Supporting Information for

Deuteration of boranes: catalysed versus non-catalysed processes

David J. Nelson, Jonathan B. Egbert and Steven P. Nolan*
EaStCHEM, School of Chemistry, University of St. Andrews, Purdie Building,
North Haugh, St. Andrews, Fife, KY16 9ST, Scotland.

Contents

Experimental Details S2
  General
  Deuteration Experiments

NMR Spectra of Reaction Products S3
  Pseudostoichiometric reactions with Ir
  Preparative Reactions
Experimental Details

**General.** All air-sensitive manipulations were carried out in an Argon-filled MBraun or Innovative Technologies glovebox; solutions of iridium complexes 8-10 are highly sensitive to oxygen. Dichloromethane-$d_2$ was dried overnight on calcium hydride, distilled, and degassed by freeze-pump-thaw cycles. Tetrahydrofuran-$d_8$ was dried overnight on sodium/benzophenone, distilled, and degassed by freeze-pump-thaw cycles. Tetrahydrofuran was obtained from an MBraun solvent purification system and degassed by purging with dry oxygen-free nitrogen. All boranes were obtained from commercial sources, except for BH$_3$·THF where both commercial and freshly-prepared borane was used (see the manuscript text). NMR analyses were conducted using either a Bruker AV300 (1H obs. at 300 MHz; 11B obs. at 96 MHz), a Bruker AV400 (1H obs. at 400 MHz; 11B obs. at 128 MHz) or a Bruker AV500 (2H obs. at 77 MHz). Chemical shifts are in ppm, relative to tetramethylsilane (for 1H), tetramethylsilane-$d_{12}$ (for 2H) or Et$_2$O·BF$_3$ (for 11B); coupling constants are in Hertz.

**Deuteration Experiments.** In a glovebox, the iridium complex (when used; typically ca. 1 to 2 mg) was weighed into a vial, and the borane (typically ca. 2 mmol) was weighed into a second vial. The borane was dissolved in solvent (0.5 mL CD$_2$Cl$_2$ for pinacolborane 2, catecholborane 3, and Me$_2$S·BH$_3$ 5; 2 mL THF for 9-BBN 4; 1 was used as a 1 mol L$^{-1}$ solution in THF; 2.5 mL CD$_2$Cl$_2$ for morpholine-borane 6 and N-methylmorpholine-borane 7) and added to the iridium complex. The solution was then transferred to a ca. 100 mL flask fitted with valve, containing a stirrer bar. The valve was closed, the flask was removed from the glovebox and then connected to a Schlenk line. The solution was frozen and the flask was placed under vacuum. The flask was filled with D$_2$ and evacuated twice, before filling with D$_2$ to ca. 10 psi. The reaction was stirred for the specified time. Once this time had elapsed, the reactions of 2, 3, 5, 6 and 7 were transferred to NMR tubes and analysed by $^1$H and $^{11}$B NMR spectroscopy. For 4, the solvent was stripped under vacuum and a portion of the solid was dissolved in THF-$d_8$ and analysed by $^1$H and $^{11}$B NMR spectroscopy. For these reactions, the conversion was quantified by integrating the B-H peak versus other peaks on the $^1$H NMR spectrum. For 1, a portion of the reaction was transferred to an NMR tube, a small quantity (ca. 100 μL) of dry CD$_2$Cl$_2$ or THF-$d_8$ was added, and the sample was analysed by $^1$H and $^{11}$B NMR spectroscopy. Conversion was estimated in this case by inspection of the $^{11}$B NMR spectrum; BH$_3$ exhibits a distinctive quartet resonance, while BD$_3$ manifests as a single broad signal (see spectra).
Sample $^1$H and $^{11}$B NMR Spectra

Where sample spectra are integrated, $\frac{1}{2}$ of the B-H signal is often considered to avoid e.g. solvent peaks. In these cases, this is taken to represent 0.5 H and so the quoted conversions in the manuscript are correct.

Pseudostoichiometric reactions

Ir-complex and ca. 3-5 equiv. of HBpin combined in CD$_2$Cl$_2$ and transferred to a J. Young NMR tube for analysis, in order to probe for interesting new complexes.

8 + HBpin
$8 + 9$-BBN

$^1$H before 9-BBN

$^1$H of $1 + 9$-BBN, 1 h at rt
Preparative Reactions: Sample spectra from reactions carried out under D$_2$ in order to show that reaction has occurred.

THF.BH$_3$ 1-$d_3$ (commercial material in THF) NB: Extra peaks are also present in a new, untouched bottle of commercial THF-BH$_3$, stored carefully in a glovebox at -40°C and only opened in an Argon-filled glovebox; one can be ascribed to B$_2$H$_6$. 

![11B spectrum](image1)

![11B spectrum](image2)
THF.BH$_3$ 1-$d_3$ (freshly prepared in THF) A solution of BH$_3$·THF in THF was prepared according to the procedure of Brown (*Inorganic Chemistry*, 2000, **39**, 1795) and exposed to D$_2$ under the same reaction conditions as commercial material. $^{11}$B NMR analysis confirmed that only BH$_3$ was present in the starting material; $^{11}$B{¹H} analysis showed that the quartet structure arose from coupling to protons.
Pinacolborane $2-d_1$ (with Ir, in CD$_2$Cl$_2$)

$^1$H

$^{11}$B (reaction mixture in blue, substrate in red)
Catecholborane 3-$d_1$ (with Ir, in CD$_2$Cl$_2$)

$^1$H

$^{11}$B

Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2013
9-BBN 4-$d_1$ (in THF)

No B-H signal on 1H NMR; no visible B-H coupling ($J \sim 170$ Hz) in $^{11}$B NMR, thus > 95% conversion.
DMS.BH$_3$ 5 (in THF)
Morpholine-borane 6 (in THF)
$N$-methylmorpholine borane 7 (in THF)
Attempted deuteration of NaBH₄

![Graphical representation of attempted deuteration of NaBH₄]