

Transition Metal Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids

William R.H. Wright, Emily R. Berkeley, Laif R. Alden, R. Tom Baker, and Larry G. Sneddon

General Experimental Section

All manipulations were carried out using standard high-vacuum or glove box techniques unless stated otherwise. Ammonia-borane was purchased from Aviator (97% minimum purity) or GFS chemicals, in both instances being used as a free flowing powder. The ionic liquids 1-butyl-3-methylimidazolium chloride [bmim][Cl], 1-butyl-2,3-dimethylimidazolium chloride [bmmim][Cl], 1-ethyl-2,3-dimethylimidazolium ethylsulfate [emmim][EtSO₄], were dried using azeotropic distillation from toluene, while the ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][N(Tf)₂] and 1-ethyl-3-methylimidazolium ethylsulfate [emim][O₃SOEt] were dried under vacuum at 75 °C for over 16 h. All solvents were dried using standard protocols with THF being dried over sodium and distilled prior to use. Anhydrous metal complexes purchased commercially and handled under inert atmosphere included [Rh(COD)Cl₂], NiCl₂ (Aldrich), Pd(DBA)₂ (Acros), RhCl₃, RuCl₃, Ru(COD)Cl₂ and Ni(COD)₂ (Strem). The complex RuCl₂(PMe₃)₄ was prepared from RuCl₂(PPh₃)₃ (Strem) using standard literature procedures.ⁱ Routine ¹¹B NMR spectra were collected on a Bruker Avance 500 while IR spectra were collected using a Varian 640 FT-IR spectrometer using an ATR attachment.

Physical Measurements

Automated Gas Burette Measurements

The automated gas burette used was based on the design reported by Zheng *et al.*ⁱⁱ but employed all glass connections with a cold trap (-78 °C) inserted between the reaction flask and burette to allow trapping of any volatiles that might have been produced during the reaction. A more complete description of the automated gas burette is available in previous communications.ⁱⁱⁱ

For reactions using the automated gas burette, AB (150 mg, 4.87 mmol) was loaded into ~100 mL flasks with calibrated volumes, along with the ionic liquid (150 mg) and required metal catalysts (5 mol%). Under a flow of helium, the flask was attached to the burette system and the system was then evacuated for 30 min. Next, the apparatus was then back-filled with helium and allowed to equilibrate to atmospheric pressure for ~30 min. Once the system pressure equalized, the data collection program was started and the flask was immersed in the preheated oil bath (Chart 1, 3).

Non-Automated Gas Burette Measurements

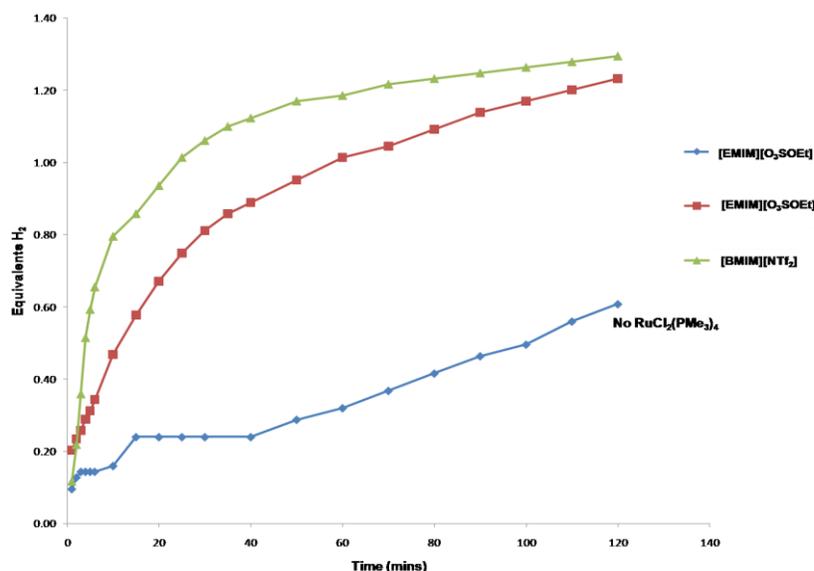
The volume of H₂ was quantitatively measured using a gas burette with pressure equalizing against atmospheric pressure. Standard atmospheric pressure was assumed along with ideal gas behavior. As in previous investigations the burette was filled with water,^{iv} or mineral oil, with identical H₂ release being obtained in each instance. When water displacement was recorded, the vapor pressure of water was considered when calculating the partial pressure of H₂.

