Supporting Information for

Activation of Hydrogen and Hydrogenation Catalysis by a Borenium Cation

By:

Jeffrey M. Farrell, Jillian A. Hatnean and Douglas W. Stephan*

Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, CANADA M5S 3H6

General considerations

All synthetic manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an MBraun glove box and a Schlenk vacuum-line. Pentane and toluene were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Bromobenzene-d_5, chlorobenzene, dichloromethane, and dichloromethane-d_2 were each dried over CaH_2, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. Toluene-d_8 was dried over Na/benzophenone, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer unless otherwise noted. Commercially available substrates and 9-BBN dimer were obtained from Sigma-Aldrich. Liquid substrates were stored over 4 Å molecular sieves or distilled from tri*iso*buylaluminum and stored in an inert atmosphere glovebox. Solid substrates were dried *in vacuo* and stored in an inert atmosphere glovebox. Tris(pentafluorophenyl)borane was purchased from Boulder Scientific and used without further purification. Trityl tetrakis(pentafluorophenyl)borate was obtained from Nova Chemicals and used without further purification.. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure^{TM} gas purifier. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{11}B: 15% $(Et_2O)BF_3$;

^{19}F: 15% $(Et_2O)BF_3$; ^{31}P: 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Mass spectrometry was carried out using and AB/Sciex QStar mass spectrometer with an ESI source. The compounds 1,3-di*iso*propylimidazol-2-ylidene[1] and $[^tBu_3PH][B(C_6F_5)_4]$[2] were prepared using literature methods.

Synthesis of 1,3-di*iso*propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (I^iPr_2)(HBC_8H_{14}) (1).

In an inert atmosphere glovebox, 1,3-di*iso*propylimidazol-2-ylidene (813.8 mg, 5.276 mmol, 2 equiv.) and 9-BBN dimer (707.3 mg, 2.638 mmol, 1 equiv.) were weighed into vials. 9-BBN was stirred in 7 mL toluene as a solution of 1,3-di*iso*propylimidazol-2-ylidene in 5 mL toluene was added dropwise with 2 × 1 mL additional toluene. The vial was capped and stirred for four hours at room temperature. The solution was concentrated *in vacuo* to approximately 2 mL and recrystallized in a –35 °C glovebox freezer. The supernatant was decanted and the colorless crystals were washed with cold pentane (3 × 1 mL) and dried *in vacuo* to give (I^iPr_2)(HBC_8H_{14}) (1.1533g , 75.8% yield) as a white crystalline solid. ^1H NMR (400 MHz, C_6D_5Br, 298 K): δ 6.55 (s, 2H), 5.20 (m(7), 2H, $^3J_{HH}$ = 7Hz), 2.40-1.36 (br, 14H), 1.11 (d, 12H, $^3J_{HH}$ = 7Hz), No observable B-H peak. ^{11}B NMR (128 MHz, C_6D_5Br, 298 K): δ –16.64 (d, $^1J_{BH}$ = 80Hz). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br, 298 K): 125.6, 115.5, 48.2, 38.2, 31.6, 25.5, 24.0, 23.6, 23.4 (br). Anal. Calcd. for $C_{17}H_{32}BN_2$: C 74.18%, H 11.72%, N 10.18%. Found: C 74.36%, H 11.44%, N 10.16%

Synthesis of [1,3-di*iso*propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane] [tetrakis (pentafluorophenyl)borate] [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$]• 0.66 C_6H_5Cl (2 • 0.66 C_6H_5Cl).

[1] Schaub, T.; Backes, M.; Radius, U. *Organometallics* **2006,** *25,* 4196-4206.

[2] Yoon, S.-C.; Won, Y.-C.; Park, Y.-W.; Chun, S.-H.; Choi, D.-S.; Kim, W.-K; Lim, T.-S.; Kim, H.; Lee, J.-M.; Paik, K.-L., Method Of Producing Cyclic Olefin Polymers Having Polar Functional Groups, Olefin Polymer Produced Using The Method And Optical Anisotropic Film Comprising The Same. Patent: *WO 2006004376* , July 5, 2005.

In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (1.161 g, 4.233 mmol, 1 equiv.) was dissolved in 10 mL dry toluene in a 100 mL Shlenk flask equipped with a stir bar. Trityl tetrakis(pentafluorophenyl)borate (3.904 g, 4.233 mmol, 1 equiv.) was weighed into a vial and transferred with 20 + 10 mL toluene to the solution of I^iPr_2-BBN while stirring. The mixture was stirred overnight during which time a gelatinous precipitate was generated. The solvent was removed *in vacuo* and the off-white residue redissolved in 20 mL chlorobenzene. This solution was cooled to –35 °C in a glovebox freezer to afford colourless crystals. The chlorobenzene was decanted and the crystals washed with 5 × 1 mL pentane to give an off-white powder. This powder was again dissolved in 20 mL chlorobenzene and cooled to –35 °C in a glovebox freezer to afford colourless crystals. The chlorobenzene was decanted and the crystals washed with 5 × 1 mL pentane. The sample was dried *in vacuo* at room temperature for 24 hours to give [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$]•0.66 C_6H_5Cl as a white powder (3.521 g, 81.0% yield). Ratio of C_6H_5Cl to [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$] was determined by ^{1}H NMR and confirmed by elemental analysis. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) (C_6H_5Cl omitted): δ 7.55 (s, 2H), 4.65 (m(7), 2H, $^3J_{HH}$ = 6.7 Hz), 2.34-2.13 (m, br, 6H), 2.08-2.01 (m, br, 2H), 1.99-1.85 (m, br, 4H), 1.62-1.50 (m, br, 2H), 1.58 (d, 12H, $^3J_{HH}$ = 6.7 Hz). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 83.8 (br), –16.7. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K, partial) (C_6H_5Cl omitted): δ 122.0, 53.5, 34.9, 33.9 (br), 24.1, 22.8. ^{19}F NMR (376 MHz, CD_2Cl_2, 298K): δ –134.1 (*o*-F, m), –164.7 (*p*-F, t, $^3J_{FF}$ = 20 Hz), –168.6 (*m*-F, m). Anal. Calcd. for $C_{41}H_{30}B_2F_{20}N_2$• 0.66(C_6H_5Cl): C 52.61%, H 3.27%, N 2.73%. Found: C 52.56%, H 3.46%, N 2.64%.

In situ **generation of [1,3-di*iso*propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane] [tetrakis(pentafluorophenyl)borate] [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$] (2).**

