramolecular Lewis Base

Jiancheng Li,[a] Yanbo Mei,[a] and Liu Leo Liu*[a]

[a] Dr. J. Li, Dr. Y. Mei, Prof. Dr. L. L. Liu
Department of Chemistry and Shenzhen Grubbs Institute and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology
Shenzhen 518055 (China)
E-mail: liuleoliu@sustech.edu.cn
Homepage: liuleoliu.com

Abstract: Phosphaborenes are P/B analogs of alkynes. Herein, we describe the isolation of a phosphaborene stabilized by an intramolecular Lewis base. This species is achieved via the installation of the phosphaborene with a sterically encumbering phosphino substituent. Although this species features an aromatic P_2B three-membered ring, the ring strain allows the hemi-labile behavior of the P-B donor-acceptor bond, thereby exhibiting frustrated Lewis pair reactivity. Our finding paves the way for further exploration of the reactivity patterns of monomeric phosphaborenes.

Introduction

Iminoboranes ($R^1B^{\delta-}{\equiv}N^{\delta+}R^2$), pioneered by Paetzold in 1979,[1] have been extensively explored.[2] These species feature a polarized B≡N triple bond, as demonstrated by short B-N bond lengths and the linear geometry at both B and N atoms.[2] However, much less has been known about their phosphorus congeners, namely phosphaborenes $R^1B{=}PR^2$. These species are P/B analogs of alkynes. Early attempts to prepare such compounds date back to the late 1980s, but remain unsuccessful as dimerization or oligomerization to the favored diphosphadiboretanes with a P_2B_2 four-membered ring or oligomers, respectively, often occurs.[3] Indeed, the theoretical studies showed a bent geometry of HP=BH with the localization of the lone pair at P and a vacant p orbital at B. This resulted in a highly exothermic dimerization of HP=BH by over 54 kcal/mol.[3g, 4]

It was until 1990 that Nöth reported on the first isolation of a monomeric phosphaborene complex **A** (Figure 1).[5] The key to isolating **A** was attributed to the coordination of P to $Cr(CO)_5$, which quenches P-basicity and provides kinetic protection. Following this, **B** was formed at low temperature via the coordination of P to $AlBr_3$.[3a] Power employed a reverse stabilization strategy involving the coordination of an external Lewis base to B, which compensates for the electron deficiency and provides kinetic protection as well, leading to the isolation of **C**.[6] In a similar fashion, Cowley described **F** and **G**.[7] More recently, Cowley demonstrated the solution-phase trapping of a transient phosphaborene[8] with Lewis bases at 80 °C, generating **D** and **E**.[8b] Andrada isolated **H** bearing a trimethylsilyl (TMS) functionality at the P-terminal, which enables facile P-center metathesis reactions to give diverse phosphaborene derivatives.[9] Gilliard and Wilson disclosed the synthesis of BP-doped phenanthryne **I** with a characteristic B=P double bond ligated by a carbene donor.[10] Nonetheless, the isolation of a phosphaborene in its free state has eluded the synthetic skills of scientists.

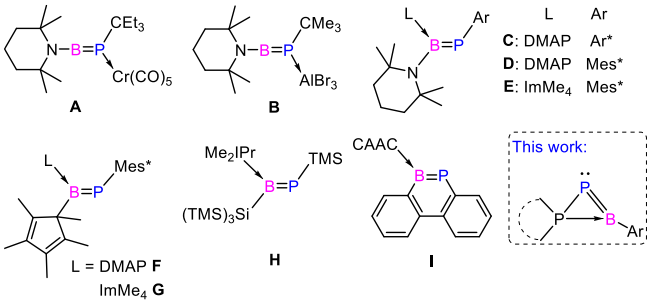

Figure 1. Examples of monomeric phosphaborenes stabilized by Lewis acids (**A**, **B**) or Lewis bases (**C**-**H**). A BP-doped phenanthryne **I**. DMAP = 4-dimethylaminopyridine. Ar* = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)C$_6$H$_3$, Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$; ImMe$_4$ = tetramethylimidazol-2-ylidene; Me$_2$IPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; CAAC = cyclic(alkyl)(amino) carbene.

