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

Yiheng Wang,^a Zhen Hua Li[®] and Huadong Wang^{*} ^{*ab}

Reaction of $Mes_2P(O)$ Li with $(C_6F_5)_2BCl$ gave access to an oxygen-linked germinal intramolecular frustrated Lewis pair $Mes_2P(O)B(C_6F_5)_2$ (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.

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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 threemembered ring. Attempts to introduce frequently applied -B(C₆F₅)₂ and -PtBu₂ functionalities to C1-linked FLPs were thwarted by facile intramolecular nucleophilic substitution of fluoride on the C₆F₅ ring by the phosphine moiety (I).⁴ To circumvent this problem, Slootweg, Lammertsma and coworkers employed -BPh2 instead of -B(C₆F₅)2 functionality and synthesized a CH2-bridged tBu2PCH2BPh2 (II).5 It was

Results and discussion

Synthesis of **1** was achieved by treatment of Mes₂P(O)H with nBuLi and subsequently (C₆F₅)₂BCl 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 Ph₂-P(OMe) (117 ppm). ¹⁵ In the ¹¹B NMR spectrum of **1** a broad

discovered that this germinal FLP can activate H2, CO2 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 employ $ing - BFxyl_2$ (Fxyl = 3,5-bis(trifluoromethyl)phenyl) as the Lewis acid center (III) or less nucleophilic -P(C₆F₅)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 CO2.14 Since the nucleophilicity of phosphinite is markedly lower than alkyl- or alkenyl-substituted phosphine, we reasoned that an oxygen-linked germinal FLP containing -B(C₆F₅)₂ and -PMes₂ 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).

^aDepartment of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Songhu Road 2005, Shanghai, 200438, China ^bState Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China. E-mail: huadongwang@fudan.edu.cn

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$$F = \begin{bmatrix} \text{(OC)}_5 \\ \text{F} \\ \text{V} \end{bmatrix}$$

$$F = \begin{bmatrix} \text{(OC)}_5 \\ \text{POBC}_2 \\ \text{POBC}_2 \end{bmatrix}$$

$$F = \begin{bmatrix} \text{(OC)}_5 \\ \text{Mes}_2 \\ \text{POBC}_2 \end{bmatrix}$$

$$F = \begin{bmatrix} \text{(OC)}_5 \\ \text{Mes}_2 \\ \text{Mes}_2 \\ \text{Mes}_2 \\ \text{Mes}_2 \end{bmatrix}$$

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$$F = \begin{bmatrix} \text{(OC)}_5 \\ \text{Mes}_2 \\ \text{Mes}_2 \\ \text{Mes}_2 \\ \text{Mes}_2 \end{bmatrix}$$

Germinal 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 $^{19}\mathrm{F}$ 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 tBu₂PCH₂B(Fxyl)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 substitutent (Fig. 2b). The LUMO is largely distributed over the boron center as well as one C₆F₅ 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).

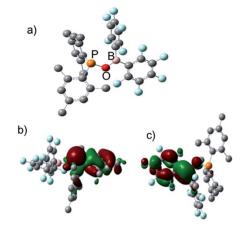


Fig. 2 (a) calculated structure of 1; (b) HOMO of 1; (c) LUMO of 1.

While 1 does not react with H₂ under 6 bar at room temperature, it reacts with H₂ 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 Mes₂P(O)H and HB(C₆F₅)₂. Existence of a P-H moiety was confirmed by the appearance of a doublet at δ 31.5 ppm $\binom{1}{I_{P-H}}$ = 514 Hz) in the 31 P NMR spectrum, with a corresponding doublet at δ 8.02 ppm (${}^{1}J_{P-H} = 514 \text{ Hz}$) observed in the ${}^{1}H$ NMR spectrum. However, both the ¹¹B and ¹¹B{¹H} 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 CO₂ (1.8 bar) at room temperature in hexane resulted in formation of a CO2 adduct 5, in an analogous way with other germinal 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 germinal B/P FLPs II^{5a} and III,⁶ the solution of 5 in C₆D₆ slowly released CO₂ under N₂ atmosphere at room temperature. In a sealed

Scheme 2 Reaction of 1 with H₂.

