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Synthesis of an oxygen-linked germinal frustrated Lewis pair and its application in small molecule activation†

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Reaction of $\text{Mes}_2\text{P}(\text{O})\text{Li}$ with $(\text{C}_6\text{F}_5)_2\text{BCl}$ gave access to an oxygen-linked germinal intramolecular frustrated Lewis pair $\text{Mes}_2\text{P}(\text{O})\text{B}(\text{C}_6\text{F}_5)_2$ (**1**). Compound **1** is stable at room temperature and only decomposes when heated to 90 °C. NMR analysis and theoretical analysis revealed the frustrated nature between the boron and phosphorus centers. Compound **1** shows typical frustrated Lewis pair reactivity when treated with dihydrogen, carbon dioxide, alkyne and alkene. The reaction of **1** with isoprene resulted in selective formation of 3,4-phosphoryl/boryl addition product **8**.

Introduction

Ever since the groundbreaking discovery by Stephan *et al.* that an unquenched phosphine/borane pair can activate dihydrogen under ambient conditions, the concept of a “frustrated Lewis pair” (FLP) has been successfully applied in small-molecule activation, organic synthesis and catalysis.¹ Mechanism investigations revealed that one of the most prominent features of FLP mediated reactions is that substrates are usually synergistically activated by both the Lewis acid and base centers.² To enhance such a synergistic effect, the most often employed strategy is to pre-organize Lewis acid and base functionalities through a linker.³ Among a variety of intramolecular FLPs, germinal FLPs in which donor and acceptor sites are separated by one atom have attracted substantial attention because the proximity of their Lewis acid and base centers can facilitate their synergistic reactivities against small molecules. Furthermore, despite such proximity, intramolecular interaction between Lewis acid and base centers in germinal FLPs is largely excluded because of the high constrain of formation of a three-membered ring. Attempts to introduce frequently applied $-\text{B}(\text{C}_6\text{F}_5)_2$ and $-\text{PtBu}_2$ functionalities to C1-linked FLPs were thwarted by facile intramolecular nucleophilic substitution of fluoride on the C_6F_5 ring by the phosphine moiety (**I**).⁴ To circumvent this problem, Slootweg, Lammertsma and coworkers employed $-\text{BPh}_2$ instead of $-\text{B}(\text{C}_6\text{F}_5)_2$ functionality and synthesized a CH_2 -bridged $t\text{Bu}_2\text{PCH}_2\text{BPh}_2$ (**II**).⁵ It was

discovered that this germinal FLP can activate H_2 , CO_2 and other unsaturated substrates despite of the mild Lewis acidity of the boron center. The groups of Wagner⁶ and Erker⁷ also reported a number of methylene-bridged germinal FLPs employing $-\text{BFxyl}_2$ ($\text{Fxyl} = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$) as the Lewis acid center (**III**) or less nucleophilic $-\text{P}(\text{C}_6\text{F}_5)_2$ as the Lewis base center (**IV**). Besides of methylene linkers, alkylidene moiety was also employed as a linker for germinal FLPs. Uhl and coworkers prepared a series of alkylidene-bridged Al/P based FLPs (**V**) which can not only coordinate to a variety of substrates,⁸ but also function as phase transfer catalyst⁹ or B–N dehydrogenation catalyst.¹⁰ Additionally, a few alkylidene-bridged FLPs based on Ga/P,¹¹ B/P¹² and Zr/P¹³ functionalities were reported by Uhl and Erker groups. In spite of the progress in the study of germinal FLPs, the linker is almost exclusively based on carbon. Only very recently, Streubel and coworkers synthesized an anionic oxygen-linked germinal FLP (**VI**) and investigated its reactivity against CO_2 .¹⁴ Since the nucleophilicity of phosphinite is markedly lower than alkyl- or alkenyl-substituted phosphine, we reasoned that an oxygen-linked germinal FLP containing $-\text{B}(\text{C}_6\text{F}_5)_2$ and $-\text{PMes}_2$ functionalities (**1**) would be less susceptible to intramolecular nucleophilic substitution, which could render this FLP stable enough for isolation. Herein, we report the synthesis of oxygen-linked germinal FLP **1** and its reactivity against small molecules (Fig. 1).