On the other hand, the development of low-valent main group compounds featuring hemi-labile ancillary donors has allowed the exploration of unique chemical behaviors.[11] Noting that the aforesaid monomeric phosphaborene systems **A**-**I** are all stabilized by an external Lewis acid or base (Figure 1), we thus envisaged the likelihood of stabilizing a phosphaborene with an intramolecular hemi-labile Lewis base. The versatile coordination capabilities afforded by the hemi-labile donor may enable the phosphaborene to participate in frustrated Lewis pair (FLP) chemistry.[12] In this paper, we document the first example of a phosphaborene of this sort as well as its unusual reactivity with 4-dimethylaminopyridine (DMAP).

Results and Discussion

Strategies including thermo and Lewis base promoted elimination of Me_3SiCl have been commonly used to generate iminoboranes and other singly or multiply bonded main group systems.[2a, 2b, 9] We speculated the formation of phosphaborenes with an intramolecular donor-acceptor stabilization if the P atom of phosphaborenes is substituted with a Lewis basic phosphino group. To this end, we chose compound **2** (^{31}P NMR: 151.7 and -147.0 ppm) bearing a diazaphospholidine substituent as the precursor (Figure 2). This compound was prepared via a salt metathesis reaction of the corresponding chlorodiazaphospholidine **1**[13] and potassium bis(trimethylsilyl)phosphide in 87 % yield. As double elimilation of TMSCl was supposed to produce the targeted B=P double system, we initially reacted **2** with equal equivalent of terphenyl dichloroborane $TerBCl_2$ (Ter = 2,6-(2,4,6-$Me_3C_6H_2$)C_6H_3).[14] However, monitoring the reaction mixture via ^{31}P NMR

spectroscopy showed the undesired cleavage of the P-P bond in **2**, which gave **1** along with other unidentified products. Alternatively, compound **2** was first desilylated by potassium *tert*-butoxide in toluene, which then reacted with $TerBCl_2$ in toluene. Gratifyingly, phosphinoborane **3** (^{31}P NMR: 138.7 and -3.4 ppm) was isolated as colorless solids in 75 % yield after workup.

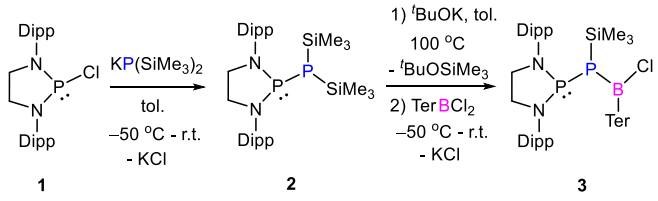

Figure 2. Two-step synthesis of phosphinoborane **3**. Dipp = 2,6-$^{i}Pr_2C_6H_3$; Ter = 2,6-(2,4,6-$Me_3C_6H_2$)C_6H_3.

Compounds **2** and **3** were further characterized by X-ray diffraction (Figures 3a and 3b). The sum of angles at P(1) (310°) and P(2) (325°) of **2** clearly manifests their triangular pyramid geometry. The bond length of P(1)-P(2) appears to be 2.242(1) Å, which is comparable to that for the P-P single bond in semblable structure of $[CH_2N(Dipp)]_2P\text{-}PH_2$ (2.277(1) Å).[15] In the asymmetric unit of the crystal lattice of **3**, two independent molecules are included as a monomer. The P(2) atom possesses planar geometry with the sum of angles around P(2) of 360° and 354°. This is in line with the degree of double-bond character between P(2) and B(1) featured by their relatively shorter distance (1.845(2) and 1.854(2) Å) compared to that of the P-B single bond (1.958(3) Å) in Ar*P(H)–B(Br)tmp (tmp = 2,2,6,6-tetramethylpiperidinyl).[6] The P(1)-P(2) bond length is 2.257(1) Å, while the P(1)-B(1) separation is longer than 3.45 Å, indicative of no interaction between these geminal Lewis base and acid centers.

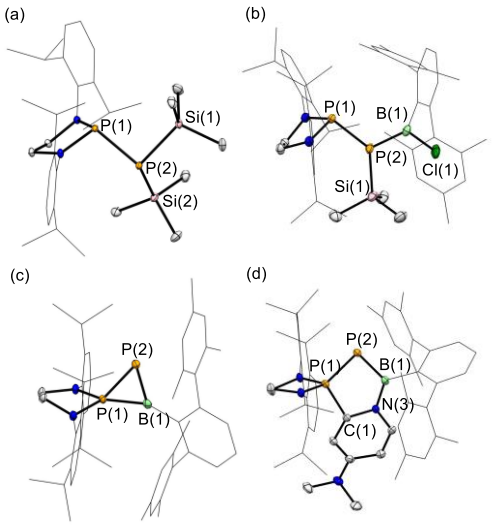

Figure 3. Solid-state structures of **2** (a), **3** (b) **4** (c) and **5** (d). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

