

Supporting Information

Dehydrogenation of Ammonia-Borane by Shvo's Catalyst

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I. General Procedures

All air and water sensitive procedures were carried out either in a Vacuum Atmosphere glove box under nitrogen (2-10 ppm O_2 for all manipulations) or using standard Schlenk techniques under nitrogen. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. Benzene- d_6 , THF- d_8 , and diethylene glycol dimethyl ether (diglyme, J. T. Baker) were dried over sodium benzophenone ketyl and distilled prior to use. Shvo's catalyst was purchased from Strem Chemicals. Ammonia borane (NH_3BH_3 , AB) was purchased from Sigma Aldrich. Borazine was synthesized and purified by the method used by Wideman and Sneddon.¹ ^1H and ^{11}B NMR spectra were obtained on a Varian 400-MR spectrometer (400 MHz in ^1H , 128 MHz in ^{11}B) with chemical shifts reported in units of ppm. All ^1H chemical shifts are referenced to the residual ^1H solvent (relative to TMS). All ^{11}B chemical shifts are referenced to a $\text{BF}_3\cdot\text{OEt}_2$ in diglyme co-axial external standard (0 ppm). NMR spectra were taken in 8" J-Young tubes (Wilmad) with Teflon valve plugs. The NMR tubes were shaken vigorously for several minutes with chlorotrimethylsilane then dried in vacuo on a Schlenk line prior to use. Reactions for the quantification of evolved hydrogen gas were carried out in flame dried 2 mL Schlenk tubes with Teflon valve plugs. The side arm was attached to an inverted buret (eudiometer) using Tygon tubing.

Safety Note. Extreme caution should be used when carrying out these reactions as the release of hydrogen can lead to sudden pressurization of reaction vessels.

II. Hydrogen Quantification

In a typical reaction, 7.7 mg AB (0.25 mmol) was combined with Shvo's catalyst (**1**, 13.6 mg, 5.0 mol %) in a 2 mL Schlenk tube equipped with a Teflon stir bar while in a glovebox under nitrogen. Diglyme (0.4 mL) and benzene (0.2 mL) were added to the tube. In reactions in which ethanol was added, it was delivered from a stock solution in diglyme so that the total reaction volume is the same as above. For example, in a 2.0 mol % ethanol experiment, a stock solution of ethanol in diglyme was prepared in the glove box from 3.7 μ L ethanol and 5.0 mL diglyme. This was delivered (0.4 mL) in place of neat diglyme. The eudiometer was constructed as follows (Figure S2). The side arm of the valve was connected to a piece of Tygon tubing, which was adapted to 20 gauge (0.03") Teflon tubing with a needle. This tubing was threaded through a porous septum that was sized to fit over the open end of a buret that was flame sealed on the other end. The role of the septum is to help keep the tubing inside the buret during the reaction. The buret was filled with water and the septum was attached. The entire apparatus was then inverted into a one-liter cylinder filled with water and clamped onto a metal ring stand. The reaction flask was heated for 1.5 minutes in a regulated oil bath to equilibrate its temperature (suspected initiation period) then the reactor's valve was opened to release gas from the reactor headspace. The volume of liberated gas was recorded periodically until gas evolution ceased. Liberated hydrogen was quantified by recording its volume displacement in the eudiometer and correcting its volume for water content (Figure S1). This implementation matches prior reports of eudiometric studies of AB dehydrogenation.²

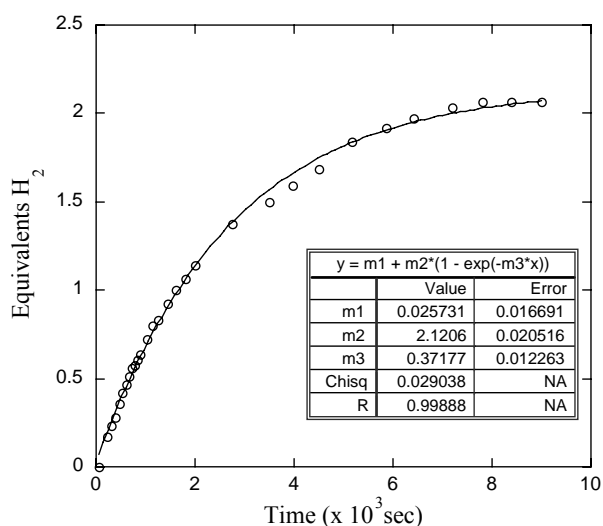


Figure S1. Time course of dehydrogenation of AB from Figure 1 (left) measured by eudiometry. Data are fit to an exponential growth curve with $k_{\text{obs}} = 3.72(12) \times 10^{-4} \text{ s}^{-1}$; $[\text{AB}] = 0.417 \text{ M}$; 5.0 mol % **1**, 2.0 mol % ethanol in 2:1 diglyme/benzene at 70 °C

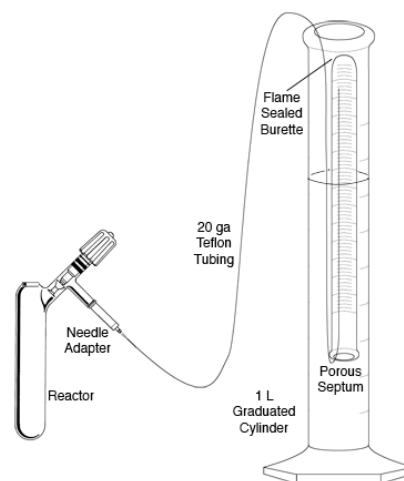
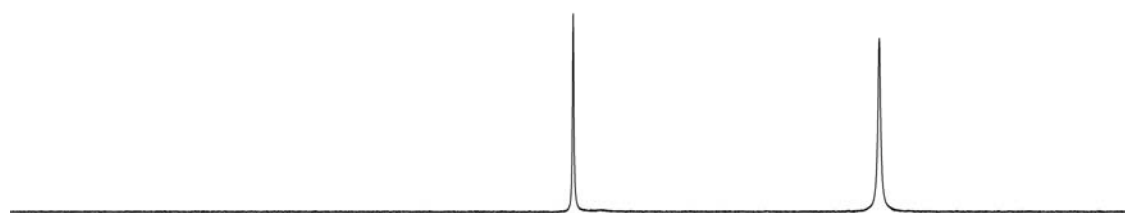


Figure S2. Schematic diagram of eudiometer.