Results and discussion

Synthesis of **1** was achieved by treatment of $\text{Mes}_2\text{P}(\text{O})\text{H}$ with $n\text{BuLi}$ and subsequently $(\text{C}_6\text{F}_5)_2\text{BCl}$ in hexane and it can be isolated as a pale yellow oil with 83% yield after workup (Scheme 1). Compound **1** was characterized by multinuclear NMR analysis. The ³¹P NMR spectrum of **1** showed a resonance at δ 126.4 ppm, similar to that observed for phosphinite $\text{Ph}_2\text{P}(\text{OMe})$ (117 ppm).¹⁵ In the ¹¹B NMR spectrum of **1** a broad

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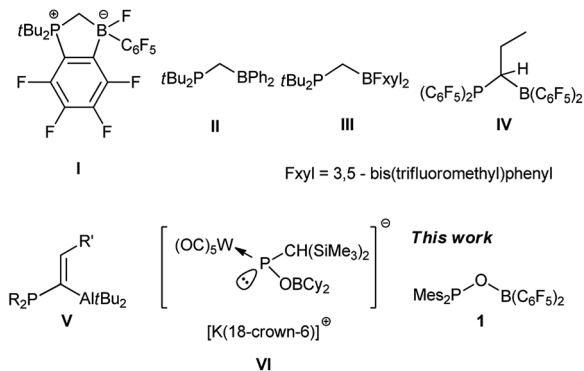
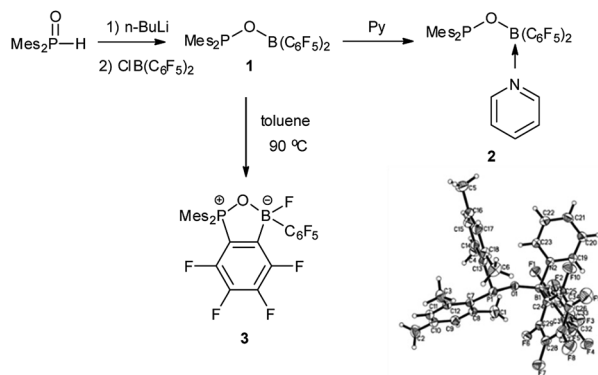
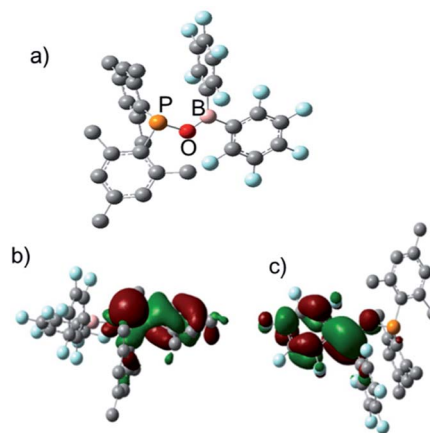


Fig. 1 Geminal intramolecular FLPs.

Scheme 1 Synthesis and thermolysis of **1** and molecular structure of **2** (thermal ellipsoids are shown with 30% probability).

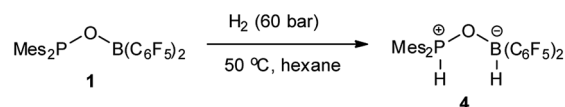
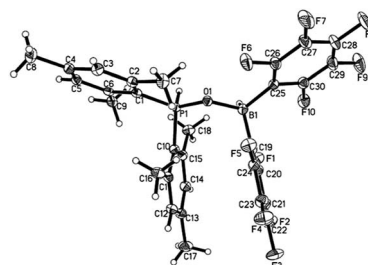
singlet was observed at δ 42.4 ppm, indicating the existence of a tri-coordinated boron center. This was corroborated by the appearance of signals at δ -131.4, -148.8, -161.2 ppm in the ^{19}F NMR spectrum of **1**. The identity of **1** was further confirmed by derivatization. Addition of equimolar of pyridine to **1** in hexane resulted in quantitative formation of adduct **2**, which was characterized by X-ray crystal structure analysis. Compound **1** is stable at room temperature both in solution and neat form. Upon heating to 90 °C in a toluene solution, **1** undergoes intramolecular nucleophilic substitution to afford **3** (Scheme 1), which was isolated in 36% yield and fully characterized by NMR spectroscopy and X-ray analysis.

To understand the electronic structure of **1**, DFT (M06-2X) calculation¹⁶ was carried out. In the calculated structure, the P–O–B bond angle is 114° and the distance between the P and B atoms is 2.57 Å (Fig. 2a), which is shorter than the observed intramolecular P...B distance in $t\text{Bu}_2\text{PCH}_2\text{B}(\text{Fxy1})_2$ (2.90 Å).⁶ Population analysis suggested that the interaction between the P and B atoms is very weak and the covalent P–B Wiberg bond order is only 0.02. The HOMO of **1** mainly corresponds to the lone pair on phosphorus, with some contribution from π orbital of the mesityl substituent (Fig. 2b). The LUMO is largely distributed over the boron center as well as one C_6F_5 ring and the oxygen linker, indicative of π electron donation from the oxygen atom to the empty p orbital of the boron center (Fig. 2c).

