

Facile dihydrogen release from phosphino-borinate ester Lewis pairs.

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Supplementary Information

General Remarks.

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of argon using standard schlenk-line and glovebox (M-Braun, O₂ < 0.1 ppm, H₂O < 0.1 ppm) techniques, and all glassware was oven dried (200 °C) overnight and allowed to cool under vacuum prior to use. Standard reagents isobutylene oxide (Sigma-Aldrich) and 2,2-di(trifluoromethyl)oxarine (Apollo Scientific) were degassed using three freeze-pump-thaw cycles then distilled under argon prior to use. The compounds chlorobis(perfluorophenyl)boron bis(perfluorophenyl)borane¹ were prepared according to a literature procedure. Solvents were purified and pre-dried using an Anhydrous Engineering column purification system then distilled from the appropriate drying agent prior to use. NMR spectra were recorded using a JEOL ECP 300 spectrometer at 300 MHz, and a Varian 400 spectrometer at 400 MHz (using the appropriate deuterated solvent (purchased from Cambridge Isotope Labs and purified by standard techniques) and referenced to an internal standard (residual solvent signal for ¹H, BF₃·OEt₂ for ¹¹B, 85% H₃PO₄ for ³¹P, and FCCL₃ for ¹⁹F. Microanalysis was carried out by the Microanalytical Laboratory, University of Bristol using a Carlo Erba spectrometer. X-ray crystal structures were solved by members of the Structural Chemistry group, University of Bristol

Synthesis of compounds **1a-1d** and **2a-2d**.

1a. *t*-Bu₃PCH₂C(Me)₂OH

A 100 mL round-bottomed flask fitted with a gas inlet and dropping funnel was charged with a magnetic stir bar, di-*t*-butylphosphine (16 mmol) and THF (30 mL) then cooled to -78°C in a acetone-dry ice bath. The dropping funnel was charged with *n*-BuLi (10 mL, 16 mmol) which was subsequently added dropwise to the THF solution over 15 mins. Once the addition was complete, the bath was removed and the flask was allowed to warm to ambient temperature. After stirring for 2 h a bright yellow colour developed. The solution was again cooled to -78°C and isobutylene oxide (1.42 mL, 16 mmol) was added dropwise by syringe, discharging the yellow colour. The solution was allowed to warm to ambient temperature overnight leaving the cooling bath in place. After 16 hours stirring the reaction mixture was pale yellow and slightly turbid. The ³¹P {¹H} spectrum of the crude reaction mixture indicated only one species (identified as **2a**). The solvent was removed under vacuum and the resulting residue taken up in degassed diethyl ether (20 mL) and water (20 mL). The mixture was transferred to a separating funnel via cannula and allowed to settle. The ether layer was transferred via cannula to separate argon filled flask charged with MgSO₄. The aqueous layer was extracted twice more and diethyl ether (20 mL portions) which were combined with the initial extract. After 1 hour stirring with MgSO₄ the solution was filtered and the solvent removed to leave colourless oil which was left under high vacuum for 1 hour. The oil was isolated inside the glove box and crystallised upon standing to give the product as a crystalline solid. Yield. 3.04 g, 13.9 mmol, 87% ¹H NMR (benzene-d₆): δ 2.37 (br. s, 1H, OH), 1.56 (d, ²J_{HP} = 5.34 Hz, 2H, CH₂), 1.27 (d, ⁴J_{HP} = 0.73 Hz, 6H, C(CH₃)₂), 1.06 (d, ³J_{HP} = 11.10 Hz, 18H, C(CH₃)₃). ³¹P {¹H} (benzene-d₆): δ 16.4 (s). ¹³C {¹H} (benzene-d₆): δ 70.1 (d, ²J_{CP} = 20.1 Hz, C(CH₃)₂), 36.1 (d, ¹J_{CP} = 23.1 Hz, CH₂) 32.1 (d, ³J_{CP} = 5.2