Measuring Ru-Initiated H₂ Release at Varying Temperatures using a Gas Burette

AB (80 mg, 2.58 mmol), [emim][O₃SOEt] (200 mg) and RuCl₂(PMe₃)₄ (4 mg, 0.008 mmol) were weighed into a round bottom Schlenk flask fitted with a side arm. The flask was attached to the hydrogen burette *via* tubing and the vessel was lowered into an oil bath of the desired temperature (55 °C, 65 °C, 75 °C or 85 °C). Agitation was provided using a stirrer bar and care was taken to ensure that the rate of agitation was comparable in each run, with the same type of stirrer bar used in each instance. After a short reaction period (*ca* 30 seconds) the reaction vessel was opened to the burette enabling readings to commence. The start of the reaction was assumed to be the moment the flask was lowered into the oil bath and the burette pressure was equalized before each reading. This procedure was repeated but with AB (80 mg, 2.58 mmol), [emim][O₃SOEt] (200 mg) in the absence of any Ru salts at the temperatures 55 °C, 65 °C, 75 °C, and 85 °C (Chart 2).

The above procedure was also utilized to assess the relative capacity of the $\text{RuCl}_2(\text{PMe}_3)_4$ pre-catalyst to dehydrogenate AB at 75°C in the ionic liquids $[\text{bmim}][\text{NTf}_2]$ and $[\text{emim}][\text{O}_3\text{SOEt}]$ (Chart S1 and Table S1). Reaction solutions were prepared using AB (80 mg, 2.58 mmol), the desired IL (200 mg) as well as $\text{RuCl}_2(\text{PMe}_3)_4$ (8 mg, 0.017 mmol). Finally, a reaction solution was analysed comprising of just AB (80 mg, 2.58 mmol) and $[\text{emim}][\text{O}_3\text{SOEt}]$ (200 mg) (Chart S1).

Chart S1 and Table S1 – Dehydrogenation of AB in alternate ILs at 75°C using $\text{RuCl}_2(\text{PMe}_3)_4$



Time	System	Equivalents H ₂ released
17h and 25 min	$[\text{emim}][\text{O}_3\text{SOEt}]$ and $\text{RuCl}_2(\text{PMe}_3)_4$	2.09
17 h and 28 min	$[\text{emim}][\text{O}_3\text{SOEt}]$ with no $\text{RuCl}_2(\text{PMe}_3)_4$	1.85
17 h and 16 min	$[\text{bmim}][\text{NTf}_2]$ and $\text{RuCl}_2(\text{PMe}_3)_4$	1.64

Evaluating the Selectivity of the $\text{RuCl}_2(\text{PMe}_3)_4$ Pre-Catalyst in Alternate ILs

AB (40 mg, 0.75 mmol) was dissolved in $[\text{bmim}][\text{NTf}_2]$ (2 g) and to this mixture was added $\text{RuCl}_2(\text{PMe}_3)_4$ (4 mg, 0.008 mmol). This reaction solution was allowed to stir for 48 h, inducing the formation of a white precipitate. The reaction solution was analysed using ^{11}B NMR spectroscopy, with the resulting spectra presenting broad ^{11}B NMR resonances (Figure S1). An aliquot of the reaction mixture was diluted in excess THF and the ^{11}B NMR spectrum recorded (Figure S2). The white solid was examined using IR spectroscopy, with the resulting spectra being consistent with the formation of insoluble, linear poly(aminoborane) (Figure S3).