Fig. 2 (a) calculated structure of **1**; (b) HOMO of **1**; (c) LUMO of **1**.

While **1** does not react with H_2 under 6 bar at room temperature, it reacts with H_2 under harsher conditions (60 bar, 50 °C) to afford compound **4** with 58% yield after workup (Scheme 2). Compound **4** can be also independently synthesized from $\text{Mes}_2\text{P}(\text{O})\text{H}$ and $\text{HB}(\text{C}_6\text{F}_5)_2$. Existence of a P–H moiety was confirmed by the appearance of a doublet at δ 31.5 ppm ($^1J_{\text{P-H}} = 514$ Hz) in the ^{31}P NMR spectrum, with a corresponding doublet at δ 8.02 ppm ($^1J_{\text{P-H}} = 514$ Hz) observed in the ^1H NMR spectrum. However, both the ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra displayed a broad signal at -4.79 ppm, excluding study of the coupling constant with the adjacent H atom. The ^1H NMR spectrum displayed a broad singlet at δ 4.59 ppm with integration of 1, which was assigned to the BH moiety. The identity of **4** was further validated by X-ray crystal structure analysis (Fig. 3).

Treatment of **1** with CO_2 (1.8 bar) at room temperature in hexane resulted in formation of a CO_2 adduct **5**, in an analogous way with other geminal FLPs (Scheme 3).^{5a,6,8a,11,13b,14} **5** was characterized by both NMR spectroscopy and X-ray analysis (Fig. 4). **5** is stable infinitely as solid. But unlike geminal B/P FLPs **II**^{5a} and **III**,⁶ the solution of **5** in C_6D_6 slowly released CO_2 under N_2 atmosphere at room temperature. In a sealed

Scheme 2 Reaction of **1** with H_2 .Fig. 3 Molecular structure of **4** (thermal ellipsoids are shown with 30% probability).

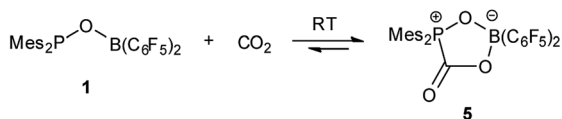
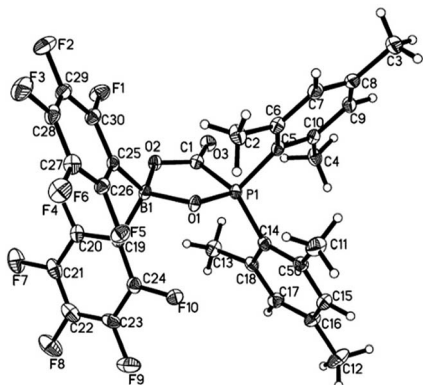
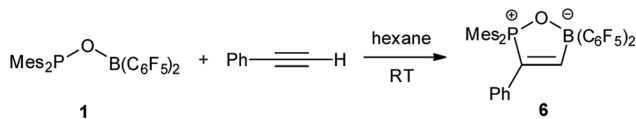
Scheme 3 Reaction of 1 with CO₂.

Fig. 4 Molecular structure of 5 (thermal ellipsoids are shown with 30% probability).

NMR tube at room temperature, equilibrium was reached after 24 hours and about 25% of 5 was converted to 1.

Reaction of 1 with phenylacetylene in hexane led to addition of both phosphoryl and boryl moieties to the C≡C bond to give 6 in 73% yield (Scheme 4). This is in line with the discovery by Stephan¹⁷ and Erker⁷ that FLPs with phosphine moiety of low basicity tend to afford addition products. In the solid structure of 6 (Fig. 5), the distances of B–O and P–O are similar to those observed in *t*Bu₂P(μ-O)(μ-C₆H₄)B(C₆F₅)₂ (P–O 1.546, B–O 1.550 Å) reported by Wagner.⁶



Scheme 4 Reaction of 1 with phenylacetylene.