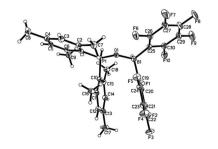


Fig. 3 Molecular structure of 4 (thermal ellipsoids are shown with 30% probability).

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$$\operatorname{Mes_2P} \overset{\bigoplus}{\longrightarrow} \operatorname{B(C_6F_5)_2} + \operatorname{CO_2} \overset{\bigoplus}{\longrightarrow} \operatorname{Mes_2P} \overset{\bigoplus}{\longrightarrow} \operatorname{B(C_6F_5)_2}$$

Scheme 3 Reaction of 1 with CO₂

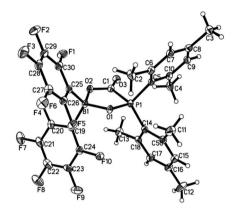


Fig. 4 Molecular structure of 5 (thermal ellipsoids are shown with 30% probability).

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 $tBu_2P(\mu\text{-O})(\mu\text{-C}_6H_4)B(C_6F_5)_2$ (P-O 1.546, B-O 1.550 Å) reported by Wagner.⁶

$$Mes_2P \xrightarrow{O}_{B(C_6F_5)_2} + Ph \xrightarrow{\qquad \qquad } H \xrightarrow{\begin{array}{c} hexane \\ RT \end{array}} Mes_2P \xrightarrow{O}_{B(C_6F_5)_2} G(C_6F_5)_2$$

Scheme 4 Reaction of 1 with phenylacetylene.

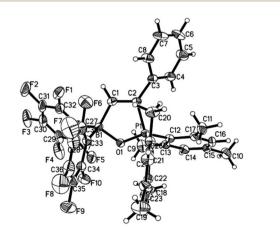


Fig. 5 Molecular structure of 6 (thermal ellipsoids are shown with 30% probability).

Scheme 5 Reaction of 1 with styrene and isoprene

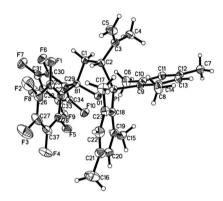


Fig. 6 Molecular structure of 8 (thermal ellipsoids are shown with 30% probability).

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. 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 $tBu_3P/B(C_6F_5)_3$ or intramolecular FLP di-t-butyl-phosphaboradibenzofulvene 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 $B(C_6F_5)_2$ and nucleophilic $PMes_2$ moieties was synthesized for the first time. This intramolecular FLP readily reacts with a series of small molecules, such as H_2 , CO_2 , 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.