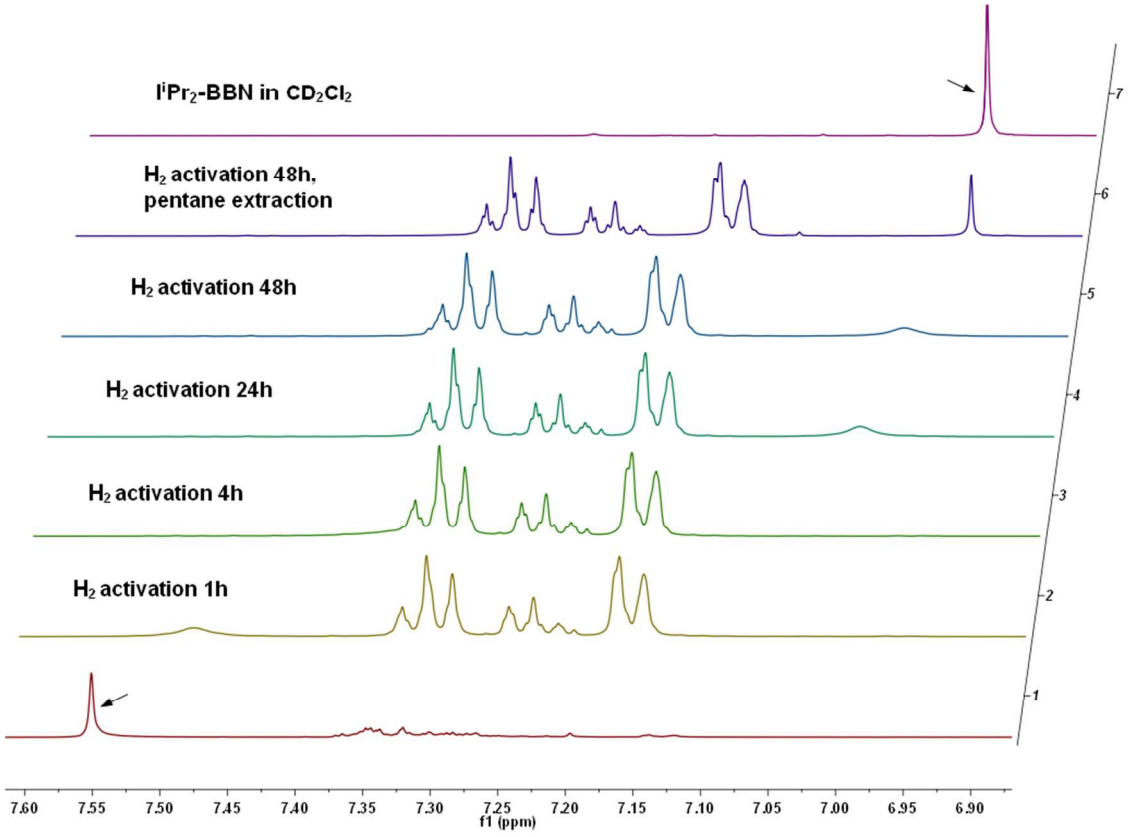
In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (17.3 mg, 0.0631 mmol, 1 equiv.) and trityl tetrakis(pentafluorophenyl)borate (58.2 mg, 0.0631 mmol. 1 equiv.) were weighed into vials. Compound **1** was dissolved in 0.2 mL CD_2Cl_2 and then trityl tetrakis(pentafluorophenyl)borate was transferred to this solution with 0.4 mL CD_2Cl_2. The mixture was transferred to a J. Young NMR tube. ^1H, ^{11}B, and ^{19}F NMR spectra were consistent with the formation of triphenylmethane and [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$].

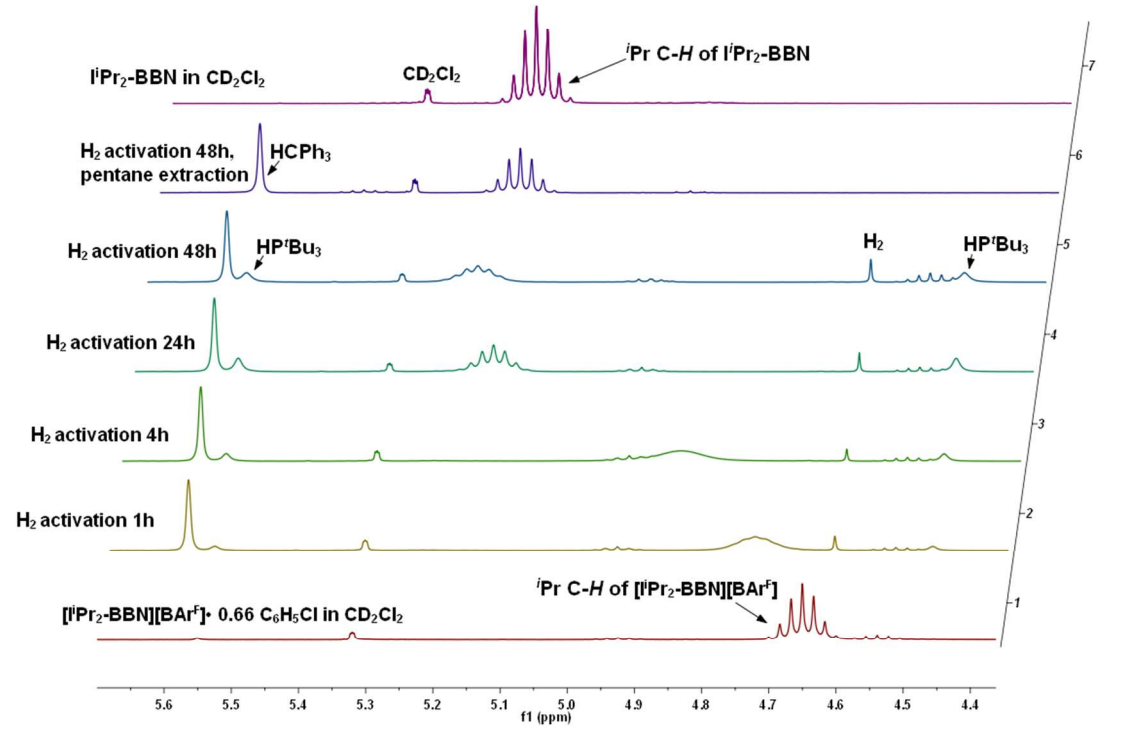
Activation of dihydrogen by compound 2 and P^tBu_3.

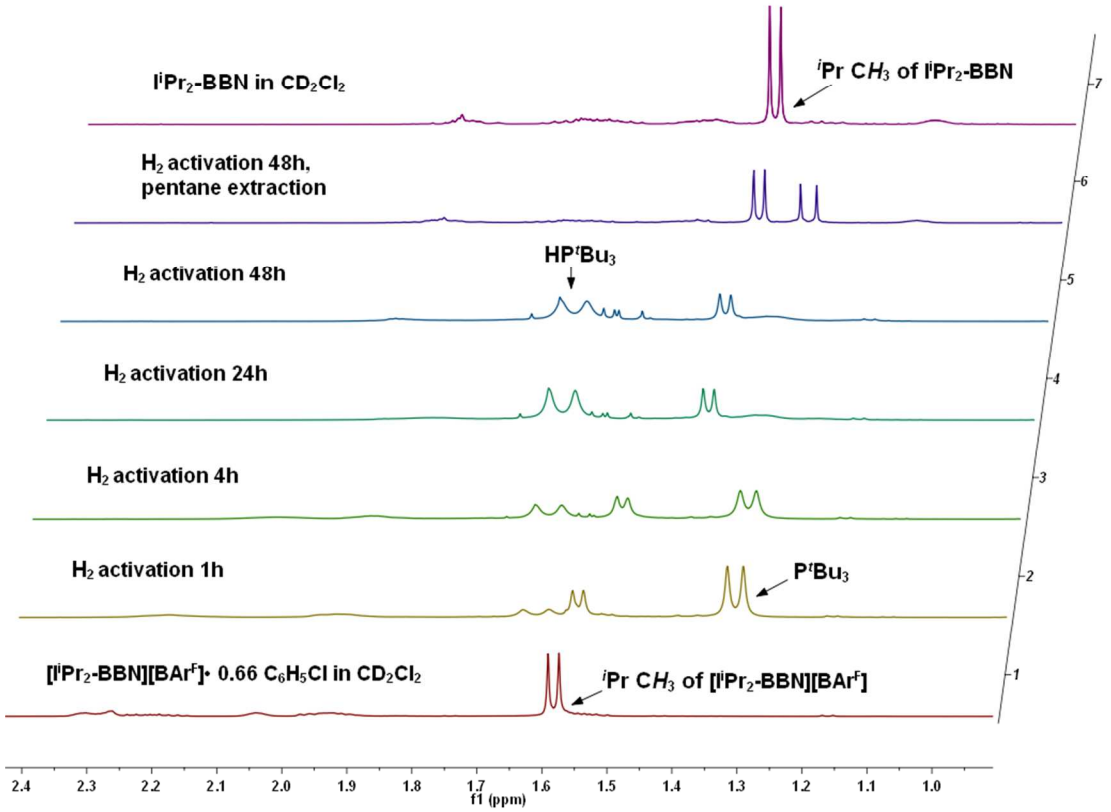
In an inert atmosphere glovebox, a sample of [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$] was generated *in situ* by a procedure similar to that described above. The sample (0.0631 mmol) was added to a vial containing P^tBu_3 (12.7 mg, 0.0631 mmol, 1 equiv.) and returned to a J. Young NMR tube. ^1H, ^{11}B, and ^{31}P NMR spectra are identical to those of the starting materials. The tube was sealed and subjected to three freeze-pump-thaw cycles. The tube was then frozen, evacuated and backfilled with hydrogen gas. The tube was thawed and hydrogen activation products were observed by ^1H, ^{11}B and ^{31}P NMR spectroscopy at 1h, 4h, 24h and 48h intervals.