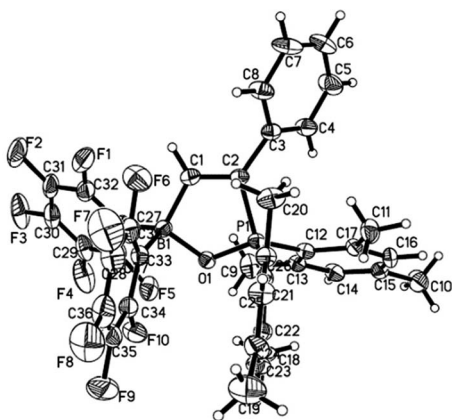
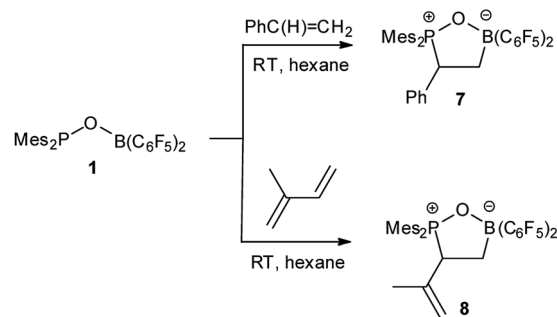


Fig. 5 Molecular structure of 6 (thermal ellipsoids are shown with 30% probability).



Scheme 5 Reaction of 1 with styrene and isoprene.

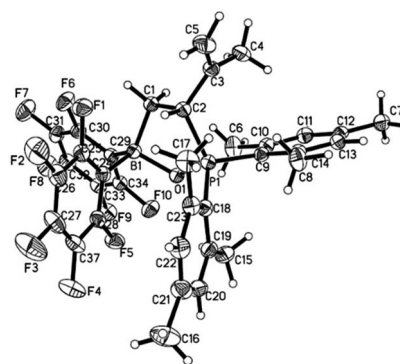


Fig. 6 Molecular structure of 8 (thermal ellipsoids are shown with 30% probability).

Compound 1 reacted with equimolar of styrene in hexane at room temperature to yield a white precipitate, which was identified as 1,2-boryl/phosphoryl addition product 7 *via* NMR spectroscopy and X-ray analysis.¹⁸ When 1 was treated with isoprene in hexane, 3,4-phosphoryl/boryl addition product 8 was formed as the only regioisomer, which can be isolated as a white solid in 79% yield (Scheme 5). 8 was characterized by both NMR spectroscopy and X-ray analysis (Fig. 6). This observed regioselectivity is in contrast to previous reports by Stephan¹⁹ and Lerner²⁰ that activation of dienes with intermolecular FLP *t*Bu₃P/B(C₆F₅)₃ or intramolecular FLP di-*t*-butylphosphoradibenzofulvene affords predominately 1,4-addition products. It is likely that in the case of intramolecular FLP 1, the favored formation of a five-member ring dictates the observed 3,4-selectivity.

Conclusions

By employing an oxygen atom as the linker, a germinal FLP containing both electrophilic B(C₆F₅)₂ and nucleophilic PMe₂ moieties was synthesized for the first time. This intramolecular FLP readily reacts with a series of small molecules, such as H₂, CO₂, phenylacetylene, styrene and isoprene. Among them, regioselective 3,4-addition to a diene is unprecedented. Current research is focusing on deoxygenation of addition adducts, which might provide a novel way for the synthesis of intramolecular FLPs.



Experimental section

General experimental methods

Solvents were dried by reflux under N₂ over sodium or CaH₂ and freshly distilled prior to use. Air-sensitive compounds were handled under a N₂ atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Bruker SPECT NMR (400 MHz for ¹H, 376 MHz for ¹⁹F, 100 MHz for ¹³C) and Bruker DMX500 NMR (500 MHz for ¹H, 160 MHz for ¹¹B) spectrometers. Most assignments were based on a series of 2D NMR experiments. HRMS analyses were performed at Bruker microTOF II. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC 1843771–1843777 (compound 2–8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. Mes₂P(O)H (Mes = 2,4,6-trimethylphenyl)²¹ and ClB(C₆F₅)₂ (ref. 22) were prepared as reported.

