Supporting Information

Iridium Catalyzed Dehydrogenation of Substituted Amine-Boranes: Kinetics, Thermodynamics and Implications for Hydrogen Storage.

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General Experimental

Unless otherwise stated, all manipulations were carried out using high vacuum techniques, under an atmosphere of argon in a glove box (Vacuum Atmospheres) or using Schlenk techniques. THF was purified by passage through a column of alumina, and pentane through columns of alumina and Q5 reactant. THF-d_8 was vacuum transferred from sodium metal/benzophenone. ($^{t\text{Bu}}$POCOP)Ir(H)$_2$ (**1**) was prepared as described in the literature (*1*). Ammonia borane and methylamine-borane were sublimed under vacuum at 65 °C and 35 °C respectively before use and stored in a glove box. All other reagents were used as received.

Solution NMR spectra were collected using Bruker AV300, DPX200 and DRX499, and AV500 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual solvent signals and shifts are reported in parts per million (ppm) downfield of tetramethylsilane. ^{11}B NMR spectra were referenced to an external sample of $BF_3.Et_2O$ set to 0 ppm. Calorimetry experiments were collected using a Setaram C80 Differential Scanning Calorimeter. IR spectra were collected using a Perkin-Elmer 1720 Infrared Fourier Transform Spectrometer. ESI-MS data was acquired on a Bruker Esquire Liquid Chromatograph - Ion Trap Mass Spectrometer.

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.*

NMR Characterization of Soluble Dehydrogenation Products

Dehydrogenation of MeAB with 1. A J-Young tube was charged with MeAB (20.0 mg, 0.45 mmol) and **1** (2.6 mg, 4.4 μmol). THF-d_8 was vacuum transferred into the tube (~0.5 mL), and a rapid color change from red to yellow along with vigorous gas evolution was observed immediately upon thawing. ^{1}H NMR (300 MHz, THF-d_8) δ 3.21 (s br, 1H, N*H*), 3.00 (s br, 2H, N*H*), 2.21 (s br, 9H, N-CH_3), 1.76 (br, 6H, BH_2). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8) δ 38-36 (multiple resonances), 36.3 (s). ^{11}B NMR (160 MHz, THF-d_8) δ −8.31 (s vbr). IR (KBR, cm^{-1}): 3447 (s br), 3275 (s), 2989 (m), 2393 (s br), 2308 (m sh) 1599 (m br), 1457 (m), 1419 (m), 1383 (m), 1356 (m), 1240 (s br), 1174 (m br), 1049 (w), 997 (w), 865 (w br).

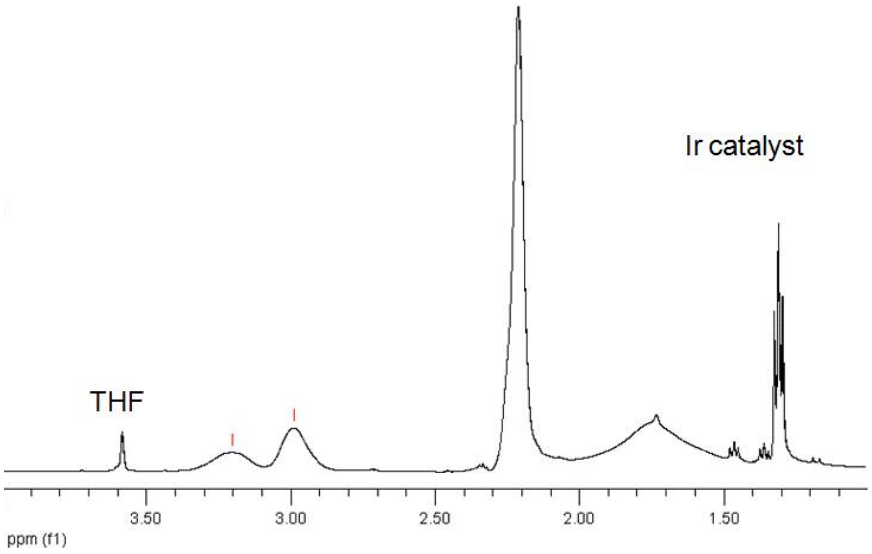

Figure 1. ^{1}H NMR spectrum of MeAB dehydrogenation product (300 MHz, THF-d_8, 298 K)

Dehydrogenation of 1:1 Mixture of AB and MeAB with 1. A J-Young tube was charged with AB (6.3 mg, 0.20 mmol), MeAB (9.3 mg, 0.21 mmol), and **1** (2.4 mg, 4.1 μmol, 1.0 mol%). THF-d_8 was vacuum transferred into the tube (~0.5 mL), and a rapid color change from red to yellow along with vigorous gas evolution was observed

immediately upon thawing. ^{1}H NMR (300 MHz, THF-d_8) δ 3.13 (br, N*H*), 2.95 (br, N*H*), 2.85 (br, N*H*), 2.80 (br, N*H*), 2.72 (br, N*H*), 2.20 (N-CH_3), 2.21 (N-CH_3), 1.91 (br, BH_2). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8) δ 37-36 (multiple resonances). ^{11}B NMR (160 MHz, THF-d_8) δ −8.7 (br), −11.4 (br). IR (KBR, cm^{-1}): 3419 (s br), 3313 (s), 3266 (s), 2986 (m), 2954 (m), 2363 (s br), 1572 (m), 1460 (m), 1365 (m), 1191 (s br), 1144 (s sh), 1049 (m), 864 (m).