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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. $Mes_2P(O)H$ (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, C_6D_6): 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, C_6D_6): δ [ppm] = 147.9 (dm, ${}^{1}J_{C-F}$ = 248 Hz, ortho- C_6F_5), 143.2 (dm, ${}^1J_{C-F} = 257$ Hz, meta- C_6F_5), 137.6 (dm, ${}^1J_{C-F} =$ 253 Hz, para- C_6F_5), 141.3 (d, ${}^2J_{P-C} = 17$ Hz, ortho-Mes), 140.2 (para-Mes), 133.3 (d, ${}^{1}J_{P-C} = 28$ Hz, ipso-Mes), 130.6 (d, ${}^{3}J_{P-C} =$ 3 Hz, meta-Mes), 22.2 (d, ${}^{3}J_{P-C} = 4$ Hz, ortho-CH₃), 20.9 (para-CH₃). ¹⁹F NMR (376 MHz, C₆D₆): δ [ppm] = -131.4 (m, ortho- C_6F_5), -148.8 (t, para- C_6F_5), -161.2 (m, meta- C_6F_5). ³¹P NMR (162 MHz, C_6D_6): δ [ppm] = 126.4. ¹¹B NMR (160 MHz, C_6D_6): 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 CH_2Cl_2 . ¹H NMR (400 MHz, C_6D_6): 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, ${}^{1}J_{C-F}$ = 240 Hz, ortho- C_6F_5), 140.8 (dm, ${}^1J_{C-F} = 251$ Hz, meta- C_6F_5), 137.8 $(dm, {}^{1}J_{C-F} = 251 \text{ Hz}, para-C_{6}F_{5}), 144.3 (ortho-Py), 141.0 (para-Py),$ 125.0 (meta-Py), 141.5 (d, ${}^{2}J_{P-C} = 17$ Hz, ortho-Mes), 138.3 (para-Mes), 136.9 (d, ${}^{1}J_{P-C} = 32$ Hz, *ipso*-Mes), 130.5 (d, ${}^{3}J_{P-C} = 2$ Hz, meta-Mes), 21.5 (d, ${}^{3}J_{P-C} = 16$ Hz, ortho-CH₃), 20.9 (para-CH₃). ¹⁹F NMR (376 MHz, C_6D_6): δ [ppm] = -131.6 (m, ortho- C_6F_5), -155.8 (t, para- C_6F_5), -163.3 (m, meta- C_6F_5). ³¹P NMR (162) MHz, C_6D_6 : δ [ppm] = 102.9. ¹¹B NMR (160 MHz, C_6D_6): 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, C_6D_6 : 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, C_6D_6): δ [ppm] = 145.2, 144.6 (d, ${}^{4}J_{P-C} = 3$ Hz, para-Mes), 143.5, 141.8 (d, ${}^{2}J_{P-C} = 12$ Hz, ortho-Mes), 132.4, 131.5 (d, ${}^{3}J_{P-C} = 13$ Hz, meta-Mes), 23.1, 21.8 $(d, {}^{3}J_{P-C} = 5 \text{ Hz}, ortho-CH_{3}), 20.9, 20.7 (d, {}^{5}J_{P-C} = 1 \text{ Hz}, p-CH_{3}).$ ¹⁹F NMR (376 MHz, C_6D_6): δ [ppm] = -129.5 (m, 2F, C_6F_4), -134.5 (m, 2F, ortho- C_6F_5), -144.1 (m, 1F, C_6F_4), -149.5 (br s, 1F, BF), -153.6 (m, 1F, C_6F_4), -158.0 (t, 1F, para- C_6F_5), -164.6(m, 2F, meta- C_6F_5). ³¹P NMR (162 MHz, C_6D_6): δ [ppm] = 58.3. ¹¹B NMR (160 MHz, C_6D_6): δ [ppm] = 8.72. HRMS (m/z): calcd for $C_{30}H_{22}OPBF_{10}Na [M + Na]^+$: 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, C_6D_6 : δ [ppm] = 8.02 (d, 1H, ${}^{1}J_{P-H}$ = 514 Hz, PH), 6.34 (d, 4H, ${}^{4}J_{P-H} = 5$ Hz, meta-Mes), 4.59 (br s, 1H, BH), 2.07 (s, 12H, ortho- CH_3), 1.86 (s, 6H, para- CH_3). ¹³C NMR (101 MHz, C_6D_6): $\delta [ppm] = 148.4 (dm, {}^{1}J_{C-F} = 240 Hz, ortho-C_{6}F_{5}), 139.9 (dm, {}^{1}J_{C-F})$ $_{\rm F} = 247$ Hz, meta- C_6 F₅), 137.4 (dm, $^1J_{\rm C-F} = 256$ Hz, para- C_6 F₅), 145.0 (d, ${}^{4}J_{P-C} = 3$ Hz, para-Mes), 143.1 (d, ${}^{2}J_{P-C} = 11$ Hz, ortho-Mes), 131.2 (d, ${}^{3}J_{P-C} = 12$ Hz, meta-Mes), 117.8 (d, ${}^{1}J_{P-C} =$ 107 Hz, *ipso*-Mes), 21.0 (d, ${}^{3}J_{P-C} = 6$ Hz, *ortho-CH*₃), 20.9 (d, ${}^{5}J_{P-C}$ = 2 Hz, para- CH_3). ¹⁹F NMR (376 MHz, C_6D_6): δ [ppm] = -133.9 $(m, ortho-C_6F_5), -159.8 (t, para-C_6F_5), -165.1 (m, meta-C_6F_5).$ ³¹P NMR (162 MHz, C_6D_6): δ [ppm] = 31.5 (d, ${}^{1}J_{P-H} = 514$ Hz). ${}^{11}B$ NMR (160 MHz, C_6D_6): 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 °C. ¹H NMR (400 MHz, C₆D₆): δ [ppm] = 6.30 (s, 4H, meta-Mes), 2.19 (s, 12H, ortho-CH₃), 1.79 (s, 6H, para-CH₃). ¹³C NMR (101 MHz, C₆D₆): δ [ppm] = 165.9 (d, ¹ J_{P-C} = 108 Hz, C=O), 148.4 (dm, ${}^{1}J_{C-F}$ = 243 Hz, ortho- $C_{6}F_{5}$), 141.0 $(dm, {}^{1}J_{C-F} = 253 \text{ Hz}, meta-C_{6}F_{5}), 137.6 (dm, {}^{1}J_{C-F} = 251 \text{ Hz}, para C_6F_5$), 145.7 (para-Mes), 143.3 (d, ${}^2J_{P-C} = 12$ Hz, ortho-Mes), 131.7 (d, ${}^{3}J_{P-C} = 13$ Hz, meta-Mes), 118.0 (d, ${}^{1}J_{P-C} = 92$ Hz, ipso-Mes), 21.8 (d, ${}^{3}J_{P-C} = 6$ Hz, ortho-CH₃), 20.9 (para-CH₃). ${}^{19}F$ 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). ³¹P NMR (162 MHz, C_6D_6): δ [ppm] = 35.0. ¹¹B NMR (160 MHz, C_6D_6): δ [ppm] = 7.94. HRMS (m/z): calcd for $C_{31}H_{22}O_3PBF_{10}Na [M + Na]^+$: 697.1138, found: 697.1123.