Synthesis of compound 1

A solution of *n*-BuLi (2.5 M, 0.80 mL, 2.0 mmol) was added to a suspension of Mes₂P(O)H (0.57 g, 2.0 mmol) in hexane (8 mL) at 0 °C, affording a pale yellow solution. After stirring for 4 h at room temperature, a solution of ClB(C₆F₅)₂ (0.76 g, 2.0 mmol) in hexane (6 mL) was added at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 12 h. The resulting white slurry was filtered and the filtrate was dried under vacuum affording **1** as a pale yellow oil (1.05 g, 81%). ¹H NMR (400 MHz, C₆D₆): δ [ppm] = 6.62 (d, 4H, ⁴J_{P-H} = 2 Hz, *meta*-Mes), 2.28 (s, 12H, *ortho*-CH₃), 2.02 (s, 6H, *para*-CH₃). ¹³C NMR (101 MHz, C₆D₆): δ [ppm] = 147.9 (dm, ¹J_{C-F} = 248 Hz, *ortho*-C₆F₅), 143.2 (dm, ¹J_{C-F} = 257 Hz, *meta*-C₆F₅), 137.6 (dm, ¹J_{C-F} = 253 Hz, *para*-C₆F₅), 141.3 (d, ²J_{P-C} = 17 Hz, *ortho*-Mes), 140.2 (*para*-Mes), 133.3 (d, ¹J_{P-C} = 28 Hz, *ipso*-Mes), 130.6 (d, ³J_{P-C} = 3 Hz, *meta*-Mes), 22.2 (d, ³J_{P-C} = 4 Hz, *ortho*-CH₃), 20.9 (*para*-CH₃). ¹⁹F NMR (376 MHz, C₆D₆): δ [ppm] = -131.4 (m, *ortho*-C₆F₅), -148.8 (t, *para*-C₆F₅), -161.2 (m, *meta*-C₆F₅). ³¹P NMR (162 MHz, C₆D₆): δ [ppm] = 126.4. ¹¹B NMR (160 MHz, C₆D₆): δ [ppm] = 42.4. HRMS (*m/z*): calcd for C₃₀H₂₃OPBF₁₀ [M + H]⁺: 631.1420, found: 631.1434.

Synthesis of compound 2

A solution of pyridine (25 mg, 0.32 mmol) in hexane (1 mL) was added to a solution of **1** (130 mg, 0.206 mmol) in hexane (2 mL), affording a white precipitate. The reaction mixture was stirred for 30 min and stored at -30 °C for 10 h. Then the supernatant was removed by filtration and the residue was washed with hexane (1 mL) and dried under vacuum, affording **2** as a white powder (118 mg, 81%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **2** in CH₂Cl₂. ¹H NMR (400 MHz, C₆D₆): δ [ppm] = 8.12 (br s, 2H, *ortho*-Py), 6.66 (s, 4H, *meta*-Mes), 6.54 (br s, 1H, *para*-Py), 6.21 (br s, 2H, *meta*-Py), 2.47 (s, 12H, *ortho*-CH₃), 2.10 (s, 6H, *para*-CH₃). ¹³C NMR (101 MHz, C₆D₆): δ [ppm] = 148.6 (dm, ¹J_{C-F} = 240 Hz, *ortho*-C₆F₅), 140.8 (dm, ¹J_{C-F} = 251 Hz, *meta*-C₆F₅), 137.8

(dm, ¹J_{C-F} = 251 Hz, *para*-C₆F₅), 144.3 (*ortho*-Py), 141.0 (*para*-Py), 125.0 (*meta*-Py), 141.5 (d, ²J_{P-C} = 17 Hz, *ortho*-Mes), 138.3 (*para*-Mes), 136.9 (d, ¹J_{P-C} = 32 Hz, *ipso*-Mes), 130.5 (d, ³J_{P-C} = 2 Hz, *meta*-Mes), 21.5 (d, ³J_{P-C} = 16 Hz, *ortho*-CH₃), 20.9 (*para*-CH₃). ¹⁹F NMR (376 MHz, C₆D₆): δ [ppm] = -131.6 (m, *ortho*-C₆F₅), -155.8 (t, *para*-C₆F₅), -163.3 (m, *meta*-C₆F₅). ³¹P NMR (162 MHz, C₆D₆): δ [ppm] = 102.9. ¹¹B NMR (160 MHz, C₆D₆): δ [ppm] = 4.37.