Dehydrogenation of 2:1 Mixtures of AB and MeAB with 1. A J-Young tube was charged with AB (8.5 mg, 0.28 mmol), MeAB (6.2 mg, 0.14 mmol), and **1** (2.3 mg, 3.9 μmol, 1.0 mol%). THF-d_8 was vacuum transferred into the tube (~0.5 mL), and a rapid color change from red to yellow along with vigorous gas evolution was observed immediately upon thawing. Formation of a white precipitate was also observed. ^{1}H NMR (300 MHz, THF-d_8) δ 3.13 (br, N*H*), 2.95 (br, N*H*), 2.85 (br, N*H*), 2.80 (br, N*H*), 2.72 (br, N*H*), 2.20 (N-CH_3), 2.21 (N-CH_3), 1.91 (br, BH_2). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8) δ 37-36 (multiple resonances). ^{11}B NMR (160 MHz, THF-d_8) δ −6.17 (br), −8.32 (br).

Insoluble precipitate: IR (nujol mull, cm^{-1}): 3299 (s), 3247 (s), 2387 (s br), 2308 (s br), 1559 (m sh), 1208 (s br), 1079 (m), 1057 (m), 843 (w br).

Dehydrogenation of 5:1 Mixtures of AB and MeAB with 1. A J-Young tube was charged with AB (10.6 mg, 0.34 mmol), MeAB (6.2 mg, 0.07 mmol), and **1** (2.4 mg, 4.1 μmol, 1.0 mol%). THF-d_8 was vacuum transferred into the tube (~0.5 mL), and a rapid color change from red to yellow along with vigorous gas evolution was observed immediately upon thawing. Formation of a white precipitate was also observed. ^{1}H NMR (300 MHz, THF-d_8) δ 3.13 (br, N*H*), 2.95 (br, N*H*), 2.85 (br, N*H*), 2.80 (br, N*H*),

2.72 (br, N*H*), 2.20 (N-CH_3), 2.21 (N-CH_3), 1.91 (br, BH_2). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8) δ 38-36 (multiple resonances). ^{11}B NMR (160 MHz, THF-d_8) δ −5.40 (br).

Insoluble precipitate: IR (nujol mull, cm^{-1}): 3300 (s), 3248 (s), 2391 (s br), 2319 (s br), 1559 (m sh), 1209 (s br), 1079 (m), 1059 (m), 970 (w), 842 (w).

Quantification of Hydrogen

Dehydrogenation of MeAB with 1. In a typical experiment, MeAB (73.4 mg, 1.64 mmol) was charged into a 10 mL round bottom flask containing a stir bar and dissolved in THF (2.2 mL). In a separate 10 mL conical vial, **1** (21.8 mg, 36.7 μmol) was dissolved in THF (1.8 mL). Both flasks were sealed with tight-fitting rubber septa. The MeAB flask was connected to a water-filled inverted buret via a needle connected to a thin Teflon tube. Catalyst solution (0.8 mL, 16.4 μmol, 1.0 mol%) was then syringed into the MeAB flask while simultaneously starting a timer. The volume of H_2 collected was monitored periodically until the reaction was complete. The procedure was repeated at different catalyst loadings by modifying the molarity of the iridium solution such that addition of 0.8 mL of solution delivered the desired amount of catalyst.

Dehydrogenation of 1:1 Mixtures of AB and MeAB with 1. The reaction was carried out as described above, using a mixture of AB (25.2 mg, 0.82 mmol) and MeAB (36.7 mg, 0.82 mmol) and the procedure was repeated at different catalyst loadings by modifying the molarity of the iridium solution such that addition of 0.8 mL of solution delivered the desired amount of catalyst.

Differential Scanning Calorimetry (DSC) Experiments

In a typical experiment, a stock solution of the appropriate amine-borane complex or mixture of complexes was made (0.16 M total amine-borane concentration). **1** (5.0 mg, 8.4 μmol, 2.5 mol%) was charged into the central chamber of a reversal mixing hastelloy vessel, and 2.0 mL of amine-borane solution (14.5 mg, 32 μmol) was syringed into the outer chamber. The vessel was sealed and placed in the DSC instrument at a constant 30 °C and allowed to equilibrate for ~2 hours. Data was collected upon inversion of the mixing vessels. Typical time to completion took 4-5 hours.