With **3** in hand, thermo- or photo-induced elimination of TMSCl by heating or radiating a C_6D_6 solution of **3** was attempted; however neither were successful as indicated by no apparent change shown in the ^{31}P NMR spectrum. Power, Cowley and co-workers have shown the generation of phosphaborenes promoted by Lewis bases.[6-7] By analogy, we treated **3** with equal equivalent of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Me_2IPr_2) at room temperature. An immediate color change from colorless to light yellow was observed. The formation of a new species **4** (Figure 4) was evidenced from the ^{31}P NMR resonances at the much lower field of δ = 167.8 (d, $^{1}J_{PP}$ = 345.2 Hz) and 43.3 ppm (d, $^{1}J_{PP}$ = 345.2 Hz) ppm relative to those of **3** (vide supra). The ^{11}B NMR spectrum of **4** reveals a broad singlet at 55.8 ppm. In the ^{1}H NMR spectrum of crude mixture, in addition to **3**, it was interesting to find a complete set of resonances ascribing to the free Me_2IPr_2 and a single peak at δ = 0.15 attributed to the free TMSCl. This suggested the catalytic nature of Me_2IPr_2 during the transformation, which is in contrast to Cowley's report where the carbene donor coordinated to the boron center.[7] Indeed, with the aid of catalytic amount of Me_2IPr_2 (5 mol%), **4** was isolated as colorless solids in the yield of 63% (Figure 4).

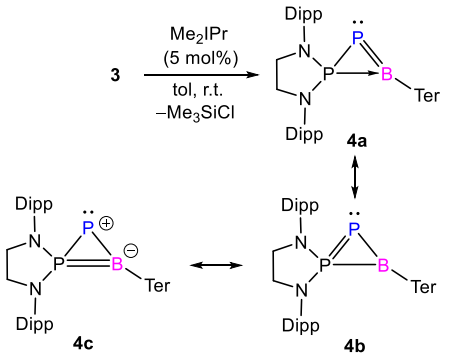

Figure 4. Synthesis of **4** via a Me_2IPr-catalyzed process. Three resonance structures of **4**.

Single crystals of **4** suitable for X-ray diffraction were obtained from a mixed *n*-hexane/toluene solution of **4** at -35 °C after two days. Structure analysis revealed a central P_2B three-membered ring system formed from the apparent coordination of P(1) to B(1) in a transient phosphaborene (Figure 3c). The P_2B triangle is almost equicrural with the nearly identical P(1)-B(1) (1.860(2) Å) and P(2)-B(1) (1.844(2) Å) bond lengths as well as nearly isometric P(2)-P(1)-B(1) (55.5(1)°) and P(1)-P(2)-B(1) (56.3(1)°) bond angles. It is worth noting that these P-B bond lengths lie between typical P-B single bond length (1.96 Å) and P=B double bond length (1.80 Å).[16] The P(1)-P(2) bond length (2.077(1) Å) is shorter than that found in **2**. The di-coordinate P(2) atom adopts a V geometry, while the P(1) is tetrahedrally configurated. The geometry of B(1) is almost planar, however around with three angles (68.2°, 138.3° and 153.4°) that are largely deviated from ideal 120°. Of note, **4** represents an extremely rare example of P_2B ring systems.[17]

Natural bond orbital (NBO) calculations at the M06-2X/def2-SVP level of theory show that the Wiberg bond indexes (WBIs) of P(1)-P(2), P(1)-B(1), and P(2)-B(1) bonds are 1.12, 1.11, 1.59, respectively. Intrinsic bond orbital (IBO) calculations,[18] which give an exact representation of any Kohn−Sham DFT wave function, illustrate the presence of a delocalized 3c-2e π bond over the P_2B ring (Figure 5a), three σ bonds in the ring (Figures 5b-5d), and a lone pair of electrons at P(2) (Figure 5d). The nucleus independent chemical shift (NICS) values[19] NICS(0) (-24.9 ppm) and NICS(1) (-15.1 ppm) unambiguously support the aromatic nature of the P_2B ring.