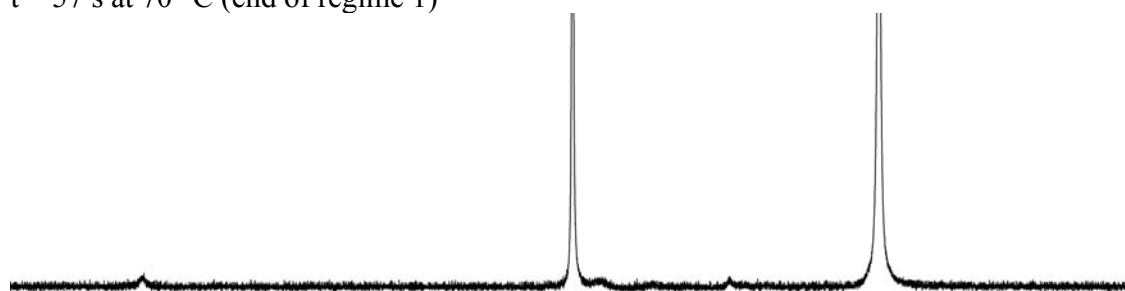
III. Mechanistic Studies Utilizing ^{11}B and ^1H NMR Spectroscopy

A. Monitoring Conversion of AB for Determination of Reaction Rate

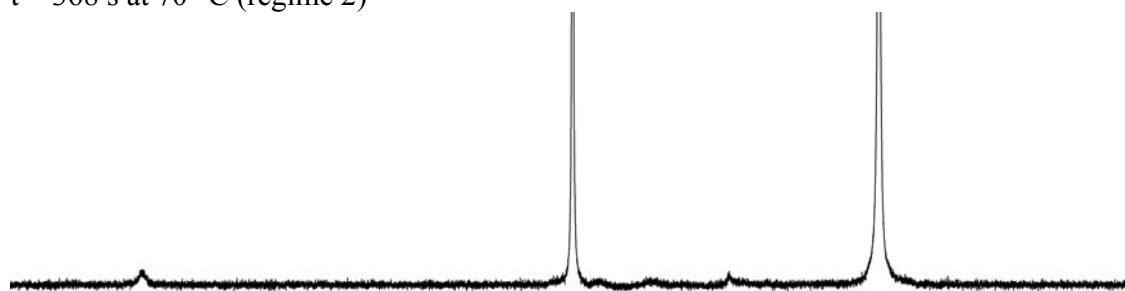
In a typical reaction, AB (7.7 mg, 0.25 mmol) was combined with Shvo's catalyst (**1**, 13.6 mg, 5.0 mol %) in an 8" J. Young tube in a glove box under nitrogen. Diglyme (0.4 mL) and benzene- d_6 (0.2 mL) were then added to the tube. A second NMR tube containing the same solvent composition was locked and shimmed at 70 °C in the probe. The sample tube was then inserted into the probe and the kinetic monitoring commenced. Disappearance of AB in the solution was monitored by the relative integration of its characteristic peak in the ^{11}B spectrum (-22 ppm) and a $\text{BF}_3\cdot\text{OEt}_2$ in diglyme co-axial external standard (0 ppm). All spectra were processed using VNMRJ software on the instrument console. The acquisition involved a 1.67 sec pulse sequence in which 32,768 complex points were recorded, followed by a 5 sec acquisition delay. A total of 16 scans were completed followed immediately by the start of another acquisition. To eliminate B—O peaks from the borosilicate NMR tube and probe, the ^{11}B FIDs were processed with back linear prediction. Typical ^{11}B spectrum with all species present are shown in Figure S3.



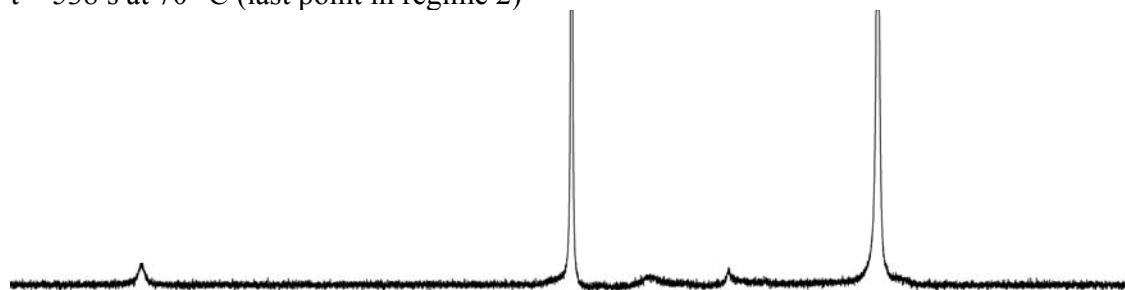
t = 57 s at 70 °C (end of regime 1)



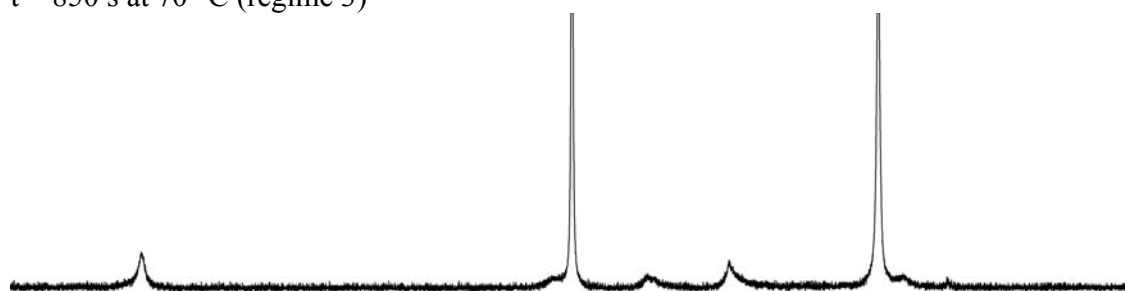
t = 368 s at 70 °C (regime 2)



t = 538 s at 70 °C (last point in regime 2)



t = 850 s at 70 °C (regime 3)



t = 2834 s at 70 °C (regime 3)