Synthesis of compound 6

PhC≡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, $^3J_{P-H}$ = 46 Hz, C= CH), 7.17 (m, 2H, PhH), 6.94 (m, 3H, PhH), 6.40 (d, 4H, ${}^{4}J_{P-H} =$ 4 Hz, meta-Mes), 2.10 (s, 12H, ortho-CH₃), 1.85 (s, 6H, para-CH₃). ¹³C NMR (101 MHz, C_6D_6): δ [ppm] = 176.7 (br s, BCH), 147.8 $(dm, {}^{1}J_{C-F} = 241 \text{ Hz}, ortho-C_{6}F_{5}), 139.9 (dm, {}^{1}J_{C-F} = 250 \text{ Hz},$ $meta-C_6F_5$), 137.1 (dm, ${}^{1}J_{C-F} = 254$ Hz, $para-C_6F_5$), 144.0 (d, ${}^{4}J_{P-C}$ = 3 Hz, para-Mes), 142.7 (d, ${}^{2}J_{P-C}$ = 11 Hz, ortho-Mes), 136.7 (d, $^{2}J_{P-C} = 21 \text{ Hz}, ipso-Ph), 135.2 (d, ^{1}J_{P-C} = 81 \text{ Hz}, PC=C), 131.5 (d, ^{1}J_{P-C} = 10 \text{ Hz}, ^{1}J_{$ $^{3}J_{P-C} = 12$ Hz, meta-Mes), 129.2 (Ph), 127.5 (d, $^{3}J_{P-C} = 5$ Hz, ortho-Ph), 124.9 (d, ${}^{1}J_{P-C} = 97$ Hz, ipso-Mes), 23.0 (d, ${}^{3}J_{P-C} =$ 5 Hz, ortho-CH₃), 20.8 (d, ${}^{5}J_{P-C} = 1$ Hz, para-CH₃). ${}^{19}F$ 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). ³¹P NMR (162 MHz, C_6D_6): δ [ppm] = 68.4 (d, ${}^{3}J_{P-H}$ = 46 Hz). ${}^{11}B$ NMR (160 MHz, $C_{6}D_{6}$): δ [ppm] = 2.65. HRMS (m/z): calcd for $C_{38}H_{28}OPBF_{10}Na [M + Na]^+$: 755.1709, found: 755.1706.