The above procedure was repeated, but with $[\text{bmim}][\text{NTf}_2]$ replaced with $[\text{emim}][\text{O}_3\text{SOEt}]$. Again after a 48 h period, the reaction mixture was analysed using ^{11}B NMR spectroscopy (Figure S4). Despite repeated attempts, it was not possible to selectively extract the amine-borane products into a less viscous solvent to obtain higher resolution.

Evaluating the Selectivity of the $\text{RuCl}_2(\text{PMe}_3)_4$ Pre-Catalyst with 27 wt% AB solutions

Reaction solutions were prepared by mixing AB (80 mg, 2.58 mmol), $[\text{emim}][\text{O}_3\text{SOEt}]$ or $[\text{bmim}][\text{NTf}_2]$ (200 mg) and $\text{RuCl}_2(\text{PMe}_3)_4$ (8 mg, 0.017 mmol). The mixtures were then heated at 75°C for 2 h and the resulting solutions were then extracted using THF (4 ml). These washings were analyzed using ^{11}B NMR spectroscopy (Figure S5 and Figure S6). This procedure was repeated for the $[\text{emim}][\text{O}_3\text{SOEt}]$ system, but with the reaction being heated for 18 h (Figure S7). Furthermore, AB (80 mg, 2.58 mmol) and $[\text{emim}][\text{O}_3\text{SOEt}]$ (200 mg) were mixed and heated at 75°C

for 18 h. Again the reaction mixture was extracted using THF and the washings analyzed using ^{11}B NMR spectroscopy (Figures S8 and S9).

Figure S1 and S2 ^{11}B NMR obtained via reaction of AB in [bmim][NTf₂] for 48 h at room temperature