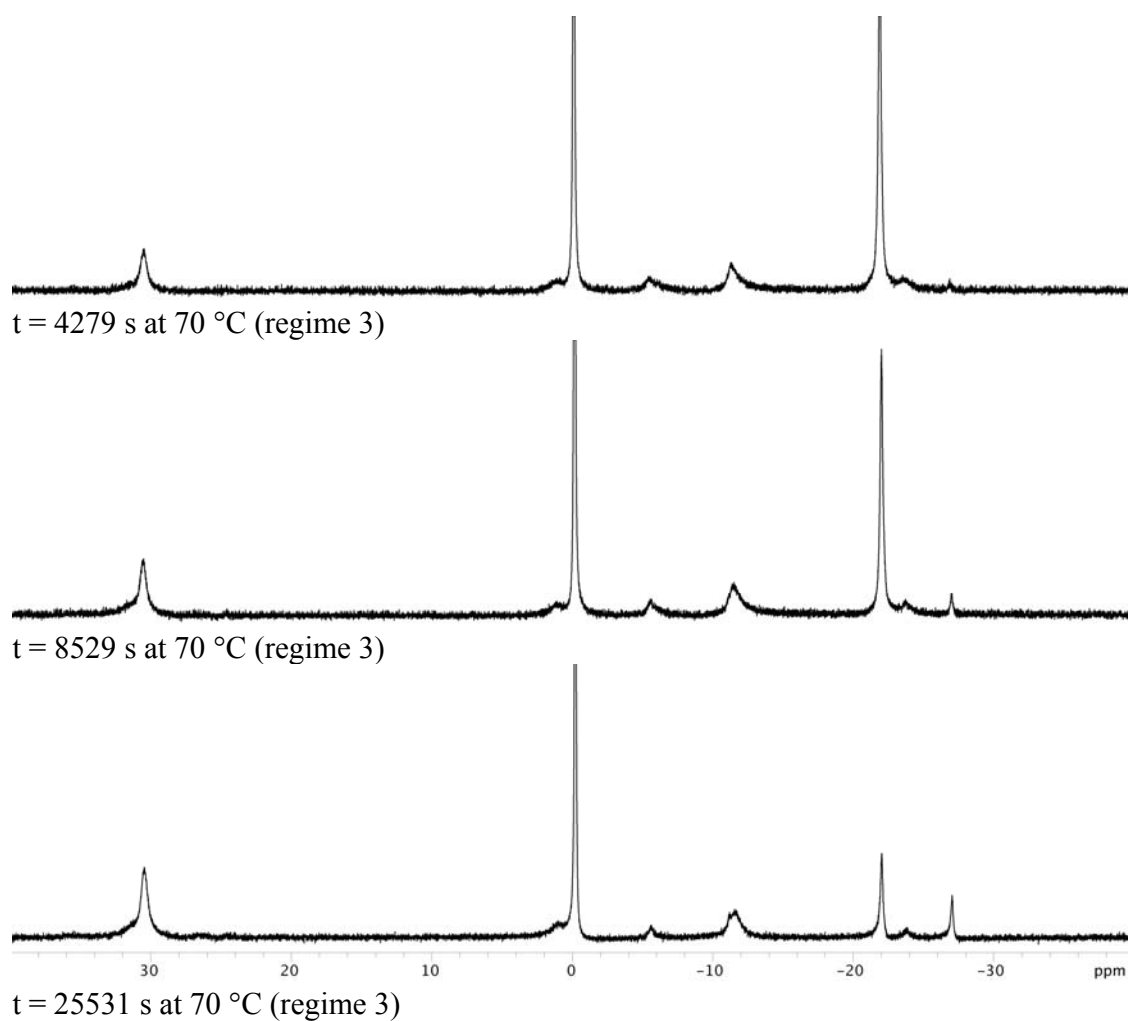


Figure S3. ^{11}B NMR spectra from a representative AB dehydrogenation run (5.0 mol % **1**). Intermediate times show borazine (32 ppm), standard (0 ppm) amine borane cyclic trimer **5** (-5, -11, -23 ppm) and AB (-22 ppm) as well as peaks at -27 ppm, 0.5 ppm, and overlapping at -11 ppm. *Note: The collection of spectra for this run was started at the very end of the initiation period. The initiation period is observed for all catalyst concentrations and in kinetic runs containing ethanol.*

B. Determination of Catalyst Order in Conversion of AB (catalytic)

The rate values for regime 2 in Figure S5. were determined using ^{11}B NMR in sealed NMR tubes, as described above. A typical treatment of the data is shown in Figure S5. and Figure S7. Catalyst concentrations were varied (**1** (mol %) = 2.5, 3.75, 5.0, 7.5). The results were plotted as a ln/ln relationship to determine order in catalyst, Figure S4.

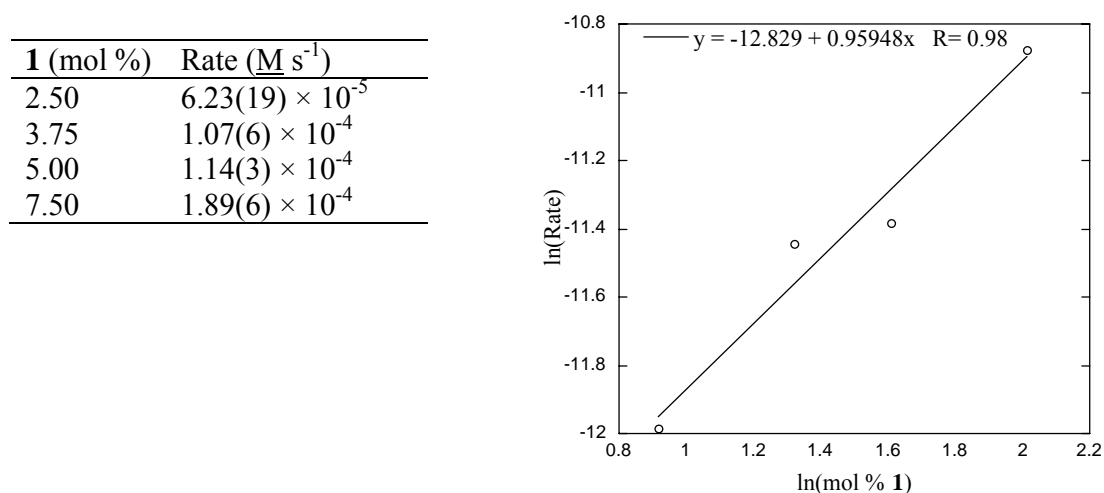


Figure S4. ln(Rate) vs. ln(mol % **1**) for determination of order in catalyst for disappearance of AB at 70.0 °C.

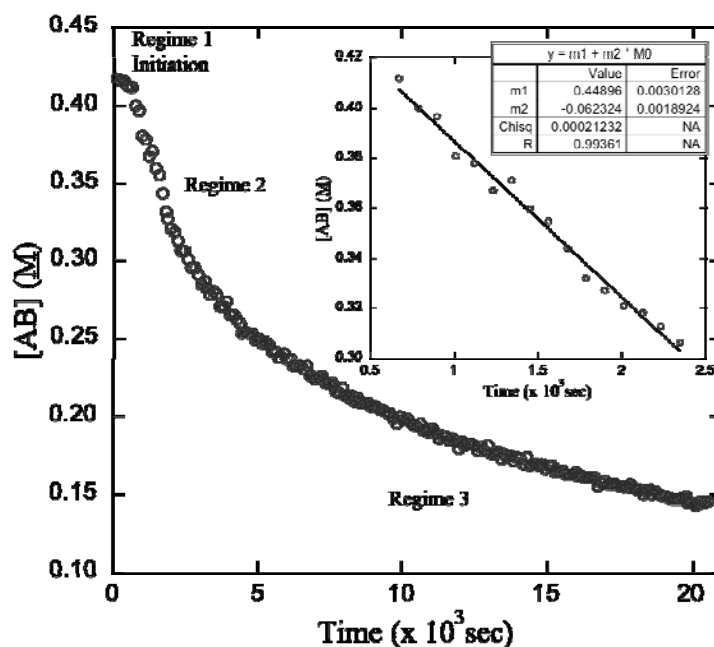


Figure S5. [AB] vs. time monitored by ^{11}B NMR in 2:1 diglyme/benzene- d_6 with 2.5 mol % **1**. Regime 1 = catalyst initiation. Regime 2 = dehydrogenation of AB. Regime 3 = dehydrogenation of AB (inhibited rate). See main text for discussion.

To determine a rate from this plot (Figure S5.) we examined regime 2 (Figure S7), as explained above. The error reported for the rate represents the data's deviation from linearity as reflected by the value of m2 (slope).