Hz, $\underline{\text{CH}_3}$), 31.6 (d, $^3J_{\text{CP}} = 20.7$ Hz, $\underline{\text{C}}(\text{CH}_3)_3$) 30.8 (d, $^2J_{\text{CP}} = 13.85$ Hz, $\underline{\text{C}}(\text{CH}_3)_2$). CI MS: m/z 219.3 ($[\text{M} + \text{H}]^+$, 100 %). Elemental Analysis: Calc. C, 66.02; H, 12.47; Found. C, 65.95.; H, 12.22

2a. *t*-Bu₃PCH₂C(Me)₂OLi

Method A

The solvent was removed from a portion of the above reaction mixture leaving a light yellow residue which was recrystallised from minimal boiling hexane and cooled to -30 °C to yield the product as white microcrystals which were collected using a swivel frit and washed with a small portion of ice-cold hexane, dried under vacuum and transferred to a glovebox. Yield. 51 mg, 0.23 mmol, 90 %

Method B

A 50 mL round-bottomed flask fitted with an inlet and capped with a septum was charged with **1a** (0.5 g, 2.29 mmol), dissolved in hexanes (5 mL) then cooled to 0 °C. *n*-BuLi (1.6 M in hexanes, 1.43 mL, 2.3 mmol) was added dropwise via syringe over 10 mins causing the solution to turn light yellow. After 30 mins the solution was slowly cooled to -78 °C causing the product to precipitate as a white powder which was separated from the supernatant by cannula filtration at -78 °C. The resulting white powder was washed with a small portion of hexane before being dried under high vacuum for 1 hour and transferred to the glovebox. Yield. 0.43 g, 1.91 mmol, 66 %. ¹H NMR (toluene-*d*₈): δ 1.75 (d, $^2J_{\text{HP}} = 5.14$ Hz, 2H, $\underline{\text{CH}_2}$), 1.58 (s, 6H, $\text{C}(\underline{\text{CH}_3})_2$), 1.22 (d, $^3J_{\text{HP}} = 10.46$ Hz, 18H, $\text{C}(\underline{\text{CH}_3})_3$). ³¹P {¹H} (toluene-*d*₈): δ 26.8 (s) ¹³C {¹H} (toluene-*d*₈): δ 71.1 (d, $^2J_{\text{CP}} = 23.8$ Hz, $\underline{\text{C}}(\text{CH}_3)_2$), 41.8 (d, $^1J_{\text{CP}} = 35.2$ Hz, $\underline{\text{CH}_2}$) 35.6 (d, $^3J_{\text{CP}} = 4.6$ Hz, $\underline{\text{CH}_3}$), 32.1 (d, $^1J_{\text{CP}} = 23.7$ Hz, $\underline{\text{C}}(\text{CH}_3)_3$) 31.2 (d, $^2J_{\text{CP}} = 13.85$ Hz, $\underline{\text{CH}_3}$). ESI MS: m/z 219.3 ($[\text{M} - \text{Li}]^-$). Elemental Analysis: Calc. C, 64.27; H, 11.69; Found. C, 64.32.; H, 11.84

1c. *t*-Bu₃PCH₂C(Me)₂OB(C₆F₅)₂.

Method A

Inside a glovebox **2a** (51.3 mg, 0.23 mmol) and chlorobis(perfluorophenyl)boron (87.0 mg, 0.23 mmol) were weighed out in to two small J-tubes, and each dissolved in toluene (2 mL). The tubes were removed, connected to a Schlenk line and cooled to -78 °C. The chlorobis(perfluorophenyl)boron solution was added dropwise via cannula over 10 mins. The mixture was immediately allowed to warm to ambient temperature, and stirred for 20 mins leaving a light white turbid solution. The tube was transferred to the glovebox, and filtered through a glass fibre plug. The solvent was removed to leave a colourless viscous oil.