In order to remove [$^tBu_3PH$][$B(C_6F_5)_4$] and hydrolysis products from the newly generated I^iPr_2-BBN, the sample was decanted after 48 h into a vial in the glovebox and concentrated *in vacuo*. The residue was extracted with 3 × 1 mL pentane, and the isolated pentane layer was concentrated *in vacuo.* This residue was redissolved in CD_2Cl_2 and ^1H, ^{11}B and ^{31}P NMR spectra were collected.

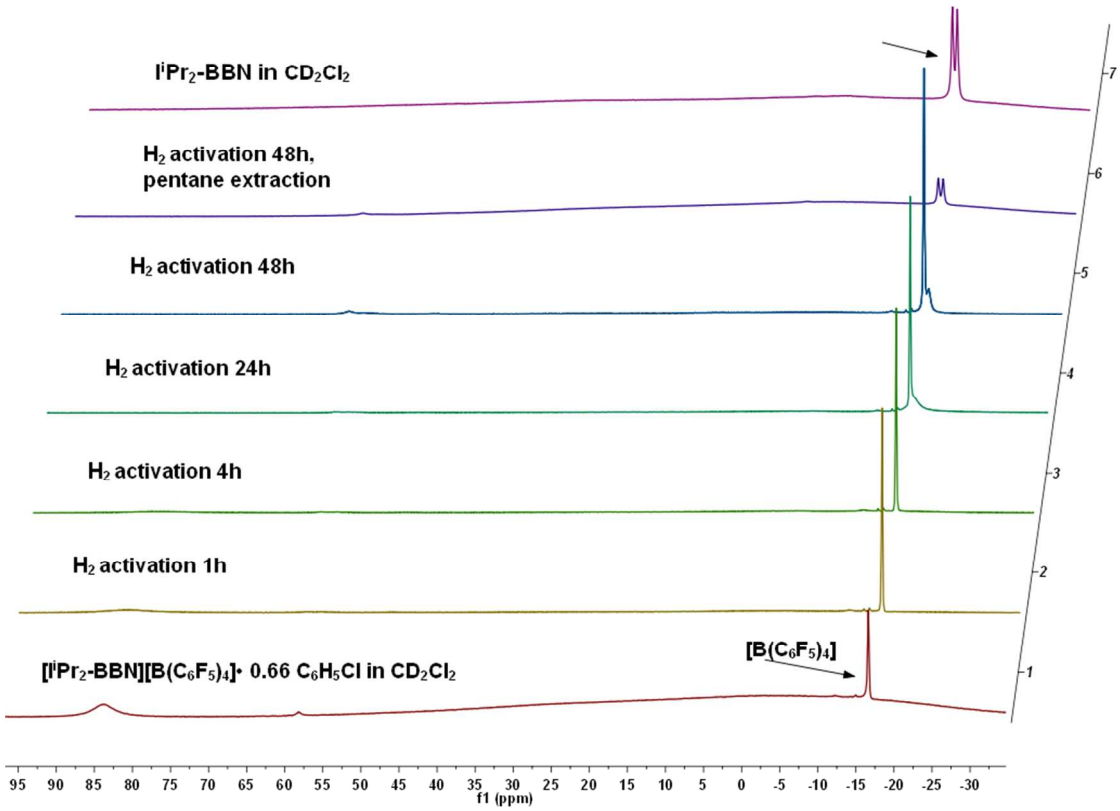
^{1}H NMR:


I^{i}Pr$_2$-BBN in CD$_2$Cl$_2$
H$_2$ activation 48h, pentane extraction
H$_2$ activation 48h
H$_2$ activation 24h
H$_2$ activation 4h
H$_2$ activation 1h
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)