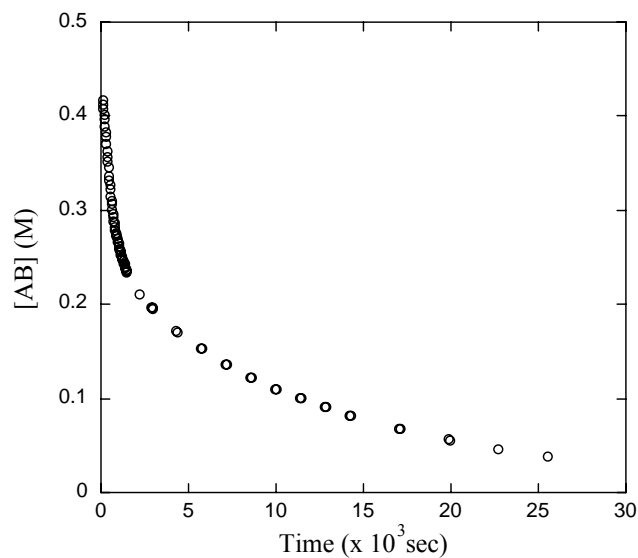
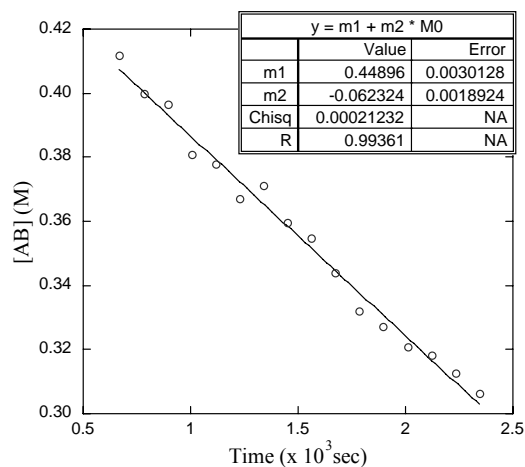
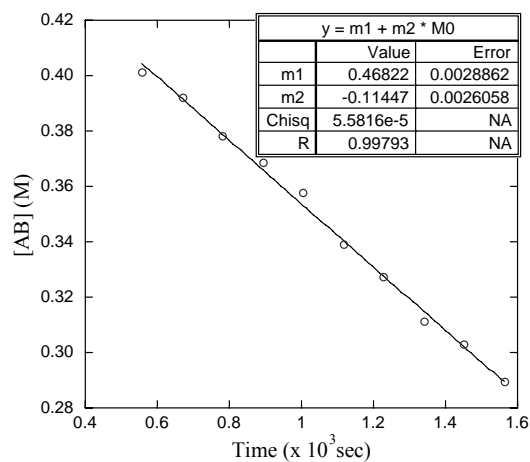


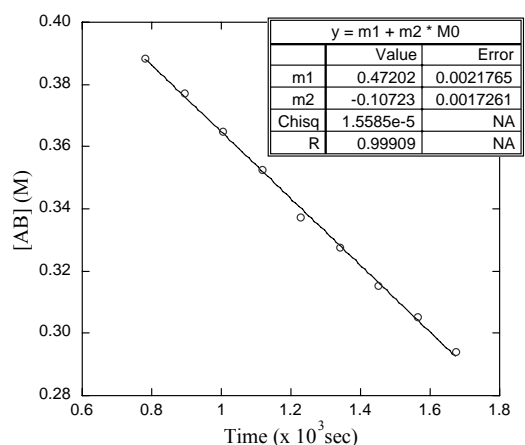
Figure S6. [AB] vs. time monitored by ^{11}B NMR in 2:1 diglyme/benzene- d_6 with 5.0 mol % **1**. Note: See Figure S3 for ^{11}B NMR spectra throughout this reaction. The collection of spectra for this run was started at the very end of the initiation period due to the need to correct an NMR instrument error. The initiation period is observed for all catalyst concentrations and in kinetic runs containing ethanol.



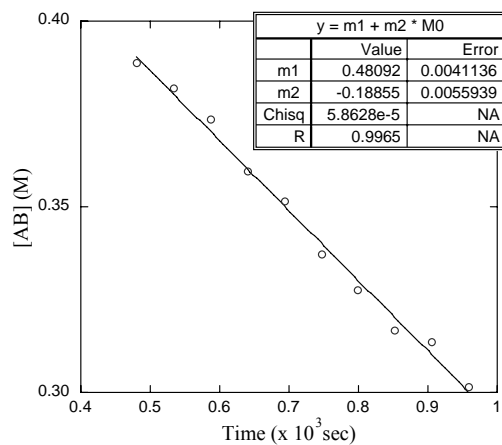
2.5 mol % **1**. Rate = $6.23(19) \times 10^{-5} \text{ M s}^{-1}$.
Conversion = 2-27%



5.0 mol % **1**. Rate = $1.14(3) \times 10^{-4} \text{ M s}^{-1}$.
Conversion = 4-31%



3.75 mol % **1**. Rate = $1.07(6) \times 10^{-4} \text{ M s}^{-1}$.
Conversion = 6-29%



7.5 mol % **1**. Rate = $1.89(6) \times 10^{-4} \text{ M s}^{-1}$.
Conversion = 6-29%

Figure S7. Regime 2 of [AB] vs. time monitored by ¹¹B NMR in 2:1 diglyme/benzene-*d*₆ with varying catalyst concentrations. Slope of the line represents the observed rate in $\text{M s}^{-1} (\times 10^{-3})$.

C. Determination of Order in AB

We originally believed that the linear nature of Regime 2 suggested that the catalysis was first order in AB. After considering several useful comments from our reviewers, we conducted a study to definitively identify the order on AB during this regime. We observed the rate of several 5.0 mol % kinetics runs at different concentrations of AB and **1** and plotted the data in a ln/ln plot (Figure S8) modeled on the rate expression below, which assumes first order behavior on [**1**] (determined in SI Section B). The resulting data (slope of the trendline) indicates that the reaction is zero-order in AB.

$$\text{Rate} = k[\text{AB}]^x [\mathbf{1}]^1$$

$$\therefore \ln\left(\frac{k_{\text{obs}}}{[\mathbf{1}]}\right) = x \ln[\text{AB}]$$

1 (mmol)	AB (mmol)	k_{obs} (s^{-1})
0.00625	0.125	$2.53(4) \times 10^{-4}$
0.00940	0.188	$4.71(10) \times 10^{-4}$
0.0125	0.250	$5.32(10) \times 10^{-4}$
0.0157	0.313	$6.46(10) \times 10^{-4}$

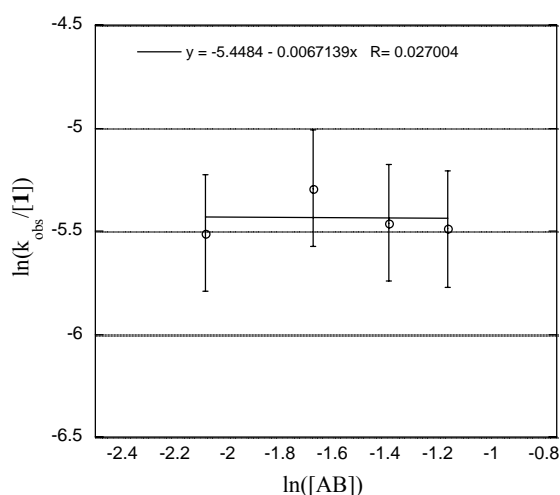


Figure S8. $\ln(k_{\text{obs}}/[\mathbf{1}])$ vs. $\ln([\text{AB}])$ for determination of order in AB for disappearance of AB at 70.0 °C. Error bars represent quality of fit.

D. Catalysis Initiation Step: Conversion of **1** to **2**

An initiation period for consumption of AB (regime 1) was observed during the NMR kinetics runs. This was attributed to the conversion of Shvo's catalyst (**1**) to a monomeric hydride. The hydride region of the ^1H NMR was convenient to study for the disappearance of **1** (-18 ppm) and appearance of **2** (-10 ppm), as shown in Figure S9. Aware that AB may have a role in the initiation, we studied the order in this reagent by varying its concentration and observing the effect on k_{obs} for conversion of **1** to **2** at 55 °C. In a 8" J. Young tube, 5.0 mg **1** (4.6×10^{-3} mmol) were heated with varying concentrations of AB (10, 20, 30, 40 equiv.) at 55 °C in a 2:1 diglyme/benzene- d_6 solvent.