Synthesis of compound 3

A solution of **1** (132 mg, 0.206 mmol) in toluene (1 mL) was heated to 90 °C for 15 h. Then, all volatiles were removed under vacuum. The resulting oily residue was extracted with hexane (2 mL). Afterwards hexane was removed under vacuum affording an oily solid. Another portion of hexane (1 mL) was introduced and an insoluble oil was formed which became crystals after standing at room temperature for 30 min. The supernatant was removed and the crystals were dried under vacuum affording **3** as a white crystalline solid (47 mg, 36%). ¹H NMR (400 MHz, C₆D₆): δ [ppm] = 6.43, 6.27 (each d, each 2H, ⁴J_{P-H} = 5 Hz, *meta*-Mes), 2.19, 2.05 (each s, each 6H, *ortho*-CH₃), 1.84, 1.71 (each s, each 3H, *para*-CH₃). ¹³C NMR (101 MHz, C₆D₆): δ [ppm] = 145.2, 144.6 (d, ⁴J_{P-C} = 3 Hz, *para*-Mes), 143.5, 141.8 (d, ²J_{P-C} = 12 Hz, *ortho*-Mes), 132.4, 131.5 (d, ³J_{P-C} = 13 Hz, *meta*-Mes), 23.1, 21.8 (d, ³J_{P-C} = 5 Hz, *ortho*-CH₃), 20.9, 20.7 (d, ⁵J_{P-C} = 1 Hz, *p*-CH₃). ¹⁹F NMR (376 MHz, C₆D₆): δ [ppm] = -129.5 (m, 2F, C₆F₄), -134.5 (m, 2F, *ortho*-C₆F₅), -144.1 (m, 1F, C₆F₄), -149.5 (br s, 1F, BF), -153.6 (m, 1F, C₆F₄), -158.0 (t, 1F, *para*-C₆F₅), -164.6 (m, 2F, *meta*-C₆F₅). ³¹P NMR (162 MHz, C₆D₆): δ [ppm] = 58.3. ¹¹B NMR (160 MHz, C₆D₆): δ [ppm] = 8.72. HRMS (*m/z*): calcd for C₃₀H₂₂OPBF₁₀Na [M + Na]⁺: 653.1239, found: 653.1258.

Synthesis of compound 4

H₂ (60 bar) was introduced to a solution of **1** (324 mg, 0.515 mmol) in hexane (2.5 mL) in an autoclave. The reaction mixture was stirred for 40 h at 50 °C, affording a white precipitate. The supernatant was removed by filtration and the solid was dried under vacuum affording **4** as a white powder (188 mg, 58%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **4** in toluene. ¹H NMR (400 MHz, C₆D₆): δ [ppm] = 8.02 (d, 1H, ¹J_{P-H} = 514 Hz, *PH*), 6.34 (d, 4H, ⁴J_{P-H} = 5 Hz, *meta*-Mes), 4.59 (br s, 1H, *BH*), 2.07 (s, 12H, *ortho*-CH₃), 1.86 (s, 6H, *para*-CH₃). ¹³C NMR (101 MHz, C₆D₆): δ [ppm] = 148.4 (dm, ¹J_{C-F} = 240 Hz, *ortho*-C₆F₅), 139.9 (dm, ¹J_{C-F} = 247 Hz, *meta*-C₆F₅), 137.4 (dm, ¹J_{C-F} = 256 Hz, *para*-C₆F₅), 145.0 (d, ⁴J_{P-C} = 3 Hz, *para*-Mes), 143.1 (d, ²J_{P-C} = 11 Hz, *ortho*-Mes), 131.2 (d, ³J_{P-C} = 12 Hz, *meta*-Mes), 117.8 (d, ¹J_{P-C} = 107 Hz, *ipso*-Mes), 21.0 (d, ³J_{P-C} = 6 Hz, *ortho*-CH₃), 20.9 (d, ⁵J_{P-C} = 2 Hz, *para*-CH₃). ¹⁹F NMR (376 MHz, C₆D₆): δ [ppm] = -133.9 (m, *ortho*-C₆F₅), -159.8 (t, *para*-C₆F₅), -165.1 (m, *meta*-C₆F₅). ³¹P NMR (162 MHz, C₆D₆): δ [ppm] = 31.5 (d, ¹J_{P-H} = 514 Hz). ¹¹B NMR (160 MHz, C₆D₆): δ [ppm] = -4.79.

Synthesis of compound 5

CO₂ (1.8 bar) was introduced to a degassed solution of **1** (551 mg, 0.875 mmol) in hexane (2.5 mL) at room temperature



