ELECTRONIC SUPPLEMENTRAY DATA

Small Molecule Activation by Solid Phase Frustrated Lewis Pairs

Jun-Yi Xing, Jean-Charles Buffet, Nicholas H. Rees, Peter Nørby and Dermot O'Hare*

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General methods and materials

All reactions were carried out on double-manifold gas-inlet (N2, H2)/vacuum line or in an MBraun 130-BG glovebox under a nitrogen atmosphere, unless indicated otherwise. H₂ (BOC) was dried by passage through a column of activated molecular sieves prior to use. Toluene was degassed by sparging with N₂, passed through a column of activated molecular sieves in a commercially available solvent-purification system, and stored over a potassium mirror under N₂. NMR solvents were dried over Na/K (C₆D₆) or CaH₂ (CD₃OD) respectively, distilled under reduced pressure, freeze-pump-thaw degassed three times prior to use. Silica (provided by SCG Chemicals) were heated to 500 °C under vacuum for 4 hours, and stored under N₂. 1,3,5,7,9,11-Octaisobutyltetracyclo[7.3.3.1^{5,11}]octasiloxaneendo-3,7-diol was purchased from Sigma-Aldrich, and used without further purification. HB(C_6F_5)₂¹ and \equiv SiOB(C₆F₅)₂^{2,3} were prepared according to published procedures. DRIFT spectra were recorded under N2 at room temperature in a transmission mode on a Bio-Rad FTS 7000 FTIR spectrometer. For background and sample spectrum, 50 scans were recorded at a resolution of 4 cm-1. Self-supporting pellets were made by pressing a finely grinded powder containing 1-2 mg of samples and 5 mg of KBr with a hand press. The sample pellets were loaded into air-tight cells with KBr windows inside the glovebox prior to measurements. Solution-state ¹H, ¹¹B ³¹P and ¹⁹F NMR spectrum were recorded at room temperature on Bruker 400 Avance III HD NanoBay 400 spectrometer using quartz NMR tubes with standard J. Young valve. All solution state NMR spectra were referenced internally to the residual protio solvent signals, and chemical shifts are reported in ppm. Solid-state ²H, ¹³C, ¹¹B, ¹⁹F and ³¹P MAS NMR spectra were collected by Dr. Nick Rees (University of Oxford) on a Bruker Avance III HD 400 MHz Solid State NMR Spectrometer. Samples were packed in 3.2mm ZrO₂ rotors and spun at the magic angle (54.71°). ²H, ¹⁹F, ³¹P and ¹¹B NMR spectra were collected at spin rates of 10, 24 kHz. Chemical shifts for all solid-state MAS NMR spectra were reported in ppm.

Preparation $[\equiv SiOB(C_6F_5)_2][^tBu_3P]$ (1)

≡SiOB(C₆F₅)₂ (100 mg, 0.048 mmol borane) and ^tBu₃P (9.7 mg, 0.048 mmol) were combined in toluene (10 mL) in an ampoule. After 2 hours of stirring at room temperature, the solid was filtered, washed with toluene (3 x 10 mL) and dried *in vacuo* for 2 h. ¹¹B{¹H}-{¹⁹F} DEPTH NMR (24 kHz MAS): δ_{iso} 1.0. ³¹P HPDEC NMR (24 kHz MAS): δ_{iso} 48. ¹⁹F DP NMR (24 kHz MAS): δ_{iso} −144 (*o*−C₆F₅), δ_{iso} −162 (*p*−C₆F₅), δ_{iso} −169 (*m*−C₆F₅). IR (cm⁻¹): 3690 (br, wk), 2946 (m), 2919 (m), 1654 (w), 1518 (m), 1496 (m), 1227 (st), 1102 (st).

Reaction of (1) with H₂ or D₂ to form $[=SiOB(C_6F_5)_2(H \text{ or } D)][^tBu_3P(H \text{ or } D)]$ (2)

A toluene slurry containing (1) (100 mg, 0.048 mmol FLP) in an ampoule was freeze-pump-thaw degassed three times, and filled with H₂ (2 bar). The mixture was left stirring in an oil bath for 72 h at 65 °C. The supernatant was removed and the solid was washed with 3 x 15 mL dry toluene followed by drying *in vacuo* for 4 hours. ¹⁹F DEPTH NMR (10 kHz MAS): $\delta_{iso} -138$ ($o-C_6F_5$), $\delta_{iso} -169$ ($p-C_6F_5$), $\delta_{iso} -172$ ($m-C_6F_5$). ¹¹B-¹H CP NMR (10 kHz MAS): $\delta_{iso} -2.14$ (B–H). ³¹P-¹H CP NMR (10 kHz MAS): $\delta_{iso} 54$ (P-H). ²H DP NMR (10 kHz MAS): $\delta_{iso} 8.5$ (v. br).

Reaction of (1) with CD₃OD to form $[=SiOB(OCD_3)(C_6F_5)_2][^tBu_3PD]$ (3)

CD₃OD (2.2 µL, 0.048 mmol) was added to a toluene slurry containing (1) (100 mg, 0.048 mmol FLP) in an ampoule. After stirring for 16 h at 25 °C, the solid was filtered, washed with dry toluene (3 x 15 mL), followed by drying *in vacuo* for 4 hours. ²H HAHNECHO NMR (10 kHz MAS): δ_{iso} 3.21 (B–OCD₃) (P–D is not observed). ¹¹B DEPTH NMR (10 kHz MAS): δ_{iso} 0 (B–OCD₃). ³¹P CP NMR (10 kHz MAS): δ_{iso} 54 (P-H) IR (cm⁻¹): 3703 (w, br), 2083 (v. w), 1648 (w), 1515 (m), 1487 (m), 1467 (m), 1212 (st), 1101 (st).