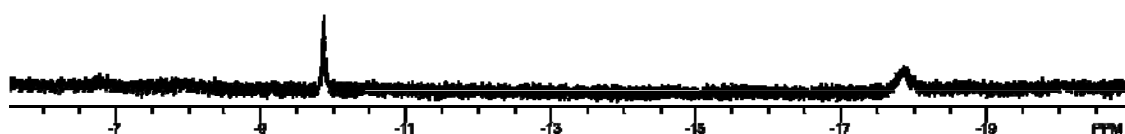


Figure S9. ^1H NMR spectrum showing the hydride region during conversion of **1** (-18 ppm) to **2** (-10 ppm).

AB (equiv.)	k_{obs} (s^{-1})
10.0	$7.96(21) \times 10^{-4}$
20.0	$7.36(29) \times 10^{-4}$
30.0	$7.52(27) \times 10^{-4}$
40.0	$6.95(27) \times 10^{-4}$

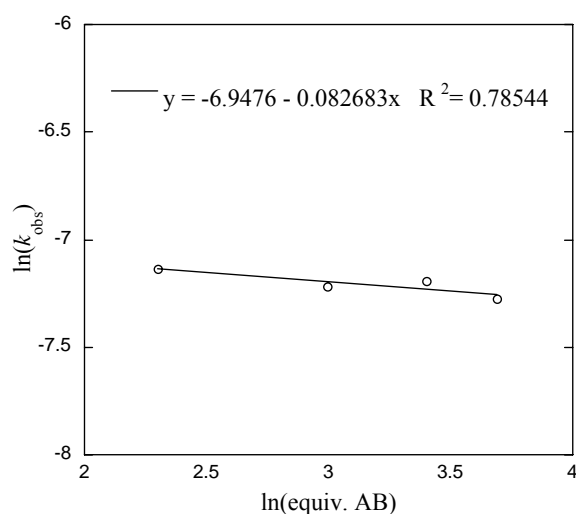


Figure S10. $\ln(k_{\text{obs}})$ vs. $\ln(\text{equiv. AB})$ for determination of order of AB on rate of conversion of bridging hydride **1** to monomeric hydride **2**.

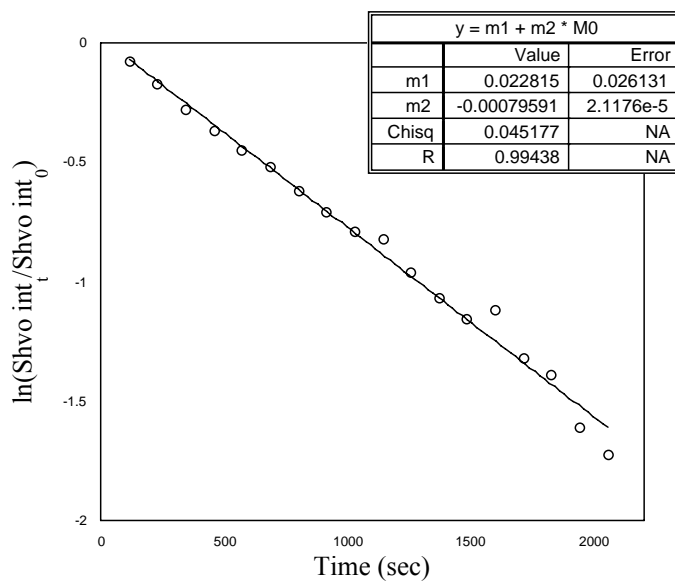


Figure S11. Plot of $\ln([1]/[1]_0)$ (Shvo integration_t/Shvo integration₀) vs. time monitored by ^1H NMR in 2:1 diglyme/benzene- d_6 with 5.0 mg **1** and 10 equiv. AB. $k_{\text{obs}} = 7.96(21) \times 10^{-4} \text{ s}^{-1}$.

E. Determination of Ethanol Dependence on Conversion of AB (catalytic)

To determine the effect of added ethanol on the reaction rate the amount of ethanol added to the solution before the tube was heated was systematically increased. Again, we analyzed regime 2 in the [AB] vs. time curve. A typical treatment of the data is shown in Figure S13. The values determined from the slopes were plotted against [EtOH] as shown in Figure S12. The relatively high y-intercept of this graph probably corresponds to an ethanol-free mechanism wherein two equivalents of **2** collide in a way that one serves as the alcohol to shuttle the proton on the other. Casey characterized this mechanism in reference 21 of the main text.

[EtOH] (mol %, M)	Rate (M s^{-1})
0.0, 0.0	$1.14(3) \times 10^{-4}$
3.4, 0.014	$1.45(4) \times 10^{-4}$
6.9, 0.029	$1.64(4) \times 10^{-4}$
10.3, 0.043	$1.98(6) \times 10^{-4}$
17.0, 0.071	$2.28(4) \times 10^{-4}$

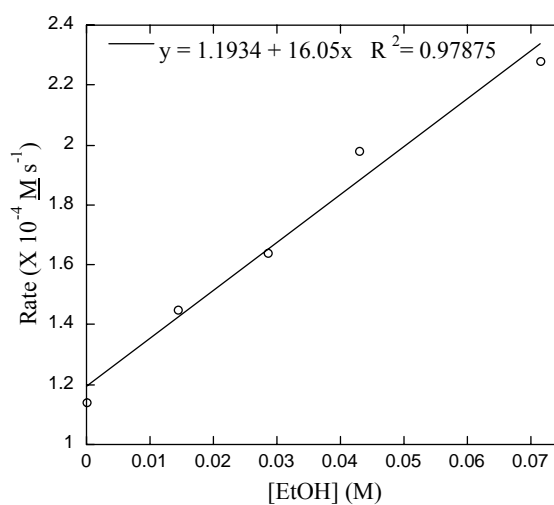


Figure S12. Dependence of reaction rate on concentration of ethanol in first dehydrogenation of AB by 5.0 mol % **1**.

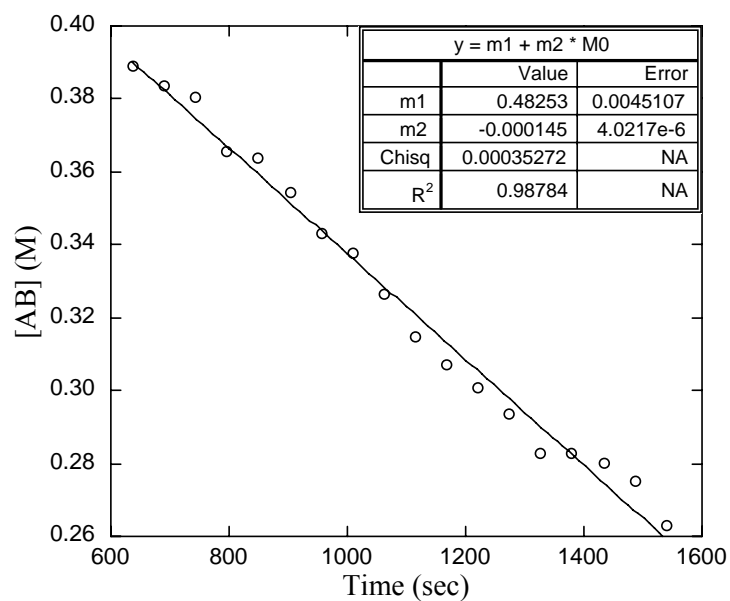


Figure S13. Regime 2 for [AB] vs. time monitored by ¹¹B NMR in 2:1 diglyme/benzene-*d*₆ at 70 °C with 5.0 mol % **1** and 3.4 mol % EtOH. Rate = 1.45(4) × 10⁻⁴ M s⁻¹.