Figure S1 before THF extraction

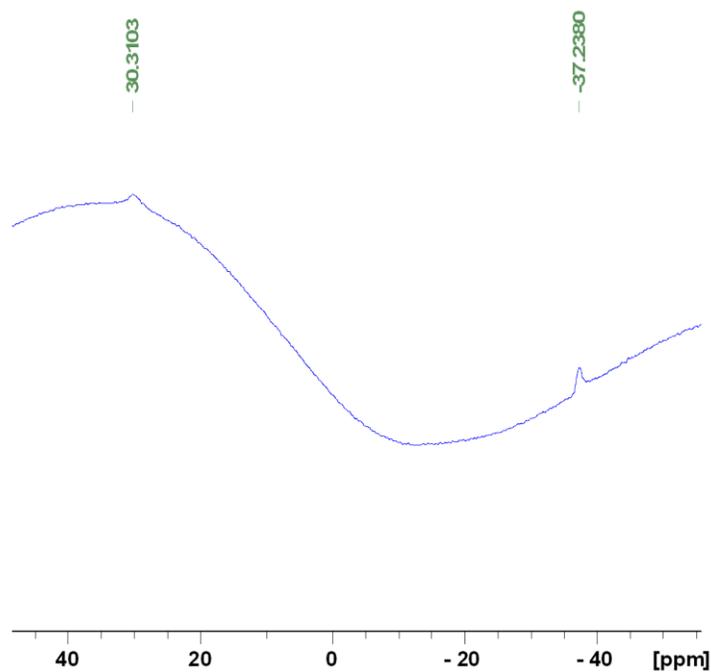


Figure S2 after THF extraction

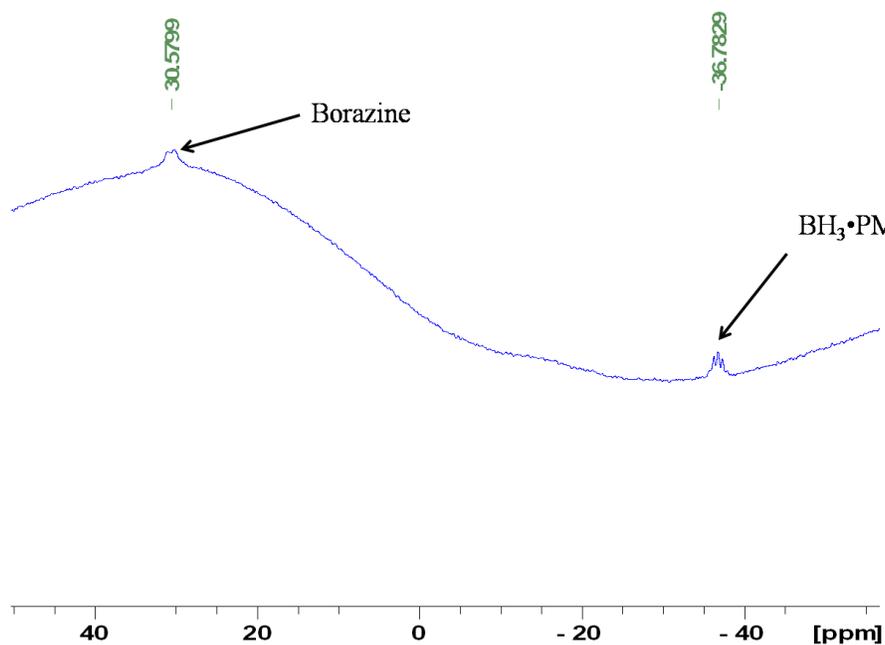


Figure S3 IR spectra of AB and the THF insoluble reaction product obtained via reaction of AB in [BMIM][NTf₂]

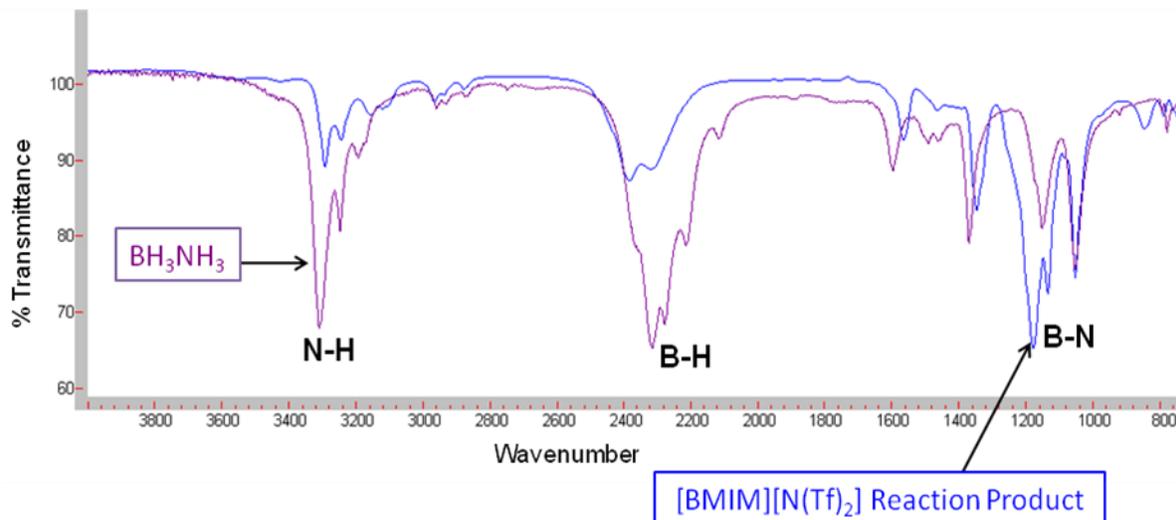


Figure S4 ¹¹B NMR spectrum obtained via reaction of AB in [emim][O₃SOEt] for 48 h at room temperature