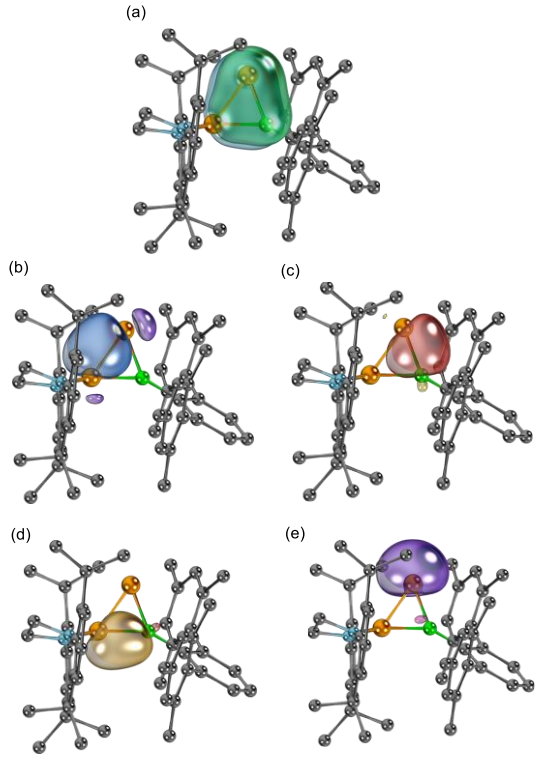

Figure 5. Depiction of selected IBOs (80% of the orbital electron's density) for **4**.

We reasoned that the ring strain of **4** may promote the hemi-labile behavior of the phosphino substituent.[20] Indeed, upon adding DMAP to **4** at room temperature, a new species **5** (^{31}P NMR: 118.4 and -187.8 ppm; ^{11}B NMR: 57.0 ppm) was formed in 4 h (Figure 6). To our surprise, an X-ray diffraction experiment of a single crystal showed **5** to be a P_2BCN non-planar five-membered ring system (Figure 3d) arising from a FLP-type addition of **4** with one aromatic C-N bond in DMAP.[21]

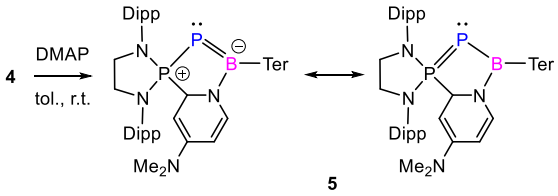

Figure 6. Reactivity of **4** with DMAP leading to **5**.

Density functional theory (DFT) investigations provide the mechanistic insights for the formation of **5** (Figure 7), involving three steps. At the outset, the hemi-labile nature of the P(1)-B(1) donor-acceptor bond gives rise to facile generation of a free phosphaborene **IN1** (4.9 kcal/mol) via **TS1** (7.3 kcal/mol). Subsequently, DMAP combines B(1) to yield **IN2** (-5.1 kcal/mol). Final attack of C(1) by P(1) produces **5** (-16.1 kcal/mol) in an exergonic manner.

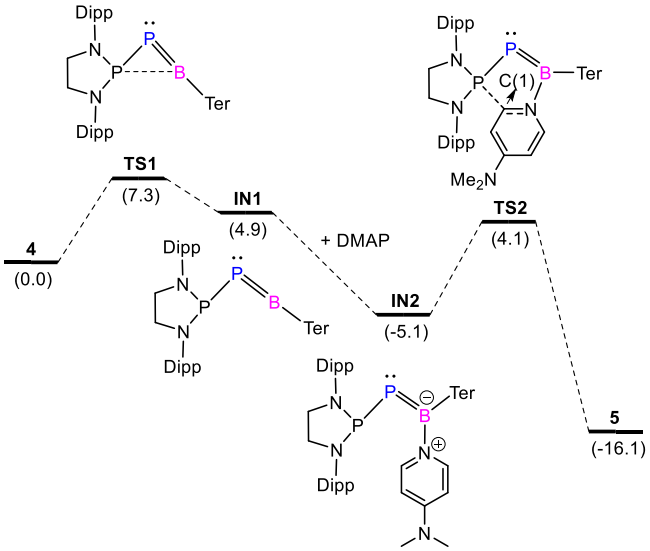

Figure 7. Free energy profile for the formation of **5**. Energies are given in kcal/mol.