F. Reusability Reactions

To test the long term stability and reusability of the catalyst we studied the kinetics of dehydrogenation of AB by loss of its resonance in the ^{11}B NMR spectrum over four sequential runs with 5.0 mol % catalyst loading at 70 °C. The first run produced the expected kinetic profile with three distinct regimes. However, the decrease in [AB] over the three successive runs fit to exponential decay, suggesting first order behavior in [AB]. Interestingly, the observed first order rate constant for these reactions *increased* as evidenced by the data below in Figure S16. During run 1, we observed the presence of cyclic trimer (**5**) as well as a prominent peak at -27 ppm, which shows up at longer reaction times. In Runs 2-4, **5** did not appear to build up in solution. Instead, it appears a significant portion of AB is converted to the species at -27 ppm, which is then converted to borazine. The ^{11}B NMR for the peak at -27 is consistent with μ -aminodiborane, $\text{B}_2\text{H}_7\text{N}$ (triplet, $J_{\text{BH}} = 134$ Hz).³ There is also a peak at -11 ppm (overlapping a resonance for **5**), which is present throughout. A wet1D protocol was used to obtain a ^1H NMR spectrum (Figure S15) at the end of the fourth run. This spectrum indicates the presence of hydride species in the 9.5-10 ppm. This evidence is not definitive for the presence of a catalytic (cyc)Ru-H species throughout the reaction but suggests it may be the case. These reactions result in the build-up of borazine in solution.

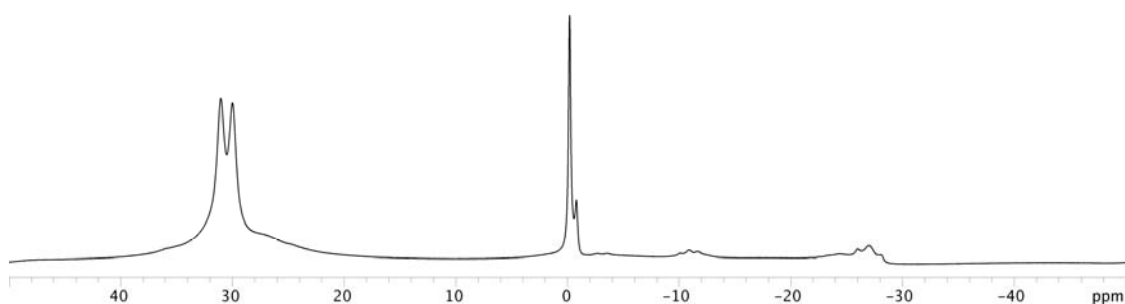


Figure S14. ^{11}B NMR (^1H coupled, 25 °C) at completion of run 4, processed and baseline corrected. Triplet at -27 ppm has $J_{\text{BH}} = 134$ Hz.

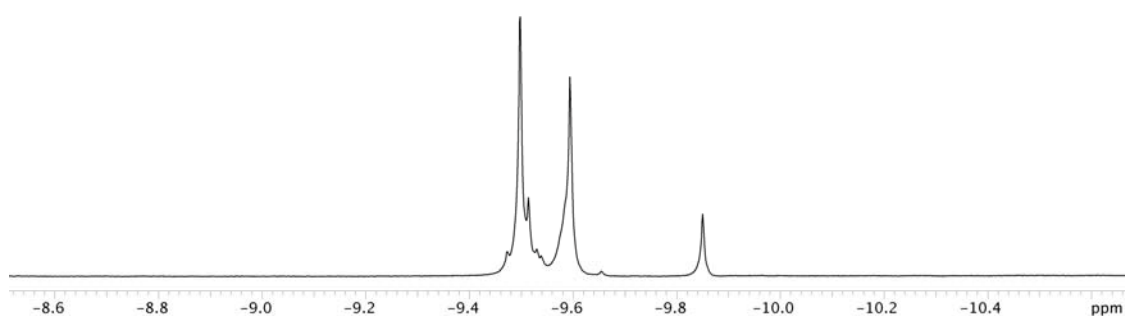


Figure S15. ^1H NMR (25 °C) of hydride peaks at completion of run 4.

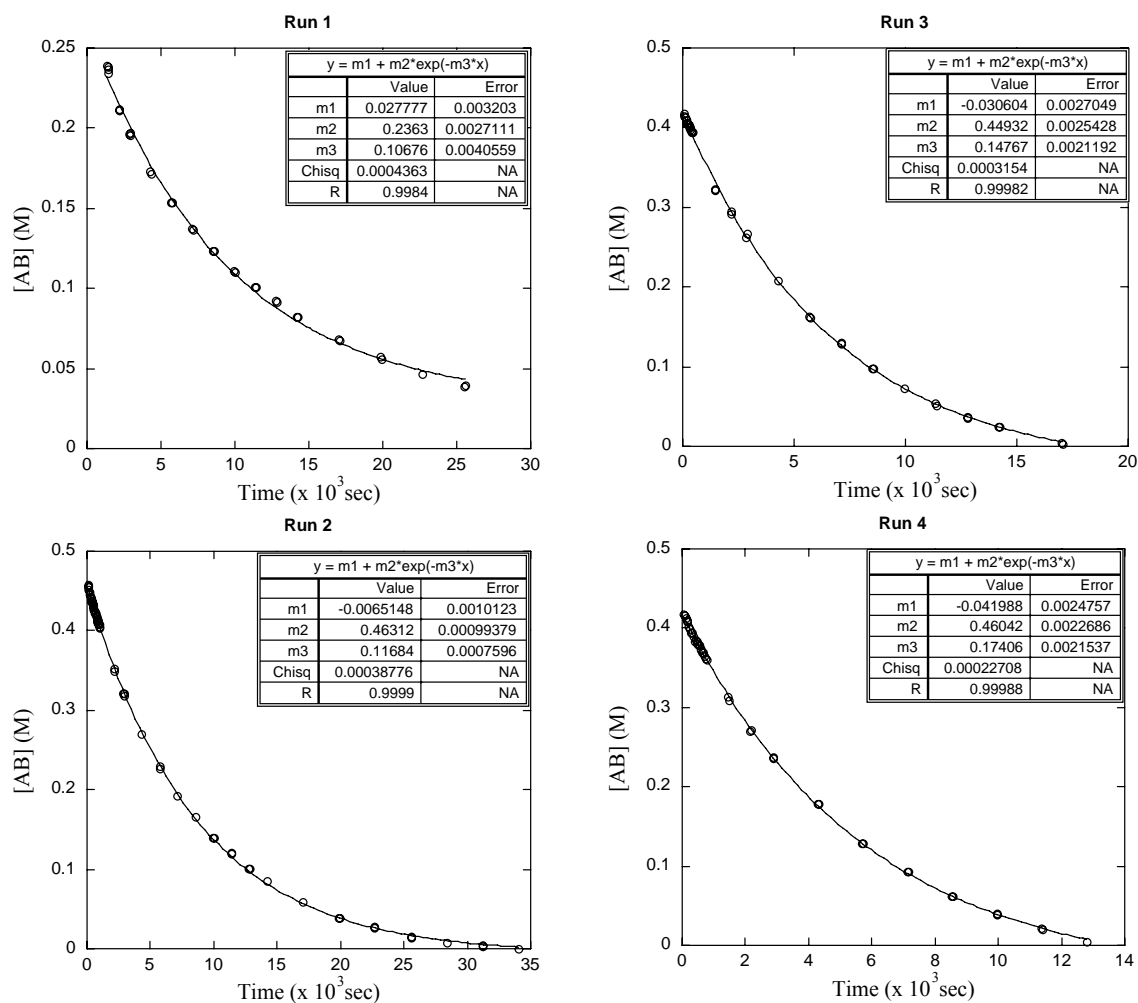


Figure S16. [AB] vs. time for successive kinetic runs of 5 mol % **1** in 2:1 diglyme/benzene-*d*₆ at 70 °C monitored by ¹¹B NMR. The plot for run 1 intentionally neglects regime 1 (initiation) and regime 2 (linear) and models regime 3. All plots fit an exponential decay function.