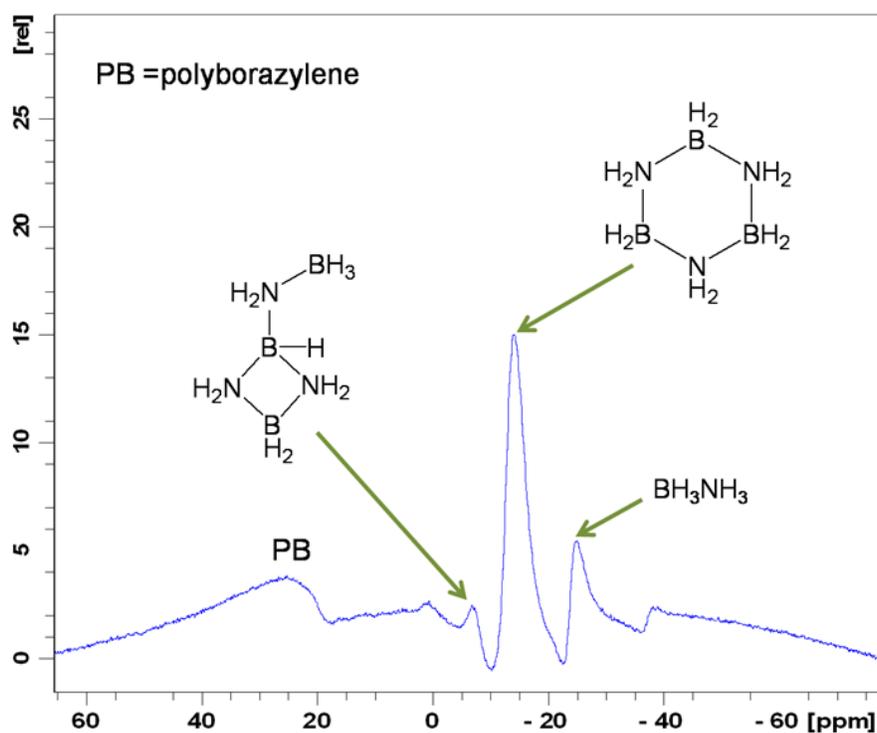


Figure S5 ^{11}B NMR spectrum (THF extract) obtained *via* Ru catalyzed reaction of AB in [emim][O₃SOEt] for 2 h at 75°C

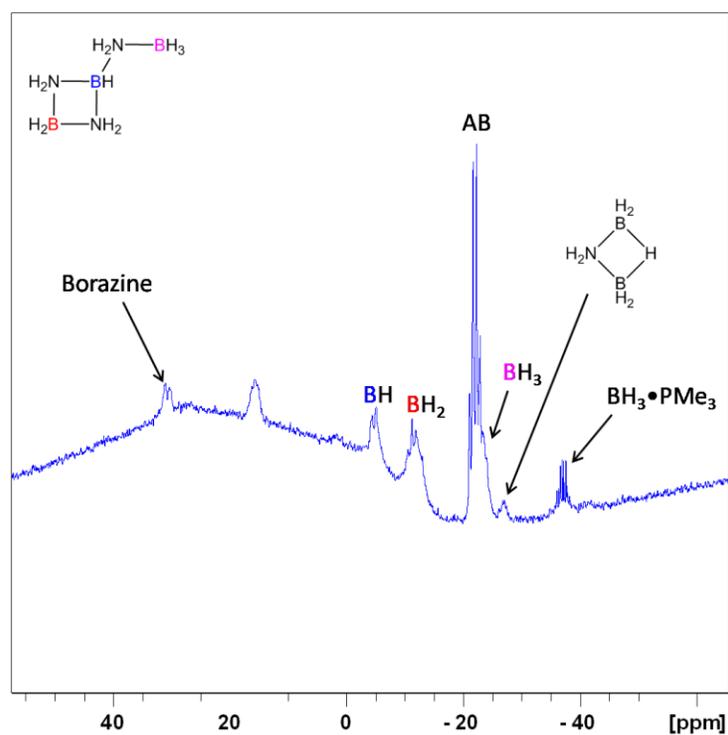


Figure S6 ^{11}B NMR spectrum (THF extract) obtained *via* Ru catalyzed reaction of AB in [bmim][NTf₂] for 2 h at 75°C