Method B

Inside the glovebox **1a** (133.1 mg, 0.61 mmol) and bis(perfluorophenyl)borane (210.9 mg, 0.61 mmol) weighed out in to two small vials, and each dissolved in toluene (5 mL). The solutions were mixed in a schlenk flask, including small toluene washes of the vial and allowed to stir for 16 hrs during which time slow evolution of gas could be observed. The reaction was monitored by the change in the ¹⁹F, ³¹P {¹H} and ¹¹B {¹H} NMR spectra. Once complete (~8 hrs), the flask was removed and the solvent removed under reduced pressure. The residue was left under high vacuum for 3 hrs leaving the product as colourless viscous oil. Yield. 337 mg, 0.60 mmol, 98%. ¹H NMR (toluene-*d*₈): δ 1.86 (d, $^2J_{\text{HP}} = 4.59$ Hz, 2H, $\underline{\text{CH}_2}$), 1.41 (s, 6H, $\text{C}(\underline{\text{CH}_3})_2$), 0.96 (d, $^3J_{\text{HP}} = 11.01$ Hz, 18H, $\text{C}(\underline{\text{CH}_3})_3$). ³¹P {¹H} (toluene-*d*₈): δ 24.5 (s) ¹¹B {¹H} (toluene-*d*₈): δ 35.6 (br.s, $\nu_{1/2} = 590$ Hz) ¹³C {¹H} (toluene-*d*₈): δ 147.6 (d, $^1J_{\text{CF}} = 246$ Hz, m- $\underline{\text{C}}$), 143.0 (d, $^1J_{\text{CF}} = 256$ Hz, p- $\underline{\text{C}}$), 138.0 (d, $^1J_{\text{CF}} =$

253 Hz, o-C), 85.3 (d, $^2J_{CP} = 25.7$ Hz, C(CH₃)₂), 35.1 (d, $^3J_{CP} = 26.5$ Hz, CH₂) 31.3 (d, $^3J_{CP} = 21.0$ Hz, CH₃), 29.65 (d, $^2J_{CP} = 13.2$ Hz, C(CH₃)₃) 29.6 (d, $^3J_{CP} = 13.27$ Hz, CH₃). Signal for ipso-C not observed. ^{19}F NMR (toluene-d₈): δ -134.69 (d, $^3J_{FF} = 20.56$ Hz, 4F, o-F), -164.11 (t, $^3J_{FF} = 20.56$ Hz, 2F, p-F), -166.84 (m, 4F, m-F). ESI MS: m/z 563.2 ([M + H]⁺, 20 %), 579.2 ([M+O+H]⁺ 50 %), 411.2 ([M+O-C₆F₅ +H]⁺ 100 %) Elemental Analysis: Calc. C, 51.27; H, 4.66; Found. C, 51.50.; H, 4.96

1d. *t*-Bu₃P(H)CH₂C(Me)₂O(H)B(C₆F₅)₂.

This was isolated by Method B above in a sealed tube, washing the colourless crystals that formed with hexane then drying under vacuum.

Yield. 96 mg, 0.17 mmol, 33 %.

^1H NMR (DCM-d₂): δ 6.08 (d, $^1J_{HP} = 486$ Hz, 1H, PH), 3.93 (br.q, $^1J_{HB} = 92.3$ Hz, 1H, BH), 2.26 (dd, $^2J_{HP} = 10.99$ Hz, $^3J_{HH} = 3.66$ Hz 2H, CH₂), 1.42 (d, $^3J_{HP} = 16.12$ Hz, 18H, C(CH₃)₃), 1.36 (d, $^4J_{HP} = 2.2$ Hz 6H, C(CH₃)₂). ^{31}P (DCM-d₂): δ 37.11 (d, $^1J_{PH} = 481$ Hz) ^{11}B (DCM-d₂): δ -11.41 (d, $^1J_{BH} = 96.43$ Hz) ^{19}F NMR (DCM-d₂): δ -134.69 (d, $^3J_{FF} = 20.56$ Hz, 4F, o-F), -164.11 (t, $^3J_{FF} = 20.56$ Hz, 2F, p-F), -166.84 (m, 4F, m-F). A satisfactory ^{13}C { ^1H } could not be obtained due to decomposition during acquisition. Elemental Analysis: Calc. C, 51.09; H, 5.00; Found. C, 51.41; H, 5.14 ESI MS: m/z 563.17 ([M-H]⁺).