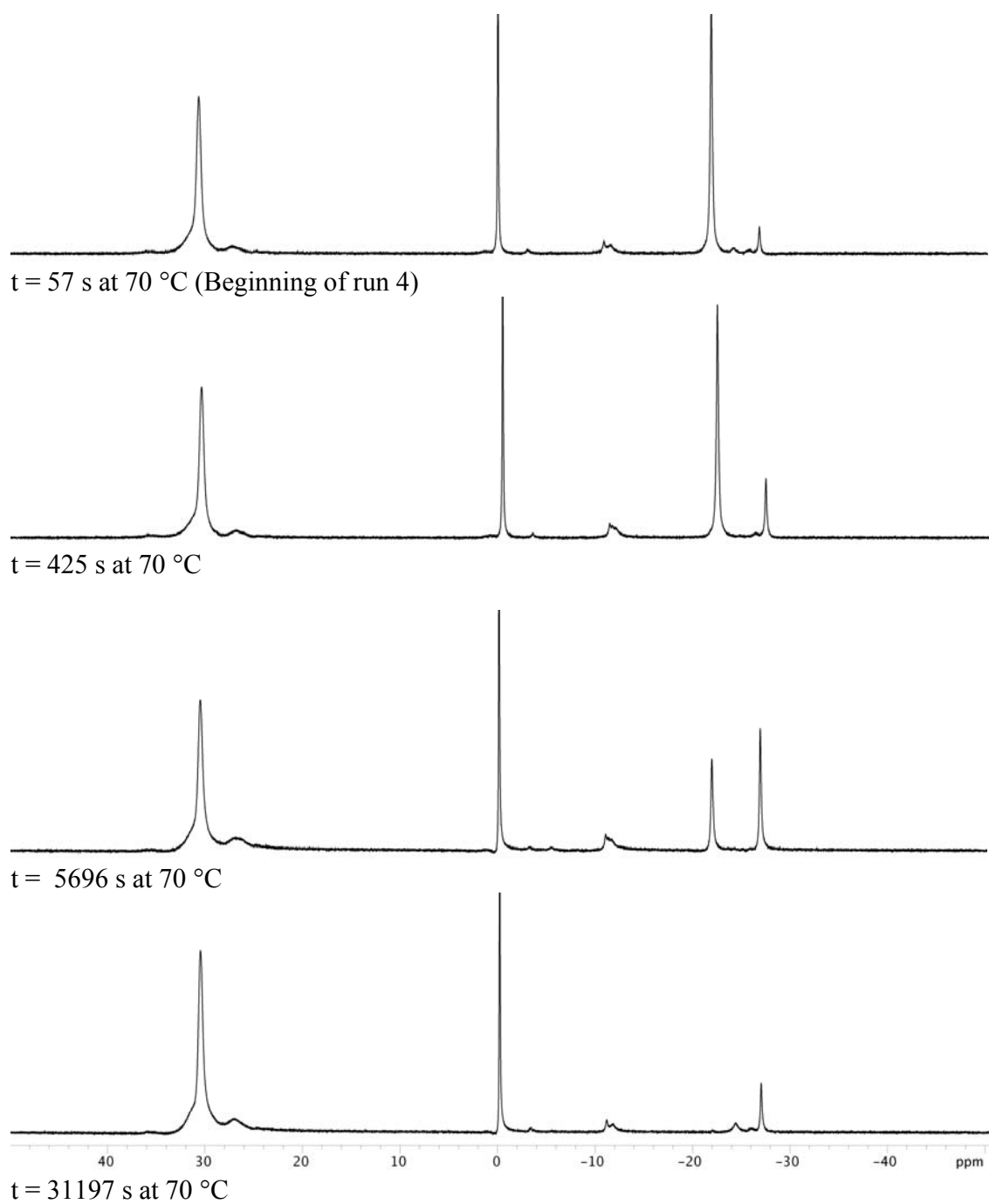


Figure S17. ^{11}B NMR spectra throughout run 4 (compare to run 1, Figure S3)

G. Dehydrogenation of AB in the Presence of Added Borazine

AB (7.7 mg, 0.25 mmol) was combined with Shvo's catalyst (**1**, 13.6 mg, 5.0 mol %) and borazine (8.3 μL , 0.083 mmol) in an 8" J. Young tube in a glove box under nitrogen. Diglyme (0.4 mL) and benzene- d_6 (0.2 mL) were then added to the tube. ^{11}B NMR kinetics were carried out at 70 $^\circ\text{C}$ as described above.

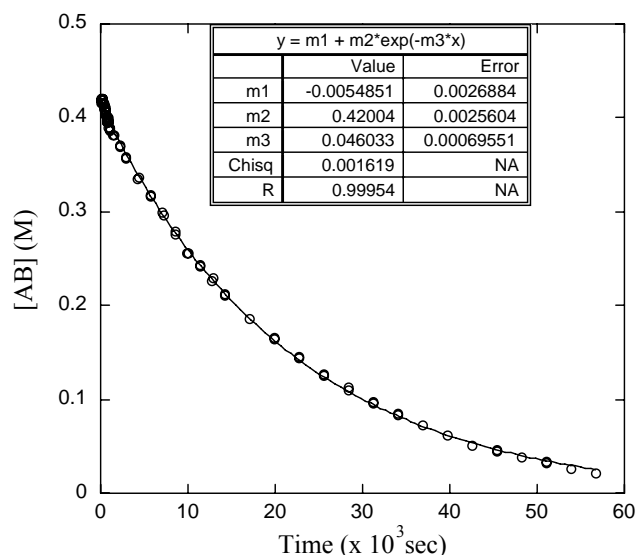


Figure S18. [AB] vs. time monitored by ^{11}B NMR in 2:1 diglyme/benzene- d_6 with 5.0 mol % **1** at 70 $^\circ\text{C}$ in the presence of 0.25 mmol added borazine. Rate = $4.60 \times 10^{-5} \text{ M s}^{-1}$

H. Derivatization of Shvo's catalyst **1** with Borazine

Borazine (8.3 μL , 0.083 mmol, 6.7 eq) and Shvo's catalyst (**1**, 13.6 mg, 0.0125 mmol) were combined in an 8" J. Young tube in a glove box under nitrogen. Diglyme (0.4 mL) and benzene- d_6 (0.2 mL) were then added to the tube. The NMR tube was heated at 50 $^\circ\text{C}$ in the NMR probe for 15 minutes, over which time the Shvo bridging hydride converted quantitatively to the hydride species show in Figure S19 and the color of the solution turns bright yellow.