Synthesis of compound 7

PhCH=CH₂ (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 CH₂Cl₂. 1 H NMR (400 MHz, C₆D₆): δ [ppm] = 6.92–6.74 (5H, Ph), 6.42 (d, 2H, $^{4}J_{P-H}$ = 3 Hz, *meta*-Mes), 6.32 (br s, 2H, *meta*-Mes), 4.76 (dt, 1H, $^{3}J_{H-H}$ = 13 Hz, $^{2}J_{P-H}$ = 6 Hz, CH), 2.96, 1.95 (each m, each 1H, BCH₂), 2.38–1.84 (18H, Mes-CH₃). 13 C NMR (101 MHz, C₆D₆): δ [ppm] = 148.1 (dm, $^{1}J_{C-F}$ = 241 Hz, *ortho-C*₆F₅), 139.7

(dm, ${}^1J_{\text{C-F}} = 248$ Hz, $meta\text{-}C_6F_5$), 137.5 (dm, ${}^1J_{\text{C-F}} = 249$ Hz, $para\text{-}C_6F_5$), 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, ${}^1J_{\text{P-C}} = 46$ Hz, PCH), 35.6 (BCH₂), 23.5, 22.4, 20.7 (Mes-CH₃). ${}^{19}\text{F}$ NMR (376 MHz, C_6D_6): δ [ppm] = -133.0 (dm, $ortho\text{-}\text{C}_6F_5$), -159.4 (t, $para\text{-}\text{C}_6F_5$), -164.4 (meta, m-C₆F₅). ${}^{31}\text{P}$ NMR (162 MHz, C₆D₆): δ [ppm] = 82.4 (d, ${}^2J_{\text{P-H}} = 39$ Hz). ${}^{11}\text{B}$ NMR (160 MHz, C₆D₆): δ [ppm] = 3.16. HRMS (m/z): calcd for $\text{C}_{38}\text{H}_{30}\text{OPBF}_{10}\text{Na}$ [M + 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 CH₂Cl₂. ¹H NMR (400 MHz, C_6D_5Br): δ [ppm] = 6.79 (s, 2H, meta-Mes), 6.76 (d, 2H, ${}^4J_{P-}$ $_{\rm H} = 4$ Hz, meta-Mes), 5.16 (d, 1H, $^2J_{\rm H-H} = 3$ Hz, C=C H_2), 5.03 (s, 1H, C= CH_2), 4.58 (dt, 1H, $^3J_{H-H} = 12$ Hz, $^2J_{P-H} = 7$ Hz, CH), 2.66, 2.02 (each m, each 1H, BCH₂), 2.57-2.01 (18H, Mes-CH₃), 1.49 (s, 3H, CH₃). ¹³C NMR (101 MHz, C₆D₅Br): δ [ppm] = 147.6 (dm, $^{1}J_{\text{C-F}} = 241 \text{ Hz}, \text{ ortho-}C_{6}F_{5}$, 139.3 (dm, $^{1}J_{\text{C-F}} = 248 \text{ Hz}, \text{ meta-}$ C_6F_5), 137.0 (dm, ${}^1J_{C-F}$ = 249 Hz, para- C_6F_5), 143.9, 143.1, (ortho-Mes and para-Mes), 142.3 (C=CH₂), 131.8, 131.3 (meta-Mes), 116.9 (d, ${}^{3}J_{P-C} = 12 \text{ Hz}$, C=CH₂), 52.1 (d, ${}^{1}J_{P-C} = 46 \text{ Hz}$, PCH), 29.9 (BCH₂), 23.4, 23.0, 21.1, 20.9 (Mes-CH₃), 19.9 (CH₃). ¹⁹F NMR (376 MHz, C_6D_5Br): $\delta -132.3$ (dm, ortho- C_6F_5), -158.9 (dt, $para-C_6F_5$, -163.6 (m, $meta-C_6F_5$). ³¹P NMR (162 MHz, C_6D_5Br): δ [ppm] = 79.8 (d, ${}^{2}J_{P-H}$ = 37 Hz). ${}^{11}B$ NMR (160 MHz, C₆D₅Br): δ [ppm] = 2.59. HRMS (m/z): calcd for C₃₅H₃₀OPBF₁₀Na [M + Na]⁺: 721.1865, found: 721.1857.

Conflicts of interest

There are no conflicts to declare.

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