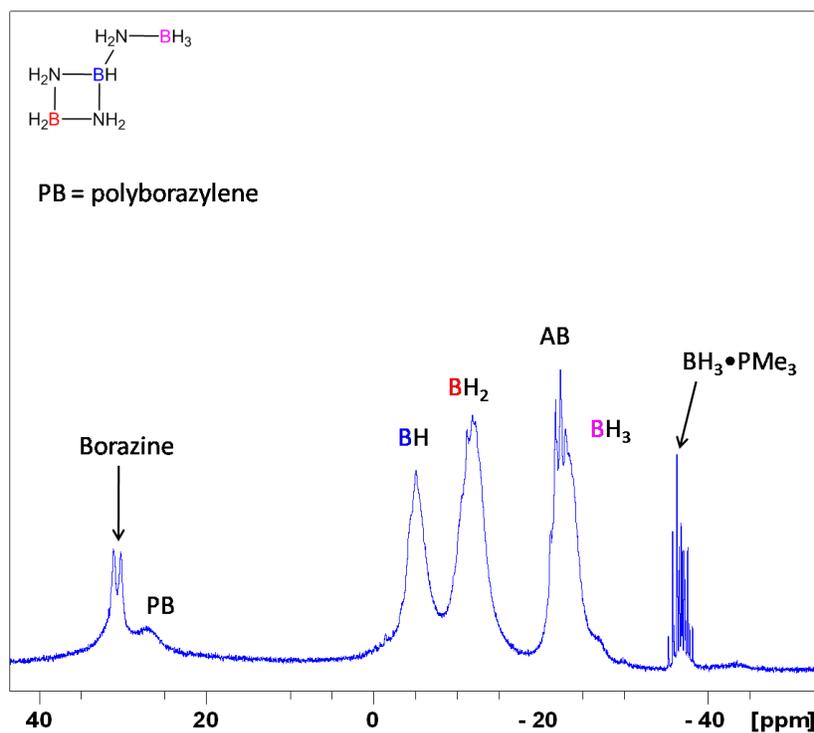


Figure S7 ^{11}B NMR spectrum (THF extract) obtained *via* Ru catalyzed reaction of AB in [emim][O₃SOEt] for 18 h at 75 °C