Conclusion

Through the installation of a phosphaborene with a bulky phosphino substituent, we have presented the first example of an isolable phosphaborene stabilized by an intramolecular Lewis base. The three-membered ring strain of **4** facilitates the hemi-labile behavior of the P-B donor-acceptor bond, thus leading to the FLP-type reactivity toward DMAP. Importantly, based on computations, a free phosphaborene **IN1** is only slightly higher in energy than **4**. With right substituents, the synthsis of free phosphaborenes is possible. We are challenging the isolation of such free species.

Experimental Section

Preparation of 2. The mixture of **1** (2 mmol, 890 mg) and $KP(SiMe_3)_2$ (2 mmol, 433 mg) was added pre-cooled (-50 °C) toluene (20 mL) at -50 °C. The reaction solution was then allowed to warm to room temperature and stirred for 4 hours. After filtration through a pad of celite, the volatiles were removed through evaporation under vacuum. The residues were washed with cold *n*-hexane (3 mL) and dried in vacuum to give a colorless solid **2** (1020 mg, 87%). Single crystals (colorless) suitable for X-ray analysis were obtained from a saturated hexane solution at -35 °C for 2 days. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 0.32 (d, $^3J_{PH}$ = 4.0 Hz, 9 H, Si*Me*$_3$), 1.36 (br, 24 H, CH*Me*$_2$), 3.15-3.21 (m, 2 H, NC*H*$_2$C*H*$_2$N), 3.63-3.71 (m, 6 H, CH*Me*$_2$ and NC*H*$_2$C*H*$_2$N), 7.13-7.17 (m, 6 H, Ar-H) ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 3.9 (d, $^2J_{PC}$ = 9.2 Hz, Si*Me*$_3$), 25.8 (br, CH*Me*$_2$), 29.0 (C*H*Me$_2$), 56.3 (NCH$_2$CH$_2$N), 56.4 (NCH$_2$*C*H$_2$N), 124.8 (Ar), 127.3 (Ar), 139.6 (Ar), 139.7 (Ar), 148.9 (Ar). ^{31}P{^{1}H} NMR (162 MHz, 298 K, C_6D_6, ppm): δ = -147.0 (d, $^1J_{PP}$ = 518.8 Hz, *P*(SiMe$_3$)$_2$), 151.7 (d, $^1J_{PP}$ = 518.8 Hz, *P*P(SiMe$_3$)$_2$). ^{29}Si NMR (119.2 MHz, 298 K, C_6D_6, ppm): δ = 0.8 (dd, $^1J_{PSi}$ = 36.0 Hz, $^2J_{PSi}$ = 17.4 Hz).

Preparation of 3. The mixture of **2** (0.2 mmol, 117.4 mg) and potassium *t*-butoxide KO^{t}Bu (0.2 mmol, 22.5 mg) was added toluene (5 mL) at room temperature. The resulting solution was heated to 100 °C and stirred for 4 hours, giving a white suspension. The in-situ ^{31}P{^{1}H} NMR spectrum suggested the complete consumption of **2** and the formation of potassium phosphide. This suspension was cooled to -40 °C followed by addition to

the cold solution of terphenyl borondichloride TerBCl$_2$ (0.2 mmol, 79 mg). The reaction solution was then allowed to warm to room temperature and stirred for overnight. After filtration to remove KCl, the volatiles were removed through evaporation under vacuum. The residues were washed with *n*-hexane (3 mL) and dried in vacuum to give a colorless solid **3** (131 mg, 75%). Single crystals (colorless) suitable for X-ray analysis were obtained from a hexane saturated solution at room temperature within one day. ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 0.42 (d, $^3J_{PH}$ = 5.1 Hz, 9 H, Si*Me*$_3$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6 H,CH*Me*$_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 6 H,CH*Me*$_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6 H,CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 6 H,CH*Me*$_2$), 1.65 (br, 6 H, Mes-*o*-*Me*), 2.25 (br, 6 H, Mes-*o*-*Me*), 2.27 (s, 6 H, Mes-*p*-*Me*), 2.96-3.00 (m, 2 H, (NC*H*$_2$CH$_2$N)), 3.36 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H,C*H*Me$_2$), 3.40-3.42 (m, 2 H, (NCH$_2$C*H*$_2$N)), 3.49 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H,C*H*Me$_2$), 6.25 (br, 2 H, Mes-*H*), 6.78 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Ter-2,5-H), 6.82 (br, 2 H, Mes-*H*), 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, Ter-4-H), 7.13-7.14 (m, 2 H, Dipp-*H*), 7.19-7.20 (m, 2 H, Dipp-*H*), 7.24-7.27 (m, 2 H, Dipp-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 4.26 (d, $^2J_{PC}$ = 9.6 Hz, Si*Me*$_3$), 21.3, 21.8, 23.7, 24.9, 26.2, 28.9, 29.0, 29.1, 56.2 (NCH$_2$CH$_2$N), 56.3 (NCH$_2$CH$_2$N), 125.0, 125.4, 135.7, 135.9, 136.9, 139.2, 139.3, 140.3, 144.1, 144.2, 148.6, 150.1. ^{31}P{^{1}H} NMR (162 MHz, 298 K, C_6D_6, ppm): δ = -3.4 (d, $^1J_{PP}$ = 639.9 Hz, *P*(SiMe$_3$)), 138.7 (d, $^1J_{PP}$ = 639.9 Hz, *P*P(SiMe$_3$)). ^{29}Si NMR (119.2 MHz, 298 K, C_6D_6, ppm): δ = 0.2 (dd, $^1J_{PSi}$ = 34.3 Hz, $^2J_{PSi}$ = 6.4 Hz).