2a. *t*-Bu₂PCH₂C(CF₃)₂OH

As for **1a** but with 2,2-di(trifluoromethyl)oxarine (0.56 g, 3.11 mmol), recrystallised from hexane. Yield. 0.89 g, 2.73 mmol, 87 %. ^1H NMR (toluene-d₈): δ 4.29 (br. s, 1H, OH), 2.07 (d, $^2J_{HP} = 3.67$ Hz, 2H, CH₂), 0.90 (d, $^3J_{HP} = 12.11$ Hz, 18H, C(CH₃)₃). ^{31}P { ^1H } (toluene-d₈): δ 4.90 (septet, $^4J_{PF} = 9.30$ Hz). ^{13}C { ^1H } (toluene-d₈): δ 124.06 (q, $^1J_{CF} = 287.8$ Hz, CF₃) 71.1 (d of septets, $^2J_{CF} = 28.9$ Hz, $^2J_{CP} = 12.11$ Hz, C(CF₃)₂), 31.7 (d, $^1J_{CP} = 17.88$ Hz, CH₂) 29.7 (d, $^3J_{CP} = 12.69$ Hz, CH₃), 32.1 (d, $^1J_{CP} = 24.23$ Hz, C(CH₃)₃). ^{19}F NMR (toluene-d₈): δ -76.55 (d, $^4J_{FP} = 8.66$ Hz). ESI MS: 327.13 ([M+H]⁺) Elemental Analysis: Calc. C, 44.18; H, 6.49; Found. C, 44.49.; H, 6.51

2b. *t*-Bu₃PCH₂C(CF₃)₂OLi

As for **2a** except using *t*-Bu₃PCH₂C(CF₃)₂OH (122 mg, 0.37 mmol). Yield. 104 mg, 0.31 mmol, 85 % ^1H NMR (toluene-d₈): δ 2.13 (d, $^2J_{HP} = 5.62$ Hz, 2H, CH₂), 1.07 (d, $^3J_{HP} = 11.98$ Hz, 18H, C(CH₃)₃). ^{31}P { ^1H } (toluene-d₈): δ 11.48 (br s). ^{19}F NMR (toluene-d₈): δ -77.92 (dt, $^4J_{FP} = 10.41$ Hz, $^4J_{FH} = 5.2$ Hz). ESI MS: 327.13 ([M-Li+2H]⁺) Elemental Analysis: Calc. C, 43.39; H, 6.07; Found. C, 43.71.; H, 5.90

2c. *t*-Bu₃PCH₂C(CF₃)₂OB(C₆F₅)₂.

Inside a glovebox, **2b** (100 mg, 0.3 mmol) and chlorobis(perfluorophenyl)boron (115 mg, 0.3 mmol) were weighed out in to two vials, and each dissolved in toluene (5 mL). The chlorobis(perfluorophenyl)boron solution was added dropwise via syringe over 10 mins with stirring. The mixture immediately became turbid. After 30 mins stirring, the solution was filtered through a glass fibre plug into a schlenk flask. The flask was removed, and the solution concentrated to ca. 2 mL, precipitating a white crystalline material. The supernatant was removed via cannula and the solids washed with hexane (5 mL), which was again removed via cannula. The solids were dried under vacuum, transferred to a glove box and isolated Yield. 67 mg, 0.10 mmol, 65 %. ^1H NMR (DCM-d₂): δ 2.53 (d, $^2J_{HP} = 9.53$ Hz, 2H, CH₂), 1.41 (d, $^3J_{HP} = 13.92$ Hz, 18H, C(CH₃)₃). ^{31}P { ^1H } (DCM-d₂): δ 47.5 (br s, $\nu_{1/2} = 120$ Hz). ^{11}B { ^1H } (DCM-d₂): δ 4.5 (s). ^{13}C { ^1H } (toluene-d₈): δ 146.6 (d, $^1J_{CF} = 236$