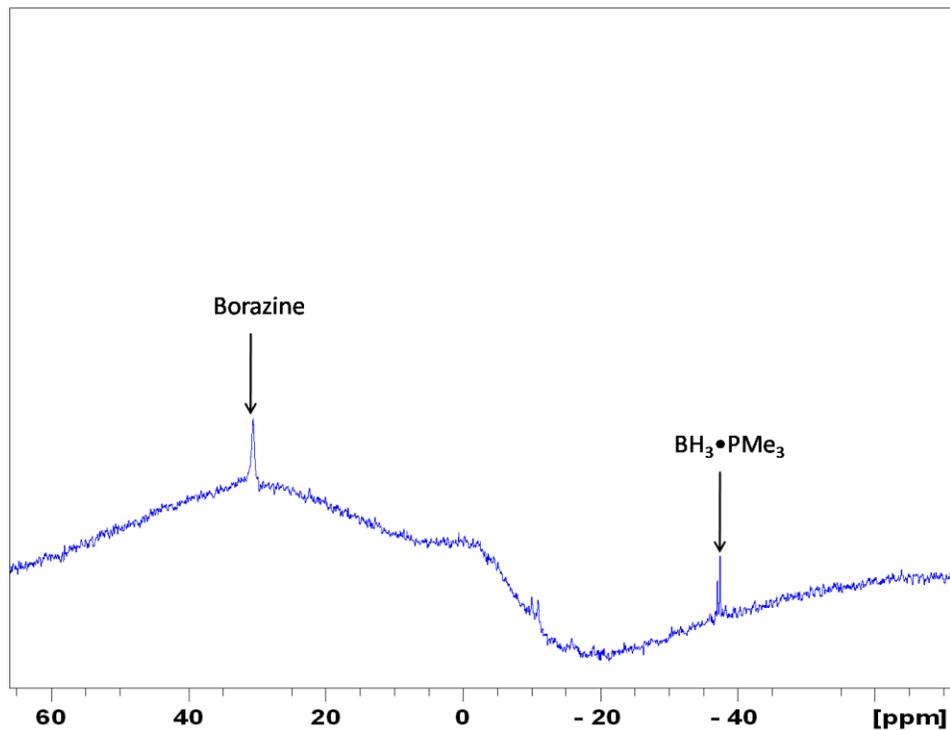


Figure S8 ^{11}B NMR spectrum (THF extract) obtained *via* IL promoted reaction of AB in [emim][O₃SOEt] for 18 h at 75 °C

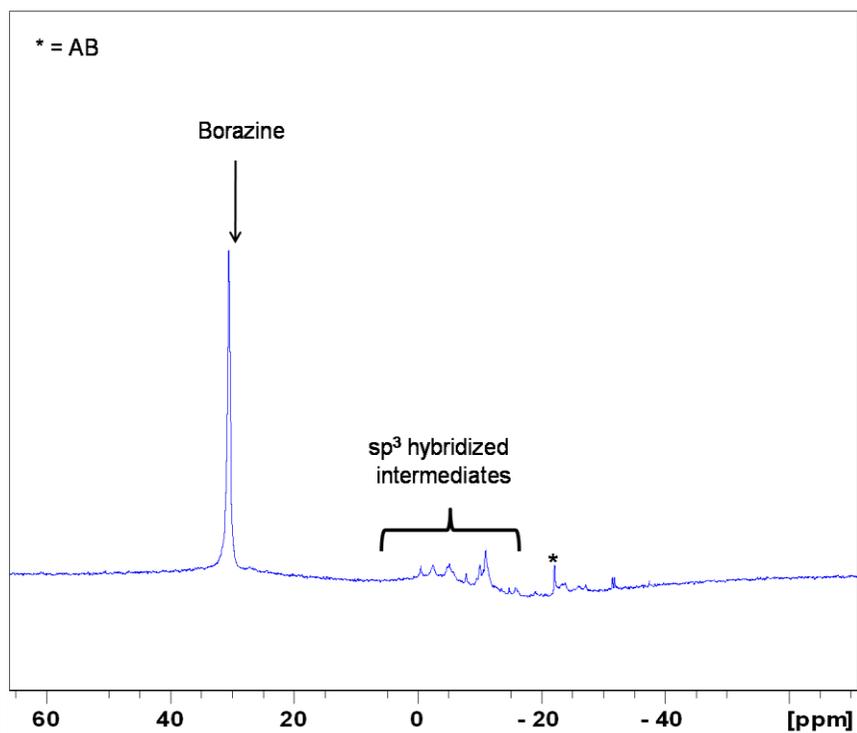
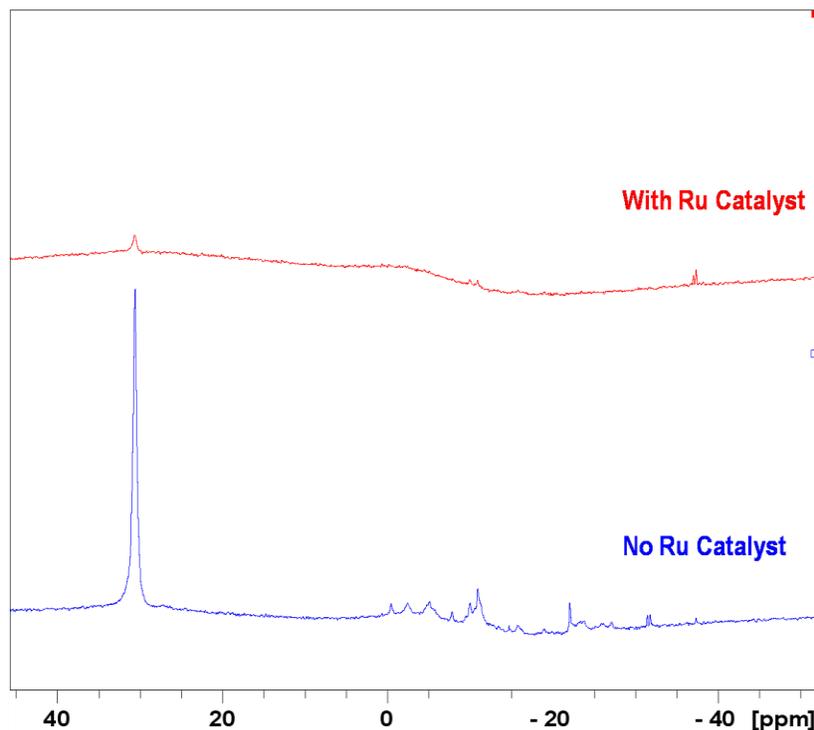