Preparation of 4. At room temperature, solid Me$_2$IPr$_2$ (5 mol%, 1.5 mg) was added to a toluene solution of **3** (0.15 mmol, 131 mg) (5 mL) and the resulting solution was stirred for overnight. Then the volatiles were removed through evaporation under vacuum. The residues were washed with cold *n*-hexane (3 mL) and dried in vacuum to give a colorless solid **4** (72 mg, 63%). Single crystals (colorless) suitable for X-ray analysis were obtained from a hexane saturated solution at room temperature for three days. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.09 (d, $^3J_{HH}$ = 7.0 Hz, 6 H,CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 6 H,CH*Me*$_2$), 1.16 (m, 12 H,CH*Me*$_2$), 1.98 (s, 12 H, Mes-*o*-*Me*), 2.23 (s, 6 H, Mes-*p*-*Me*), 3.21-3.22 (m, 2 H, (NC*H*$_2$CH$_2$N)), 3.30 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H,C*H*Me$_2$), 3.43 (br, 2 H, (NCH$_2$C*H*$_2$N)), 3.74 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H,C*H*Me$_2$), 6.58 (s, 4 H, Mes-*H*), 6.81 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, Ter-2,5-H), 6.94 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Dipp-2,5-H), 7.02 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Dipp-2,5-H), 7.05 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, Ter-4-H), 7.05 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Dipp-4-H). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K, ppm): δ = 21.5, 21.8, 24.0, 24.7, 25.6, 26.8, 28.7, 29.4, 51.6 (NCH$_2$CH$_2$N), 51.6 (NCH$_2$CH$_2$N), 124.5, 124.6, 128.8, 129.4, 135.2, 135.8, 136.5, 136.5, 141.4, 146.0, 146.1, 149.3, 150.0. ^{31}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = 43.2 (d, $^1J_{PP}$ = 345.2 Hz, P*P*=*B*), 167.7 (d, $^1J_{PP}$ = 245.2 Hz, *P*P=B). ^{11}B NMR (192.6 MHz, 298 K, C_6D_6, ppm): δ = 55.8 (br, PP=*B*).