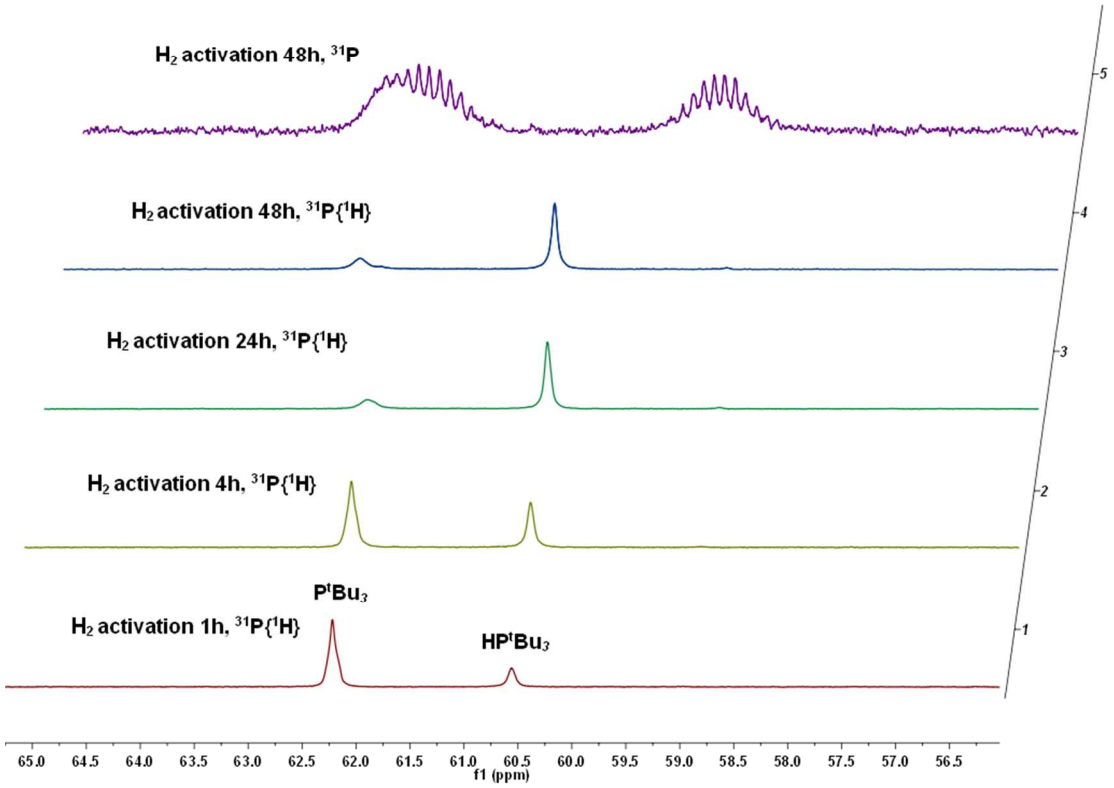

I^{i}Pr$_2$-BBN in CD$_2$Cl$_2$
CD$_2$Cl$_2$
^{i}Pr C-*H* of I^{i}Pr$_2$-BBN
H$_2$ activation 48h, pentane extraction
HCPh$_3$
H$_2$ activation 48h
HP^{t}Bu$_3$
H$_2$
HP^{t}Bu$_3$
H$_2$ activation 24h
H$_2$ activation 4h
H$_2$ activation 1h
^{i}Pr C-*H* of [I^{i}Pr$_2$-BBN][BAr^F]
[I^{i}Pr$_2$-BBN][BAr^F]• 0.66 C$_6$H$_5$Cl in CD$_2$Cl$_2$
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)


^{i}Pr CH_3 of ^{i}Pr$_2$-BBN
^{i}Pr$_2$-BBN in CD_2Cl_2
H_2 activation 48h, pentane extraction
H_2 activation 48h
HP^{t}Bu$_3$
H_2 activation 24h
H_2 activation 4h
H_2 activation 1h
P^{t}Bu$_3$
[^{i}Pr$_2$-BBN][BAr^{F}]• 0.66 C_6H_5Cl in CD_2Cl_2
^{i}Pr CH_3 of [^{i}Pr$_2$-BBN][BAr^{F}]
f1 (ppm)

^{11}B NMR:


^{i}Pr$_2$-BBN in CD_2Cl_2
H_2 activation 48h, pentane extraction
H_2 activation 48h
H_2 activation 24h
H_2 activation 4h
H_2 activation 1h
[^{i}Pr$_2$-BBN][B(C_6F_5)$_4$]• 0.66 C_6H_5Cl in CD_2Cl_2
[B(C_6F_5)$_4$]
f1 (ppm)

^{31}P NMR:



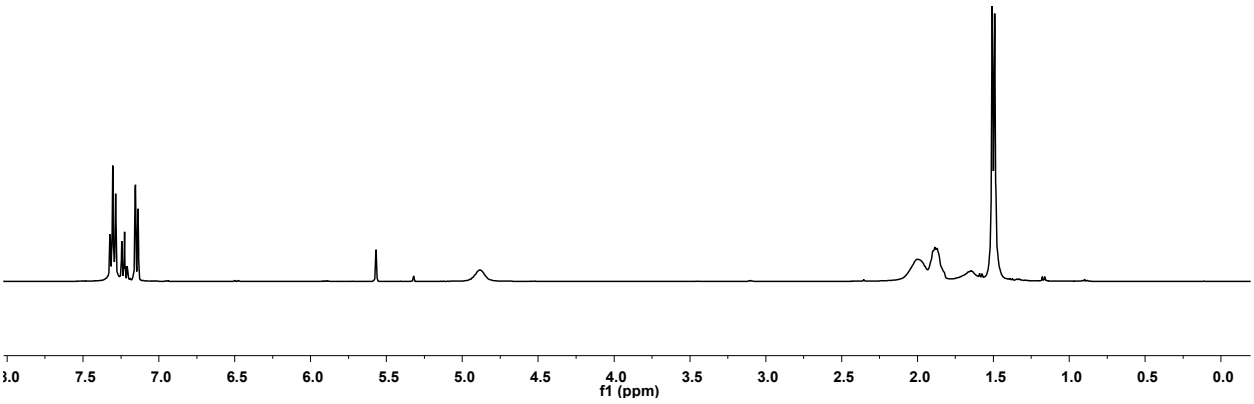
NMR spectra of mixtures containing **1** and **2** were stoichiometry-dependent at room temperature. ^{11}B NMR silence is observed in the initial stages of dihydrogen activation and ^{1}H NMR shifts corresponding to **1** and **2** coalesce at chemical shifts intermediate to each prepared independently.

To confirm that this was a stoichiometry-dependent occurrence (i.e. rapid hydride transfer or bridging hydride between **1** and **2**), a 1:1 mixture of **1** and **2** was prepared and ^{1}H and ^{11}B NMR shifts were measured.

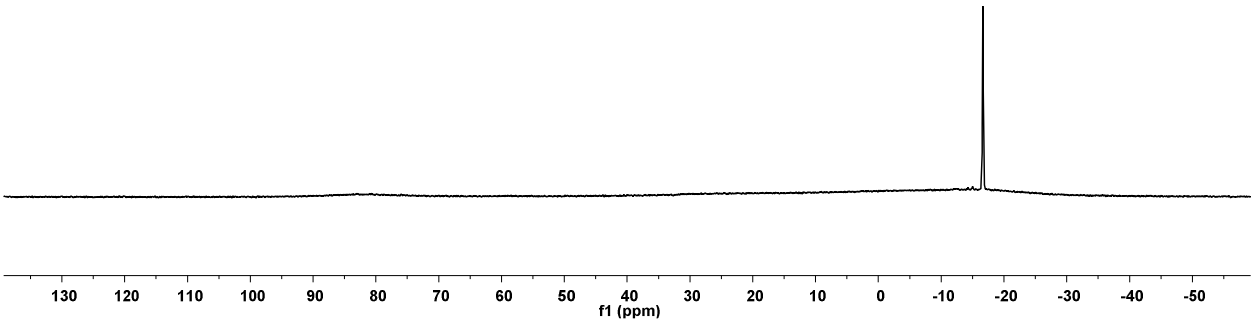
Generation of a 1:1 mixture of (I^iPr_2)(HBC_8H_{14}) (1) and [(I^iPr_2)(BC_8H_{14})][$B(C_6F_5)_4$] (2).

In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (25.0 mg, 0.0911 mmol, 2 equiv.) and trityl tetrakis(pentafluorophenyl)borate (42.0 mg, 0.0455 mmol, 1 equiv.) were weighed into vials. I^iPr_2-BBN was dissolved in 0.2 mL CD_2Cl_2 and trityl tetrakis(pentafluorophenyl)borate was transferred to this solution with 0.4 mL CD_2Cl_2. The solution was transferred to an NMR tube and ^1H and ^{11}B NMR shifts were measured:

^1H NMR:



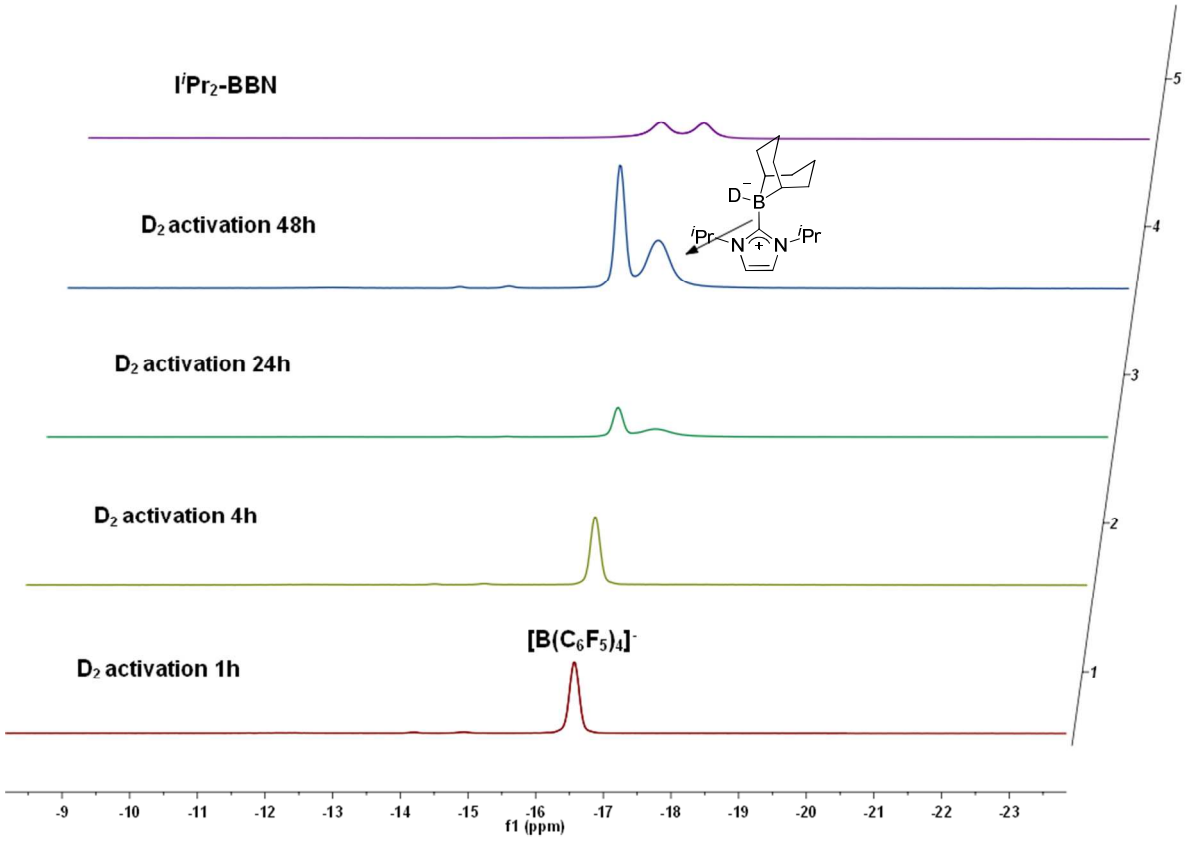
^{11}B NMR:



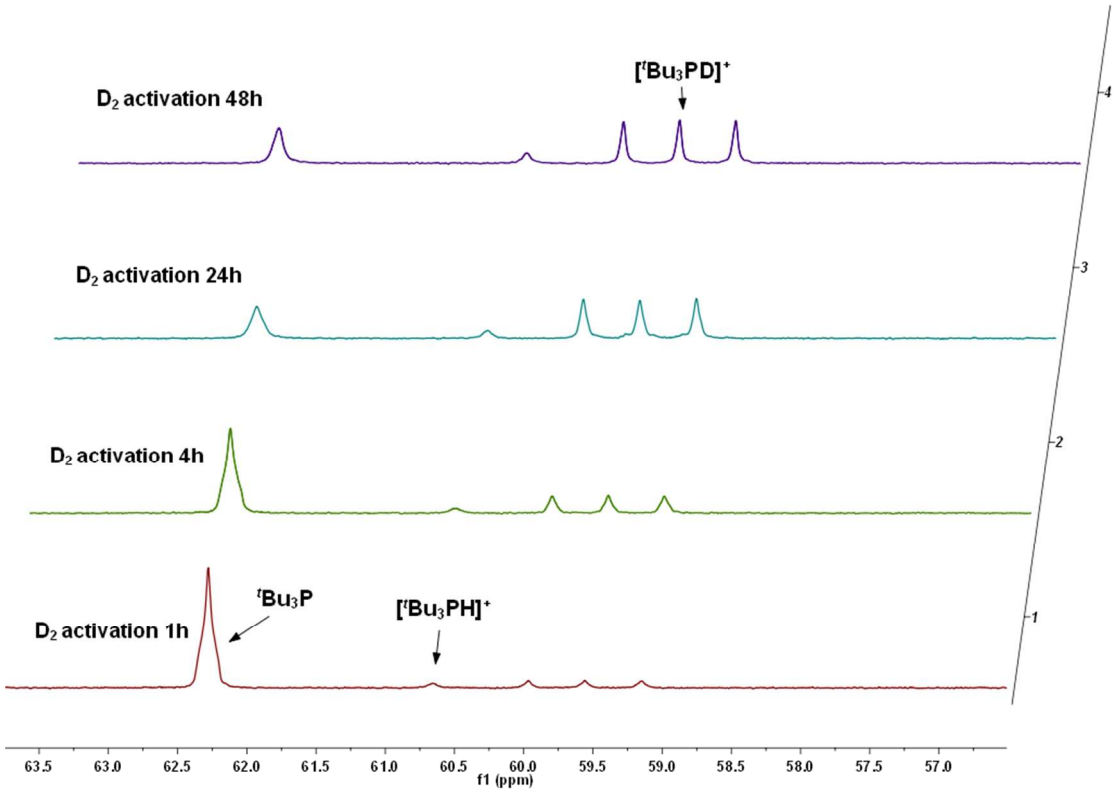
Activation of deuterium with $[(I^iPr_2)(BC_8H_{14})][B(C_6F_5)_4]$ and P^tBu_3.

Activation of D_2 was carried out in a procedure analogous to that used for the activation of dihydrogen; however, deuterium gas was used in place of hydrogen gas and CH_2Cl_2 was used in place of CD_2Cl_2.

^{11}B NMR:



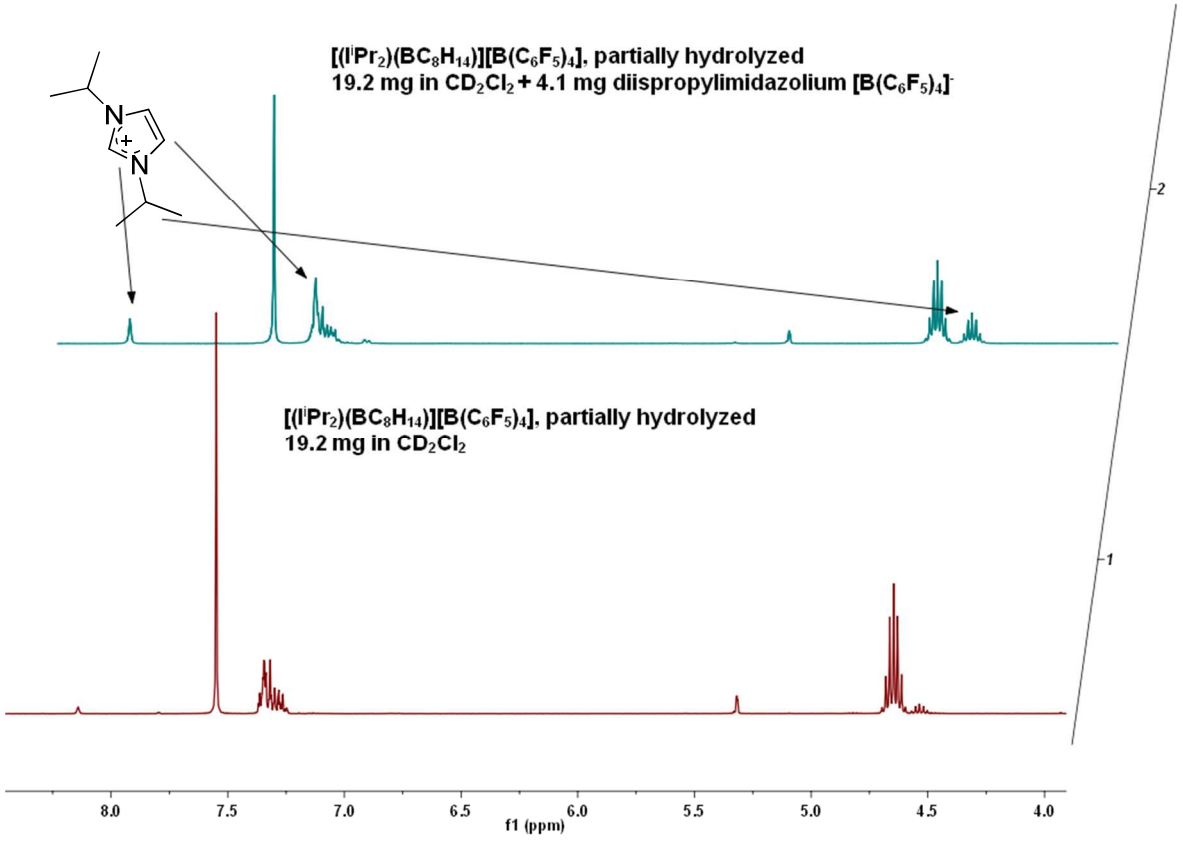
$^{31}P\{^{1}H\}$ NMR:



Minor peaks observed in some cases could be identified as hydrolysis products of $[(I^{i}Pr_2)(BC_8H_{14})][B(C_6F_5)_4]$ due to adventitious water. These peaks correspond to the known compound 9-hydroxy-9-borabicyclo[3.3.1]nonane (^{11}B NMR: δ 58)[3] and 1,3-di*iso*propyl-imidazolium tetrakis(pentafluorophenyl)borate. The compound 1,3-di*iso*propylimidazolium tetrakis(pentafluorophenyl)borate was synthesized independently and identified in partially hydrolyzed $[(I^{i}Pr_2)(BC_8H_{14})][B(C_6F_5)_4]$ through doping experiments:

[3] Köster, R.; Tsay, Y.-H.; Synoradzki, L. *Chem. Ber.* **1987**, *120*, 1117.

^{1}H NMR:



Synthesis of 1,3-di*iso*propylimidazolium tetrakis(pentafluorophenyl)borate.

A vial charged with di*iso*propylimidizolium chloride (0.05 g, 0.26 mmol, 1 equiv.) and trityl tetrakis(pentafluorophenyl)borate (0.244 g, 0.26 mmol, 1 equiv.) in 5 mL of CH_2Cl_2 was stirred for 1 h. The solvent was removed *in vacuo*, and the resultant white powder washed 3 times with 5 mL of pentane. The white solid was dried *in vacuo* to give 1,3-di*iso*propylimidazolium tetrakis(pentafluorophenyl)borate (0.18 g, 81% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.78 (s, 1H, NC*H*N); 7.34 (s, 2H, NC*H*=C*H*N); 4.61 (m(7), 2H, ^{i}Pr–C*H*, $^{3}J_{HH}$ = 6.5 Hz); 1.59 (d, 12H, ^{i}Pr–CH_3, $^{3}J_{HH}$ = 6.5 Hz). ^{11}B NMR (CD_2Cl_2, 128 MHz): δ –16.65 (s, [*B*(C_6F_5)$_4$]$^-$). ^{19}F NMR (CD_2Cl_2, 376 MHz): δ –133.11 (dm, 8F, *o*–C_6F_5, $^{3}J_{FF}$ = 18.6 Hz); –163.61 (t, 4F, *p*–C_6F_5, $^{3}J_{FF}$ = 20.6 Hz); –167.54 (dd, 8F, *m*–C_6F_5, $^{3}J_{FF}$ = 20.6 Hz, $^{3}J_{FF}$ = 18.6 Hz). ^{13}C{^{1}H}

NMR (CD_2Cl_2, 101 MHz): δ 148.64 (dm, 8C, *o*–C_6F_5, $^1J_{CF}$ = 240.15 Hz); 138.76 (dm, 4C, *p*–C_6F_5, $^1J_{CF}$ = 241.52 Hz); 138.80 (dm, 8C, *m*–C_6F_5, $^1J_{CF}$ = 245.64 Hz); 132.33 (s, 4C, *ipso*–C_6F_5); 130.18 (s, 1C, N*C*HN); 121.25 (s, 2C, N*C*H=*C*HN); 54.71 (s, 2C, *i*Pr–*C*H); 23.26 (s, 4C, *i*Pr–*C*H_3). Calcd for $C_9H_{17}N_2$: [M^+] 153.13917. Found: m/z 153.13936.

NMR scale reduction of *N*-benzylidene-*tert*-butylamine with I^iPr_2-BBN and [^{t}Bu$_3$PH][B(C_6F_5)$_4$].

In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (10.8 mg, 0.0394 mmol, 1 equiv.) and [^{t}Bu$_3$PH][B(C_6F_5)$_4$] (38.3 mg, 0.0434 mmol, 1.1 equiv.) were weighed into vials and transferred to a J. Young NMR tube with 0.6 mL C_6D_5Br. Upon mixing, no reaction could be observed between the two starting materials by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy. *N*-benzylidene-*tert*-butylamine (68.2 mg, 0.423 mmol, 10.7 equiv.) was added to the sample. ^{1}H, ^{11}B and ^{31}P NMR indicated the generation of P^{t}Bu$_3$ and [(I^iPr_2)(BC_8H_{14})][B(C_6F_5)$_4$] concomitant with the formation of ~10% *N*-benzyl-*tert*-butylamine. The tube was subjected to three freeze-pump-thaw cycles. The tube was then frozen, evacuated and backfilled with hydrogen gas. The tube was thawed and hydrogen activation products were observed by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy at 1h, 4h, 24h and 48h intervals. Further conversion of *N*-benzylidene-*tert*-butylamine to *N*-benzyl-*tert*-butylamine was monitored by ^{1}H NMR spectrsocopy at 24 h, 72 h and 120 h. At these intervals, P^{t}Bu$_3$ and [(I^iPr_2)(BC_8H_{14})][B(C_6F_5)$_4$] could be observed by ^{11}B and ^{31}P NMR spectroscopy; however, [^{t}Bu$_3$PH][B(C_6F_5)$_4$] and I^iPr_2-BBN were absent.

Procedures for elevated pressure reductions.

Procedure 1. (Entries 3, 9, 11)**:** In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (25.0 mg, 0.0912 mmol, 5 equiv. or 5.0 mg, 0.018 mmol, 1equiv.), [Ph_3C][B(C_6F_5)$_4$] (84.1 mg, 0.0912 mmol, 5 equiv. or 16.8 mg, 0.0182 mmol, 1 equiv.) and the unsaturated substrate (1.824 mmol, 100 equiv.) were weighed into vials. [Ph_3C][B(C_6F_5)$_4$] was transferred to the vial of I^iPr_2-BBN with 0.4 mL C_6H_5Cl. This solution was then transferred to the vial containing the unsaturated substrate with an additional 0.2 mL C_6H_5Cl. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was

purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in toluene-d_8 or $CDCl_3$. Conversion of unsaturated substrate to amine product was determined by ^1H NMR spectroscopy.