and the reaction mixture was stirred for 24 h, affording a white precipitate. The supernatant was removed by filtration and the residue was dried under vacuum affording **5** as a white powder (430 mg, 73%). Crystals suitable for X-ray diffraction were grown from toluene at $-30\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 6.30 (s, 4H, *meta*-Mes), 2.19 (s, 12H, *ortho*- CH_3), 1.79 (s, 6H, *para*- CH_3). ^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 165.9 (d, $^1J_{\text{P-C}} = 108\text{ Hz}$, $\text{C}=\text{O}$), 148.4 (dm, $^1J_{\text{C-F}} = 243\text{ Hz}$, *ortho*- C_6F_5), 141.0 (dm, $^1J_{\text{C-F}} = 253\text{ Hz}$, *meta*- C_6F_5), 137.6 (dm, $^1J_{\text{C-F}} = 251\text{ Hz}$, *para*- C_6F_5), 145.7 (*para*-Mes), 143.3 (d, $^2J_{\text{P-C}} = 12\text{ Hz}$, *ortho*-Mes), 131.7 (d, $^3J_{\text{P-C}} = 13\text{ Hz}$, *meta*-Mes), 118.0 (d, $^1J_{\text{P-C}} = 92\text{ Hz}$, *ipso*-Mes), 21.8 (d, $^3J_{\text{P-C}} = 6\text{ Hz}$, *ortho*- CH_3), 20.9 (*para*- CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -133.9 (*ortho*- C_6F_5), -155.9 (*para*- C_6F_5), -163.5 (*meta*- C_6F_5). ^{31}P NMR (162 MHz, C_6D_6): δ [ppm] = 35.0. ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 7.94. HRMS (m/z): calcd for $\text{C}_{31}\text{H}_{22}\text{O}_3\text{PBF}_{10}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 697.1138, found: 697.1123.

Synthesis of compound 6

$\text{PhC}\equiv\text{CH}$ (120 mg, 1.18 mmol) was added to a solution of **1** (567 mg, 0.900 mmol) in hexane (3 mL) at room temperature, affording a white precipitate. After the reaction mixture was stirred for 17 h, the supernatant was removed by filtration and the solid was dried under vacuum affording **6** as a white powder (480 mg, 73%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **6** in toluene. ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 9.01 (d, 1H, $^3J_{\text{P-H}} = 46\text{ Hz}$, $\text{C}=\text{CH}$), 7.17 (m, 2H, *PhH*), 6.94 (m, 3H, *PhH*), 6.40 (d, 4H, $^4J_{\text{P-H}} = 4\text{ Hz}$, *meta*-Mes), 2.10 (s, 12H, *ortho*- CH_3), 1.85 (s, 6H, *para*- CH_3). ^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 176.7 (br s, *BCH*), 147.8 (dm, $^1J_{\text{C-F}} = 241\text{ Hz}$, *ortho*- C_6F_5), 139.9 (dm, $^1J_{\text{C-F}} = 250\text{ Hz}$, *meta*- C_6F_5), 137.1 (dm, $^1J_{\text{C-F}} = 254\text{ Hz}$, *para*- C_6F_5), 144.0 (d, $^4J_{\text{P-C}} = 3\text{ Hz}$, *para*-Mes), 142.7 (d, $^2J_{\text{P-C}} = 11\text{ Hz}$, *ortho*-Mes), 136.7 (d, $^2J_{\text{P-C}} = 21\text{ Hz}$, *ipso*-Ph), 135.2 (d, $^1J_{\text{P-C}} = 81\text{ Hz}$, $\text{PC}=\text{C}$), 131.5 (d, $^3J_{\text{P-C}} = 12\text{ Hz}$, *meta*-Mes), 129.2 (Ph), 127.5 (d, $^3J_{\text{P-C}} = 5\text{ Hz}$, *ortho*-Ph), 124.9 (d, $^1J_{\text{P-C}} = 97\text{ Hz}$, *ipso*-Mes), 23.0 (d, $^3J_{\text{P-C}} = 5\text{ Hz}$, *ortho*- CH_3), 20.8 (d, $^5J_{\text{P-C}} = 1\text{ Hz}$, *para*- CH_3). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -132.0 (m, *ortho*- C_6F_5), -159.2 (t, *para*- C_6F_5), -164.5 (m, *meta*- C_6F_5). ^{31}P NMR (162 MHz, C_6D_6): δ [ppm] = 68.4 (d, $^3J_{\text{P-H}} = 46\text{ Hz}$). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 2.65. HRMS (m/z): calcd for $\text{C}_{38}\text{H}_{28}\text{OPBF}_{10}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 755.1709, found: 755.1706.