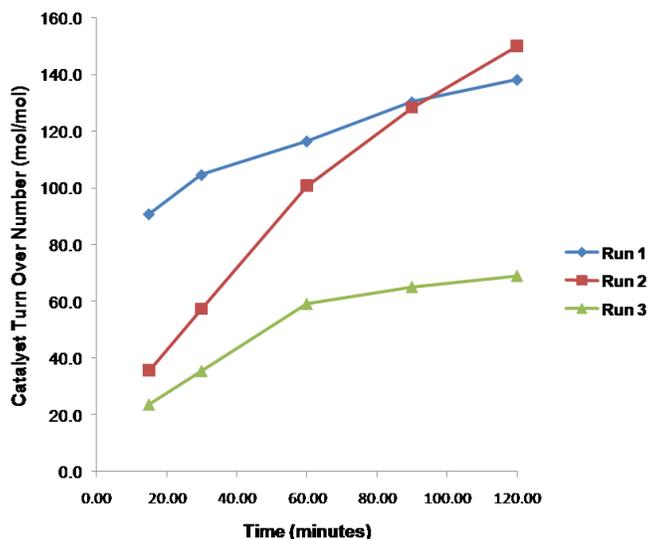
Figure S9 A comparison of ^{11}B NMR spectra (THF extract) obtained via IL promoted and metal catalyzed dehydrogenation of AB in $[\text{emim}][\text{O}_3\text{SOEt}]$ for 18h at 75°C



Evaluating the Reusability of the $\text{RuCl}_2(\text{PMe}_3)_4$ System

A reaction solution was prepared by mixing AB (80 mg, 2.58 mmol), $[\text{emim}][\text{O}_3\text{SOEt}]$ (200 mg) and $\text{RuCl}_2(\text{PMe}_3)_4$ (10 mg, 0.021 mmol). This mixture was then heated at 75°C for 2 h, and the subsequent H_2 release was measured using a gas burette (Chart S2). After cooling, further portions of AB (80 mg, 2.58 mmol) and $[\text{emim}][\text{O}_3\text{SOEt}]$ (200 mg) were added to the mixture, which was then heated, with the H_2 release again measured using a gas burette. This procedure was repeated for a third time, enabling a third recycle to be observed (Chart S2). Evidently, this system is reusable enabling a total turnover number of 357 (mol H_2 /mol Ru).

Chart S2 Reusing the $\text{RuCl}_2(\text{PMe}_3)_4$ system at 75°C



Notes and References

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- ⁱⁱ F. Zheng, S. D. Rassat, D. J. Heldebrandt, D. D. Caldwell, C. L. Aardahl, T. Autrey, J. C. Linehan and K. G. Rappe, *Rev. Sci. Instrum.*, 2008, **79**, 084103.
- ⁱⁱⁱ D. W. Himmelberger, L. R. Alden, M. E. Bluhm and L. G. Sneddon, *Inorg. Chem.*, 2009, **48**, 9883-9889.
- ^{iv} N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 14034-14035; B. L. Conley and T. J. Williams., *Chem Commun.*, 2010, **46**, 4815-4817.