Entry 9 was isolated by removal of solvent *in vacuo* followed by column chromatography using 99:1 hexanes : EtOAc using silica gel pre-treated with diethylamine.

Procedure 2. (Entries 2, 5-8, 10, 12)**:** In an inert atmosphere glovebox, $[(I^iPr_2)(BC_8H_{14})][B(C_6F_5)_4]\bullet$ 0.66 C_6H_5Cl (18.7 mg, 0.0182 mmol, 1 equiv. or 93.6 mg, 0.09115 mmol, 5 equiv.) and the unsaturated substrate (1.824 mmol, 100 equiv.) were weighed into vials. $[(I^iPr_2)(BC_8H_{14})][B(C_6F_5)_4]\bullet$ 0.66 C_6H_5Cl was transferred to the vial containing the substrate with 0.6 mL CH_2Cl_2. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in $CDCl_3$. Conversion of unsaturated substrate to amine product was determined by ^1H NMR spectroscopy.

Entries 2, 5, 6, 7, and 12 were isolated by removal of solvent *in vacuo* followed by column chromatography using 9:1 hexanes : EtOAc using silica gel pre-treated with diethylamine.

Procedure 3. (Entry 1**):** Procedure 1 was followed with modification to omit $[Ph_3C][B(C_6F_5)_4]$. I^iPr_2-BBN was transferred directly to the substrate with 0.6 mL C_6H_5Cl without prior activation.

Procedure 4. (Entry 4)**:** Procedure 1 was followed with modification that toluene was used in place of C_6H_5Cl.

Product characterization data:

Isolated products were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as mass spectrometry and compared to literature values where applicable:

N-benzyl-*tert*-butylamine: Frøyen, P.; Juvvik, P. *Tetrahedron Lett.* **1995**, *36*, 9555-9558. (colourless oil Yield: 0.235 g, 79%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 and 7.23 (m, 4H, *o* and *m*–Ph–*H*); 7.15 (tt, 1H, *p*–Ph–*H*, $^{3}J_{HH}$ = 6.9 Hz, $^{4}J_{HH}$ = 1.6 Hz); 3.65 (s, 2H, CH_2); 1.11 (s, 9H, ^{t}Bu–CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.7 MHz): δ 141.37 (s, 1C, *ipso*–Ph–*C*); 128.21, 128.10, and 126.57 (s, 5C, Ph–*C*); 50.46 (s, 1C, ^{t}Bu–*C*); 47.14 (s, 2C, *C*H_2); 29.03 (s, 3C, ^{t}Bu–*C*H_3). HR-MS Calcd for $C_{11}H_{17}N$: [M^+] 164.14392. Found: m/z 164.14460.

N-*tert*-butyl-(3-methoxybenzyl)amine: (colourless oil Yield: 0.309 g, 88%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, 1H, 5–Ph–*H*, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 8.0 Hz); 6.93 (s, 1H, 2–Ph–*H*); 6.93 (m, 1H, 4–Ph–*H*); 6.78 (dd, 1H, 6–Ph–*H*, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 2.2 Hz); 3.80 (s, 1H, OCH_3); 3.71 (s, 2H, CH_2); 1.17 (s, 9H, ^{t}Bu–CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.7 MHz): δ 158.71 (s, 1C, *ipso*–Ph–*C*OMe); 141.75 (s, 1C, *ipso*–Ph–*C*); 128.35, 119.58, 121.84, and 111.35 (s, 4C, Ph–*C*); 54.14 (s, 1C, O*C*H_3); 49.88 (s, 1C, ^{t}Bu–*C*); 46.21 (s, 2C, *C*H_2); 28.00 (s, 3C, ^{t}Bu–*C*H_3). HR-MS Calcd for $C_{12}H_{19}NO$: [M^+] 194.15449. Found: m/z 194.15513.

N-cyclohexylpiperidine: Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 7543-7546. (colourless oil Yield: 0.259 g, 85%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.34 (dd, 4H, CH_2N, $^{3}J_{HH}$ = 5.3, 5.1 Hz); 2.08 (m, 1H, C*H*); 1.68 and 1.60 (d, 2H, $^{3}J_{HH}$ = 5.9 Hz); 1.45 (d, 1H, $^{3}J_{HH}$ = 6.2 Hz); 1.41 (dd, 4H, $^{3}J_{HH}$ = 6.1, 5.9 Hz); 1.38 (d, 1H, $^{3}J_{HH}$ = 6.2 Hz); 1.25 (m, 2H); 1.05 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz); 1.04 (d, 2H, $^{3}J_{HH}$ = 9.4 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.7 MHz): δ 64.17 (s, 1C, *C*H); 49.84 (s, 2C, *C*H_2N); 28.45 (s, 2C, CH*C*H_2); 26.24 (s, 2C, *C*H_2CH_2N); 25.94 (s, 3C, CHCH_2*C*H_2*C*H_2); 24.70 (s, 1C, *C*H_2CH_2CH_2N). HR-MS Calcd for $C_{11}H_{21}N$: [M^+] 168.17522. Found: m/z 168.17514.

N-cyclopentylpiperidine: (colourless oil Yield: 0.262 g, 94%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.30 (m, 5H, C*H*$_2$N and C*H*); 1.70, 1.53, 1.46, 1.38, and 1.29 (m, 14H, C*H*$_2$C*H*$_2$CH$_2$N and CHC*H*$_2$C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.7 MHz): δ 67.95 (s, 1C, *C*H); 53.35 (s, 2C, *C*H$_2$N); 30.29 (s, 2C, CH*C*H$_2$); 25.81 (s, 2C, *C*H$_2$CH$_2$N); 24.39 (s, 1C, *C*H$_2$CH$_2$CH$_2$N); 24.05 (s, 2C, CHCH$_2$*C*H$_2$). HR-MS Calcd for $C_{10}H_{19}N$: [M^+] 154.15957. Found: m/z 154.16002.

1,2,3,3-tetramethylindoline: Tolmachev, A. A. *Khim. Geterotsikl. Soedin.* **1986**, *11*, 1474-1477. (pale yellow oil Yield: 0.301 g, 94%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (ddd, 1H, 3–C_6H_4–*H*, $^{3}J_{HH}$ = 8.9, 7.8 Hz, $^{4}J_{HH}$ = 1.1 Hz); 7.21 (dd, 1H, 5–C_6H_4–*H*, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 0.8 Hz); 6.93 (ddd, 1H, 4–C_6H_4–*H*, $^{3}J_{HH}$ = 8.9, 7.6 Hz, $^{4}J_{HH}$ = 0.8 Hz); 6.70 (d, 1H, 2–C_6H_4–*H*, $^{3}J_{HH}$ = 7.8 Hz); 3.08 (q, 1H, C*H*, $^{3}J_{HH}$ = 6.6 Hz); 2.90 (s, 3H, NC*H*$_3$); 1.52 and 1.26 (s, 6H, C*H*$_3$); 1.14 (d, 3H, CHC*H*$_3$, $^{3}J_{HH}$ = 6.6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.7 MHz): δ 152.10 (s, 1C, 1–*ipso*–*C*); 139.26 (s, 1C, 6–*ipso*–*C*); 127.52 (s, 1C, 3–C_6H_4–*C*H); 121.60 (s, 1C, 5–C_6H_4–*C*H); 118.68 (s, 1C, 4–C_6H_4–*C*H); 107.81 (s, 1C, 2–C_6H_4–*C*H); 72.37 (s, 1C, *C*H); 42.82 (s, 1C, *C*Me$_2$); 32.02 (s, 1C, N*C*H$_3$); 23.02 and 14.77 (s, 2C, C*C*H$_3$); 13.55 (s, 1C, CH*C*H$_3$). Calcd for $C_{12}H_{17}N$: [M^+] 176.14392. Found: m/z 176.14434.