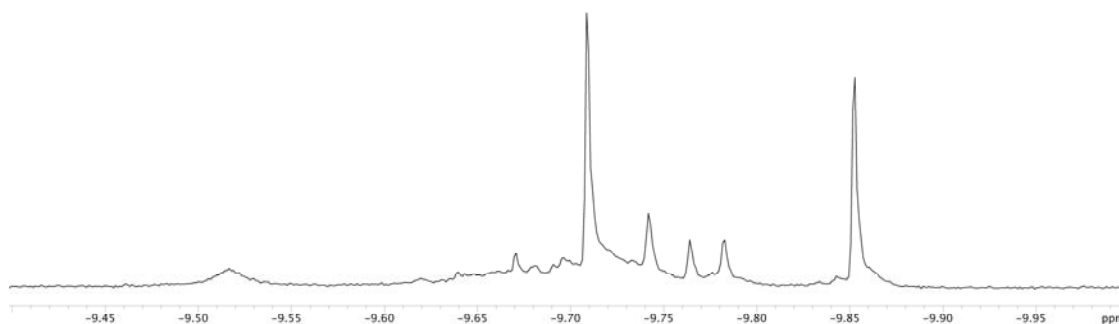


Figure S19. Hydride region of **1** heated with ~ 7 equivalents borazine at 50 $^\circ\text{C}$ for 15 min.

I. Thermal Control Reactions

Figures S20 and S21 show the *initial* rate for hydrogen loss from AB at 70 °C in the presence and absence of ethanol, respectively.

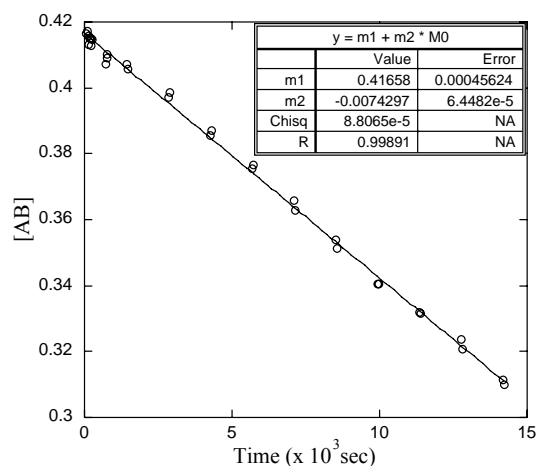


Figure S20. Thermal dehydrogenation of AB in the presence of 2.0 mol % ethanol in 2:1 diglyme/benzene-*d*₆ at 70 °C monitored by loss of AB in ¹¹B NMR. Initial rate = 7.43 × 10⁻⁶ M s⁻¹

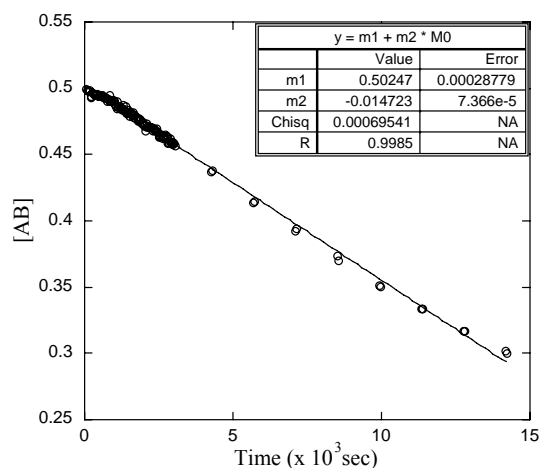


Figure S21. Thermal dehydrogenation of AB in 2:1 diglyme/benzene-*d*₆ at 70 °C monitored by loss of AB in ¹¹B NMR. Initial rate = 1.45 × 10⁻⁵ M s⁻¹

J. Rate Law for Catalysis in Regime 2

Anticipated rate law for the mechanism proposed in Scheme 2 in the presence of ethanol.

$$(1) \text{Rate} = k_1[\mathbf{2}][\text{EtOH}]$$

$$(2) [\text{Ru}_T] = [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}] \quad (\text{recall that } [\text{Ru}_T] = 2[\mathbf{1}_{\text{init}}] \text{ because } \mathbf{1} \text{ is a dimer})$$

Steady state assumption applied to $[\mathbf{3}]$:

$$(3) \frac{d[\mathbf{3}]}{dt} = 0 = k_2[\mathbf{4}] - k_3[\text{AB}][\mathbf{3}]$$

$$(4) [\mathbf{3}] = \frac{k_2[\mathbf{4}]}{k_3[\text{AB}]}$$

Steady state assumption applied to $[\mathbf{4}]$:

$$(5) \frac{d[\mathbf{4}]}{dt} = 0 = k_1[\mathbf{2}][\text{EtOH}] - k_2[\mathbf{4}]$$

$$(6) [\mathbf{4}] = \frac{k_1[\mathbf{2}][\text{EtOH}]}{k_2}$$

Substituting (5) and (6) into (2) gives, with rearrangement:

$$(7) [\mathbf{2}] = [\text{Ru}_T] - \frac{k_2}{k_3[\text{AB}]}[\mathbf{4}] - \frac{k_1}{k_2}[\mathbf{2}][\text{EtOH}]$$

Substituting (6) again gives

$$(8) [\mathbf{2}] = [\text{Ru}_T] - \frac{k_2}{k_3[\text{AB}]} \left(\frac{k_1}{k_2}[\mathbf{2}][\text{EtOH}] \right) - \frac{k_1}{k_2}[\mathbf{2}][\text{EtOH}]$$

$$(9) [2] = [Ru_T] - \frac{k_1}{k_3[AB]}[2][EtOH] - \frac{k_1}{k_2}[2][EtOH]$$

Solving (9) for $[Ru_T]/[2]$ gives

$$(10) \frac{[Ru_T]}{[2]} = 1 + \frac{k_1[EtOH]}{k_3[AB]} + \frac{k_1[EtOH]}{k_2}$$

This gives

$$(11) [2] = \frac{[Ru_T]}{1 + \frac{k_1[EtOH]}{k_3[AB]} + \frac{k_1[EtOH]}{k_2}}$$

Substituting (11) into rate law (1) give the three-term rate law (12)

$$(12) \text{Rate} = \frac{k_1[Ru_T][EtOH]}{1 + \frac{k_1[EtOH]}{k_3[AB]} + \frac{k_1[EtOH]}{k_2}}$$

In the case where $k_2 \gg k_1$, this simplifies to

$$(13) \text{Rate} = \frac{k_1[Ru_T][EtOH]}{1 + \frac{k_1[EtOH]}{k_3[AB]} + 0}$$

In the case where $k_3[AB] \gg k_1$, this further simplifies to

$$(14) \text{Rate} = \frac{k_1[Ru_T][EtOH]}{1+0+0} = k_1[Ru_T][EtOH] = 2k_1[I_{init}][EtOH]$$

IV. References

1. Wideman, T.; Sneddon, L.G. *Inorg. Chem.* **1995**, *34*, 1002-1003.
2. (a) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844-1845. (b) Blaquiere, N.; Diallo-Garcia, S.; Gorelsky, S. I.; Black, D. A.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 14034-14035.
3. (a) Schlesinger, H. I.; Ritter, D. M.; Burg, A. B. *J. Am. Chem. Soc.* **1938**, *60*, 2297-2300. (b) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1964**, *86*, 1505-1507. (c) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613-2626.