Reaction of $HB(C_6F_5)_2$ with 1,3,5,7,9,11-Octaisobutyltetracyclo[7.3.3.1^{5,11}]octasiloxane-*endo*-3,7-diol

1,3,5,7,9,11-Octaisobutyltetracyclo[7.3.3.1^{5,11}]octasiloxane-*endo*-3,7-diol (9 mg, 0.01 mmol) and HB(C₆F₅)₂ (7 mg, 0.02 mmol) were combined in BrC₆D₅ (0.5 mL) in a Young's tap quartz NMR tube. The reaction completed over night at 25 °C. ¹⁹F NMR (BrC₆D₅, 376.5 MHz): δ –132 (m, 2F, *o*-C₆F₅H), δ –149 (m, 1F, *p*-C₆F₅), δ –161.5 (m, 2F, *m*-C₆F₅). ¹¹B NMR (BrC₆D₅, 128.4 MHz): δ 40.2 (br).

Preparation of [T₈(OB(C₆F₅)₂)₂][(^tBu₃P)₂] (4)

T₈(OB(C₆F₅)₂)₂ (16 mg, 0.01 mmol borane) and P*t*Bu₃ (4.1 mg, 0.02 mmol) were combined in in BrC₆D₅ (0.5 mL) in a Young's tap quartz NMR tube. ¹⁹F NMR (BrC₆D₅, 376.5 MHz): δ –131.93 (m, 2F, *o*-C₆F₅H), δ –148.75 (m, 1F, *p*-C₆F₅), δ –161.57 (m, 2F, *m*-C₆F₅). ¹¹B NMR (BrC₆D₅, 128.4 MHz): δ 40.4 (br). ³¹P {¹H} NMR (BrC₆D₅, 162 MHz): δ 62.

Reaction of (4) with H₂ to form $[T_8(OB(H)(C_6F_5)_2)_2][(^tBu_3PH)_2]$ (5)

A Yong's tap quartz NMR tube containing a solution of (4) (20 mg, 0.01 mmol FLP in BrC₆D₅) was freeze-pump-thaw degassed three times, and pressurised with H₂ (2 bar). ¹H NMR (BrC₆D₅, 400 MHz): 5.4 (d, ¹J_{HP} = 444 Hz ¹Bu₃P–**H**), 0.64 (d, ³J_{HP} = 15.5 Hz, ((**H**₃C)₃C)₃PH)), B-**H** was not observed. ¹⁹F NMR (BrC₆D₅, 376.5 MHz): -133.03 (m, 2F, *o*-C₆F₅H), -161.45 (m, 1F, *p*-C₆F₅), -165.8 (m, 2F, *m*-C₆F₅). ¹¹B NMR (BrC₆D₅, 128.4 MHz): 2.75 (br). ³¹P NMR (BrC₆D₅, 162 MHz): 59 (dm, ¹J_{PH} = 444 Hz, ³J_{PH} = 15.5 Hz). **IR (cm⁻¹):** 2959 (m), 2929 (m), 2870 (m), 1643 (s), 1515 (s), 1482 (s), 1464 (s), 1404 (m), 1385 (m), 1366 (m), 1323 (w), 1294 (w), 1272 (w), 1262 (w), 1227 (m), 1172 (m), 1107(s), 1032, (w), 967 (m).



Figure S1. DRIFT spectrum of $[\equiv SiOB(OCD_3)(C_6F_5)_2][^tBu_3PD]$ showing C–D bond stretch at 2083 cm⁻¹.



Figure S2. Solid state ²H DP MAS NMR spectrum of 2 at 10 kHz spinning rate.



Figure S3. Solid-state ¹¹B DEPTH NMR spectrum of $[\equiv SiOB(OCD_3)(C_6F_5)_2][^tBu_3PD]$, at 10 kHz MAS.



Figure S4. Solid-state ³¹P CP NMR spectrum of $[\equiv SiOB(OCD_3)(C_6F_5)_2][^tBu_3PD]$, at 10 kHz MAS. [#]Denotes excess unreacted ^tBu_3P.



Figure S5. Solution-state ¹H NMR spectrum of compound 4 [T₈(OB(C₆F₅)₂)₂][(^tBu₃P)₂] in BrC₆D₅.



Figure S6. Solution-state ¹¹B NMR spectrum of compound 4 $[T_8(OB(C_6F_5)_2)_2][({}^tBu_3P)_2]$ in BrC₆D₅. Signal mrked by *.



Figure S7. Solution-state ³¹P NMR spectrum of compound 4 [T₈(OB(C₆F₅)₂)₂][(^tBu₃P)₂] in BrC₆D₅.



Figure S8. Solution-state ¹H NMR spectrum of compound **5** $[T_8(OB(H)(C_6F_5)_2)_2][({}^{t}Bu_3PH)_2]$ in BrC₆D₅ after 2 h reaction at room-temperature under 2 bar of H₂ showing ${}^{1}J_{H-P}$ coupling at 4.4 ppm.



Figure S9. Solution-state ³¹P NMR spectrum of compound 5 $[T_8(OB(H)(C_6F_5)_2)_2][(^{t}Bu_3PH)_2]$ in BrC₆D₅ after 2 h reaction at room-temperature under 2 bar of H₂ showing ¹J_{P-H} coupling at 59 ppm



Figure S10. Solution-state ¹¹B NMR spectrum of compound **5** $[T_8(OB(H)(C_6F_5)_2)_2][(^4Bu_3PH)_2]$ in BrC₆D₅ after 2 h reaction at room-temperature under 2 bar of H₂ Signal marked by *.

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