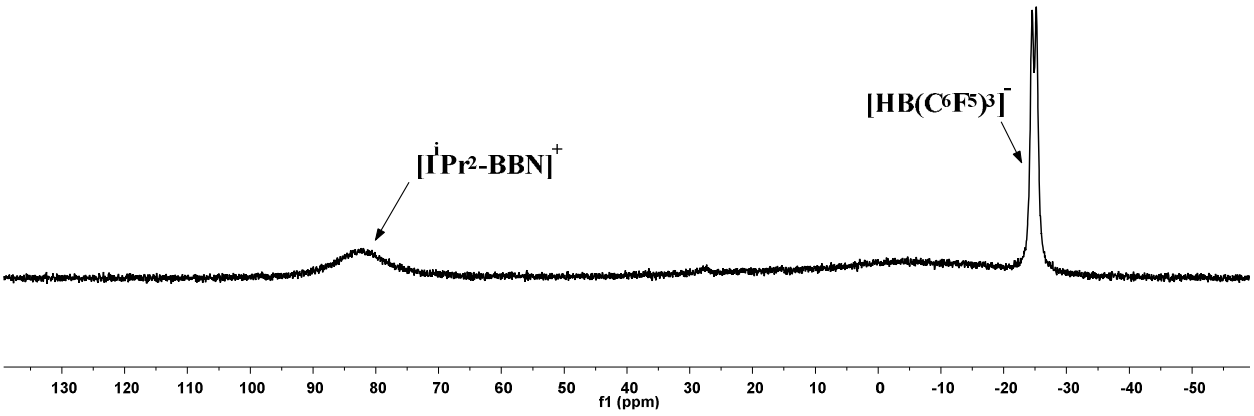
N-(1-Phenylethyl)aniline: T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, *J. Org.Chem.,* **1995**, *60*, 2677-2682. (colourless oil Yield: 0.325g, 90%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 and 7.61 (m, 4H, *o* and *m*–Ph–*H*); 7.51 (tt, 1H, *p*–Ph–*H*, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.3 Hz); 7.41 (dd, 1H, *m*–*N*–Ph–*H*, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 7.3 Hz); 6.98 (tt, 1H, *p*–*N*–Ph–*H*, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.1 Hz); 6.82 (dd, 1H, *o*–*N*–Ph–*H*, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 0.9 Hz); 4.77 (q, 3H, C*H*, $^{3}J_{HH}$ = 6.7 Hz); 4.28 (br s, 1H, NH); 1.76 (d, 3H, C*H*$_3$, $^{3}J_{HH}$ = 6.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.7 MHz): δ 147.24 and 145.18 (s, 2C, *ipso*–Ph–*C*); 129.04, 128.56, 126.78, 125.78, 117.16, and 113.29 (s, 8C, Ph–*C*); 53.31 (s, 1C, *C*H); 24.87 (s, 1C, *C*H$_3$). EI-MS Calcd for $C_{12}H_{19}NO$: [M^+] 198.1. Found: m/z 198.1.

Product conversions by ^{1}H NMR spectroscopy were determined by comparison to literature values for entry 11: 8-Methyl-1,2,3,4-tetrahydoquinoline: (Murahashi, S.-I.; Imada, Y.; Hirai, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2968-2976.**)**

Hydride transfer from (I^iPr_2)(HBC_8H_{14}) to $B(C_6F_5)_3$.

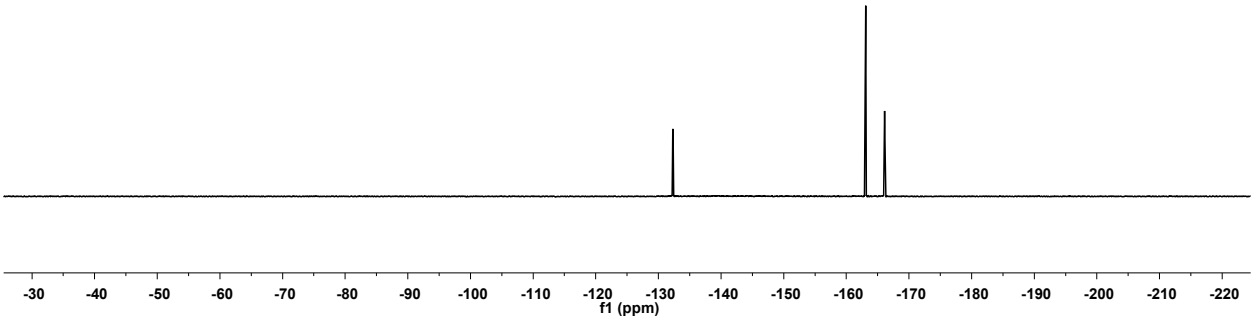
In an inert atmosphere glovebox, (I^iPr_2)(HBC_8H_{14}) (6.3 mg, 0.0230 mmol, 1 equiv.) and $B(C_6F_5)_3$ (11.7 mg, 0.230 mmol, 1 equiv.) were transferred to an NMR tube with 0.6 mL C_6D_5Br. ^{1}H, ^{11}B and ^{19}F NMR spectra were consistent with the quantitative formation of $[I^iPr_2\text{-BBN}]^+$ (reported herein) and $[HB(C_6F_5)_3]^-$.[4]

^{11}B NMR:



[4] Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.

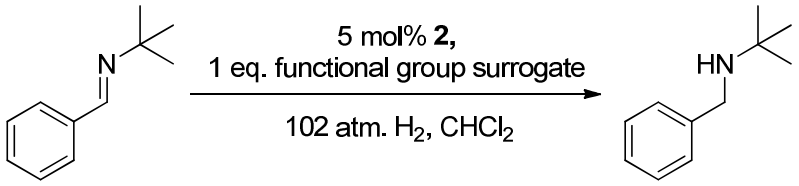
^{19}F NMR:



Procedure for surrogate functional group tolerance experiments.

In an inert atmosphere glovebox, $[(I^iPr_2)(BC_8H_{14})][B(C_6F_5)_4]$ • 0.66 C_6H_5Cl (31.2 mg, 0.0303 mmol, 1 equiv.), *N*-benzylidene-*tert*-butylamine (98 mg., 0.6074 mmol, 20 equiv.) and the functional group surrogate (0.6074 mmol, 20 equiv.) were added successively to a vial equipped with a stir bar. The sample was dissolved in 0.2 mL CH_2Cl_2 (in entry 9, 0.4 mL CH_2Cl_2 was required for complete dissolution) and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in $CDCl_3$. Conversion of unsaturated substrate to amine product was determined by ^{1}H NMR spectroscopy.

Table 1. Hydrogenation in the presence of a functional group surrogate.



entry	functional group surrogate	reaction time (h)	%yield[a]	
			Reduced substrate	Reduced surrogate
1	4,4'-dimethylbenzophenone	2	100	0
2	2,2,2-trifluoroacetophenone	2	0	0
3	8-methylquinoline	2	76	0
4	8-methylquinoline	4	100	0
5	ethyl-4-bromobenzoate	2	100	0
6	acetophenone	2	0	0
7	fenchone	2	100	0
8	2-phenylpyridine	2	100	0
9	2',6'-diisopropylacetophenone	2	0	0

[a] Yield determined by ^{1}H NMR spectroscopy.