Hz, m-C), 140.1 (d, $^1J_{CF}$ = 237 Hz, p-C), 137.2 (d, $^1J_{CF}$ = 240 Hz, o-C), δ 123.2 (q, $^1J_{CF}$ = 236 Hz, CF₃), 37.4 (d, $^1J_{CP}$ = 12.72 Hz, CH₂) 29.9 (s, CH₃), 21.2 (d, $^1J_{CP}$ = 36.1 Hz, C(CH₃)₃) 29.6 (d, $^3J_{CP}$ = 13.27 Hz, CH₃). Signal for *ipso*-C and C(CF₃)₂ not observed. ¹⁹F NMR (DCM-d₂): δ -74.84 (br. s, 6F, CF₃), -129.29 (br. s, 4F, o-F), -157.61 (t, $^2J_{FF}$ = 20.56 Hz, 2F, p-F), -164.0 (br. s, 6F, m-F), Elemental Analysis: Calc. C, 43.01; H, 3.01; Found. C, 43.21.; H, 3.31

2d. *t*-Bu₃P(H)CH₂C(CF₃)₂O(H)B(C₆F₅)₂.

Inside a glovebox **1b** (75.0 mg, 0.23 mmol) and bis(perfluorophenyl)borane (79.5 mg, 0.23 mmol) weighed out in to two small vials, and each dissolved in toluene (5 mL). The solutions were mixed in a schlenk flask, including small toluene washes of the vial. A white microcrystalline solid precipitated from the homogenous solution within *ca.* 1 min. The mixture was allowed to stand overnight before the supernatant was decanted and the solids washed with hexane. After drying, **1d** was obtained as a white solid. Yield 127.0 mg, 0.19 mmol, 83 %. ¹H NMR (DCM-d₂): δ 6.31 (d, $^1J_{HP}$ = 499 Hz 1H, PH), 4.02 (br s, 1H, BH), 2.68 (dd, $^3J_{HH}$ = 12.3 Hz, $^3J_{HP}$ = 3.67 Hz, 2H, CH₂), 1.45 (d, $^3J_{HP}$ = 16.88 Hz, 18H, C(CH₃)₃). ³¹P (DCM-d₂): δ 35.57 (doublet of multiplets, $^2J_{PH}$ = 496 Hz). ¹³C {¹H} (toluene-d₈): δ 147.6 (d, $^1J_{CF}$ = 237 Hz, m-C), 138.5 (d, $^1J_{CF}$ = 239 Hz, p-C), 136.4 (d, $^1J_{CF}$ = 240 Hz, o-C), δ 123.5 (q, $^1J_{CF}$ = 291 Hz, CF₃), 37.4 (d, $^1J_{CP}$ = 12.72 Hz, CH₂) 29.9 (s, CH₃), 21.2 (d, $^1J_{CP}$ = 36.1 Hz, C(CH₃)₃) 29.6 (d, $^3J_{CP}$ = 13.27 Hz, CH₃). Signal for *ipso*-C and C(CF₃)₂ not observed. ¹⁹F NMR (DCM-d₂): δ -71.16 (s, 6F, CF₃), -134.26 (br. s, 4F, o-F), -162.31 (t, $^2J_{FF}$ = 20.56 Hz, 2F, p-F), -166.30 (m, 6F, m-F), ESI MS: 671.12 ([M-H]⁺), Elemental Analysis: Calc. C, 42.88; H, 3.30; Found. C, 42.59; H, 3.59.

1. D. J. Parks, W.E. Piers,, and, G. P. A. Yap, *Organometallics* 1998, **17**, 5492.