Preparation of 5. At room temperature, to the solid mixture of **4** (0.033mmol, 25.5 mg) and 4-dimethylaminopyridine (0.033 mmol, 4.1 mg) toluene (0.5 mL) was added. The resulting solution was stirred for 4 hours. Then the volatiles were removed through evaporation under vacuum. The residues were washed with *n*-hexane and dried in vacuum to give a colorless solid **5** (27 mg, 91%). Single crystals (colorless) suitable for X-ray analysis were obtained from a hexane/toluene saturated solution at -35 °C for three days. ^{1}H NMR (600 MHz, C_6D_6, 298 K, ppm): δ = 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3 H,CH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6 H,CH*Me*$_2$), 1.21 (apperent triplet, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3 H,CH*Me*$_2$), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 3 H,CH*Me*$_2$), 1.59 (d, $^3J_{HH}$ = 6.8 Hz, 3 H,CH*Me*$_2$), 2.05 (s, 3 H, Mes-*Me*), 2.08 (s, 3 H, Mes-*Me*), 2.17 (s, 3 H, Mes-*Me*), 2.18 (s, 3 H, Mes-*Me*), 2.26 (s, 3 H, Mes-*Me*), 2.28 (s, 3 H, Mes-*Me*), 2.46 (s, 6 H, N*Me*$_2$), 2.91-2.99 (m, 2 H, (NC*H*$_2$CH$_2$N)), 3.33-3.36 (m, 2 H, (NCH$_2$C*H*$_2$N)), 3.57-3.61 (m, 1 H,C*H*Me$_2$), 3.66-3.70 (m, 1 H,C*H*Me$_2$), 3.71-3.76 (m, 1 H,C*H*Me$_2$), 4.02 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H,C*H*Me$_2$), 4.22 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, C$_5$*H*$_4$N), 4.55 (s, 1 H, C$_5$*H*$_4$N), 4.72 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 2.0 Hz, 1 H, C$_5$*H*$_4$N), 6.26 (m, 1 H, C$_5$*H*$_4$N), 6.27 (s, 1 H, Mes-*H*), 6.58 (s, 2 H, Mes-*H*), 6.70 (s, 1 H, Mes-*H*), 6.94 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, Ter-2,5-H), 7.04 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar-*H*), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ar-*H*), 7.14-7.18 (m, 2 H, Ar-H), 7.23-7.26 (m, 2 H, Ar-H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K, ppm): δ = 21.4, 21.6, 21.6, 22.0, 22.3, 22.5, 22.9, 23.0, 23.1, 23.8, 23.9, 24.6, 25.2, 26.6, 26.7, 27.6, 27.6, 28.3, 29.5, 29.5, 40.1, 50.7, 50.8, 52.0, 66.0, 66.1, 66.7, 66.8, 81.9, 82.0, 95.4, 106.9, 124.0. 124.6, 124.9, 134.5, 134.7, 135.0, 135.0, 135.1, 135.1, 136.6, 136.8, 137.4, 137.5, 139.9, 140.8, 143.9, 145.8, 145.9, 148.8, 149.8, 150.0, 150.9. ^{1}P{^{1}H} NMR (243 MHz, 298 K, C_6D_6, ppm): δ = -187.8 (d, $^1J_{PP}$ = 512.3 Hz, P*P*=*B*), 118.4 (d, $^1J_{PP}$ = 512.3 Hz, *P*P=B). ^{11}B NMR (192.6 MHz, 298 K, C6D6, ppm): δ = 57.0 (br, PP=*B*).

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.
Deposition Numbers 2177462-2177465 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Keywords: phosphaborene • frustrated Lewis pair • dearomative reaction • multiple bond • main group element

Corresponding Author Biography:

Liu Leo Liu received his B.Sc. degree in chemistry (2011) at Xiamen University and Ph.D. degree in organic chemistry (2016) from a joint program under the supervision of Prof. Yufen Zhao at Xiamen University and Prof. Guy Bertrand at the University of California, San Diego. He gained postdoctoral training in Prof. Douglas W. Stephan's group at the University of Toronto and in a joint group of Profs. F. Dean Toste, Kenneth N. Raymond and Robert G. Bergman in Lawrence Berkeley National Laboratory

and the University of California, Berkeley. He had been an Assistant Professor at Southern University of Science and Technology (SUSTech) since September 2020 and was promoted to Associate Professor in June 2022. His group is developing the chemistry of multi-active ambiphilic centers and extremely electron-releasing centers based on main group elements.

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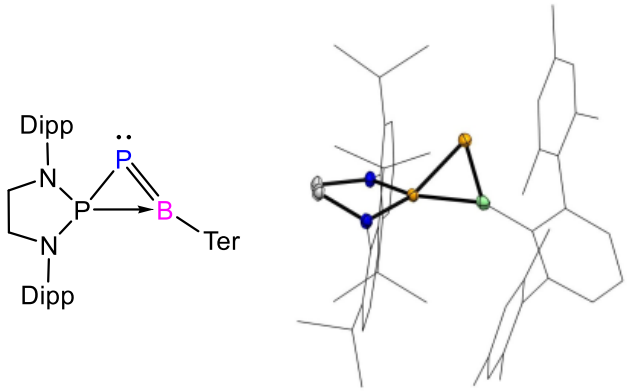

The isolation of a phosphaborene stabilized by an intramolecular donor has been described. This species features a hemi-labile P-B donor-acceptor bond and exhibits frustrated Lewis pair reactivity.

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