Synthesis of compound 7

$\text{PhCH}=\text{CH}_2$ (220 mg, 2.12 mmol) was added to a solution of **1** (1.00 g, 1.59 mmol) in hexane (6 mL) at room temperature, affording a white precipitate. After the reaction mixture was stirred for 15 h, the supernatant was removed by filtration and the solid was dried under vacuum affording **7** as a white powder (890 mg, 76%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **7** in CH_2Cl_2 . ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 6.92–6.74 (5H, Ph), 6.42 (d, 2H, $^4J_{\text{P-H}} = 3\text{ Hz}$, *meta*-Mes), 6.32 (br s, 2H, *meta*-Mes), 4.76 (dt, 1H, $^3J_{\text{H-H}} = 13\text{ Hz}$, $^2J_{\text{P-H}} = 6\text{ Hz}$, *CH*), 2.96, 1.95 (each m, each 1H, *BCH}_2*), 2.38–1.84 (18H, *Mes-CH}_3*). ^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 148.1 (dm, $^1J_{\text{C-F}} = 241\text{ Hz}$, *ortho*- C_6F_5), 139.7

(dm, $^1J_{\text{C-F}} = 248\text{ Hz}$, *meta*- C_6F_5), 137.5 (dm, $^1J_{\text{C-F}} = 249\text{ Hz}$, *para*- C_6F_5), 143.8, 143.4, 138.2 (*ortho*-Mes and *para*-Mes), 131.7, 131.4 (*meta*-Mes), 129.1, 128.5, 127.6 (Ph), 51.3 (d, $^1J_{\text{P-C}} = 46\text{ Hz}$, *PCH*), 35.6 (*BCH}_2*), 23.5, 22.4, 20.7 (*Mes-CH}_3*). ^{19}F NMR (376 MHz, C_6D_6): δ [ppm] = -133.0 (dm, *ortho*- C_6F_5), -159.4 (t, *para*- C_6F_5), -164.4 (*meta*, *m-C}_6\text{F}_5*). ^{31}P NMR (162 MHz, C_6D_6): δ [ppm] = 82.4 (d, $^2J_{\text{P-H}} = 39\text{ Hz}$). ^{11}B NMR (160 MHz, C_6D_6): δ [ppm] = 3.16. HRMS (m/z): calcd for $\text{C}_{38}\text{H}_{30}\text{OPBF}_{10}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 757.1865, found: 757.1865.

Synthesis of compound 8

Isoprene (50 mg, 0.74 mmol) was added to a solution of **1** (331 mg, 0.525 mmol) in hexane (3 mL) at room temperature, affording a white precipitate after stirring for about 24 h. The supernatant was removed by filtration and the solid was dried under vacuum affording **8** as a white powder (290 mg, 79%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of **8** in CH_2Cl_2 . ^1H NMR (400 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ [ppm] = 6.79 (s, 2H, *meta*-Mes), 6.76 (d, 2H, $^4J_{\text{P-H}} = 4\text{ Hz}$, *meta*-Mes), 5.16 (d, 1H, $^2J_{\text{H-H}} = 3\text{ Hz}$, $\text{C}=\text{CH}_2$), 5.03 (s, 1H, $\text{C}=\text{CH}_2$), 4.58 (dt, 1H, $^3J_{\text{H-H}} = 12\text{ Hz}$, $^2J_{\text{P-H}} = 7\text{ Hz}$, *CH*), 2.66, 2.02 (each m, each 1H, *BCH}_2*), 2.57–2.01 (18H, *Mes-CH}_3*), 1.49 (s, 3H, *CH}_3*). ^{13}C NMR (101 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ [ppm] = 147.6 (dm, $^1J_{\text{C-F}} = 241\text{ Hz}$, *ortho*- C_6F_5), 139.3 (dm, $^1J_{\text{C-F}} = 248\text{ Hz}$, *meta*- C_6F_5), 137.0 (dm, $^1J_{\text{C-F}} = 249\text{ Hz}$, *para*- C_6F_5), 143.9, 143.1, (*ortho*-Mes and *para*-Mes), 142.3 ($\text{C}=\text{CH}_2$), 131.8, 131.3 (*meta*-Mes), 116.9 (d, $^3J_{\text{P-C}} = 12\text{ Hz}$, $\text{C}=\text{CH}_2$), 52.1 (d, $^1J_{\text{P-C}} = 46\text{ Hz}$, *PCH*), 29.9 (*BCH}_2*), 23.4, 23.0, 21.1, 20.9 (*Mes-CH}_3*), 19.9 (*CH}_3*). ^{19}F NMR (376 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ [ppm] = -132.3 (dm, *ortho*- C_6F_5), -158.9 (dt, *para*- C_6F_5), -163.6 (m, *meta*- C_6F_5). ^{31}P NMR (162 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ [ppm] = 79.8 (d, $^2J_{\text{P-H}} = 37\text{ Hz}$). ^{11}B NMR (160 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ [ppm] = 2.59. HRMS (m/z): calcd for $\text{C}_{35}\text{H}_{30}\text{OPBF}_{10}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 721.1865, found: 721.1857.

Conflicts of interest

There are no conflicts to declare.

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