ESI-MS Experiments

ESI-MS of Soluble Dehydrogenation Products. 3.3 mmol of MeAB or the appropriate AB/MeAB mixture was added to 9.7 mg of **1** (0.5 mol%) and dissolved in 6.0 mL of THF (0.55 M in total amine-boranes). After hydrogen evolution had ceased, the products were isolated by removing the solvent *en vacuo* (in the case of the 2:1 and 5:1 mixed AB/MeAB experiments, the solvent was removed after centrifugation and removal of the insoluble precipitate). 5.0 mg of isolated product was dissolved in 1.0 mL of 10% H_2O in MeOH (NMR experiments were conducted to ensure the products were stable in this solvent mixture). The sample was infused into the ESI-MS instrument and spectra acquired at varying trap drives over regular intervals to get best possible signal to noise at various mass ranges. Spectra were also acquired while systematically varying the capillary exit and skimmer voltages to reduce the amount of any premature

fragmentation, and no significant change in the ratio of the various isotopic distribution patterns was observed.

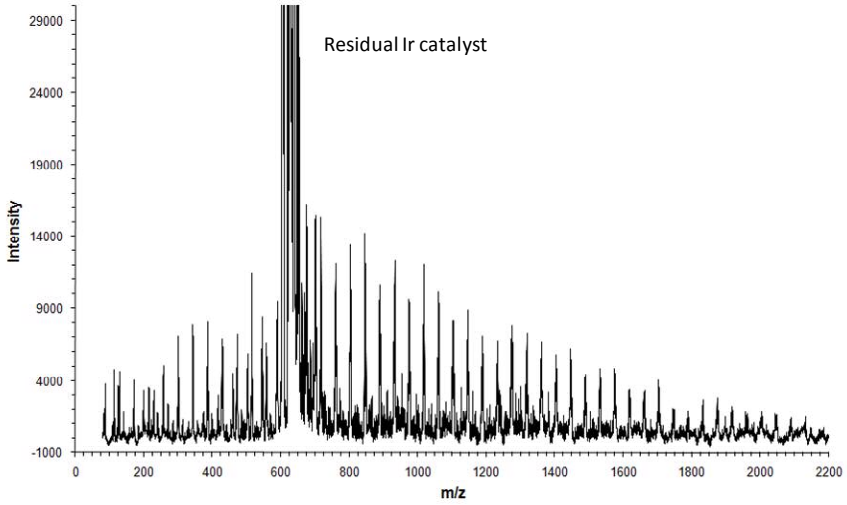

Figure 2. ESI-MS of the MeAB dehydrogenation products. Large peaks in the 600 m/z region represent numerous $[M+H]^+$ ions for various iridium species including **4**, ($^{t\text{Bu}}$POCOP)Ir(H)(OMe), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(H_2), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(OH)(H).

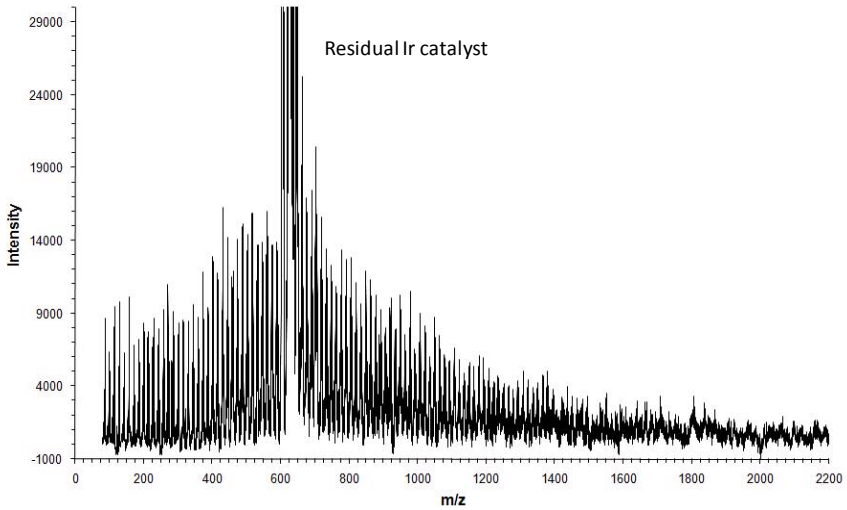

Figure 3. ESI-MS of the 1:1 mixed AB/MeAB dehydrogenation products. Large peaks in the 600 m/z region represent numerous $[M+H]^+$ ions for various iridium species including **4**, ($^{t\text{Bu}}$POCOP)Ir(H)(OMe), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(H_2), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(OH)(H).

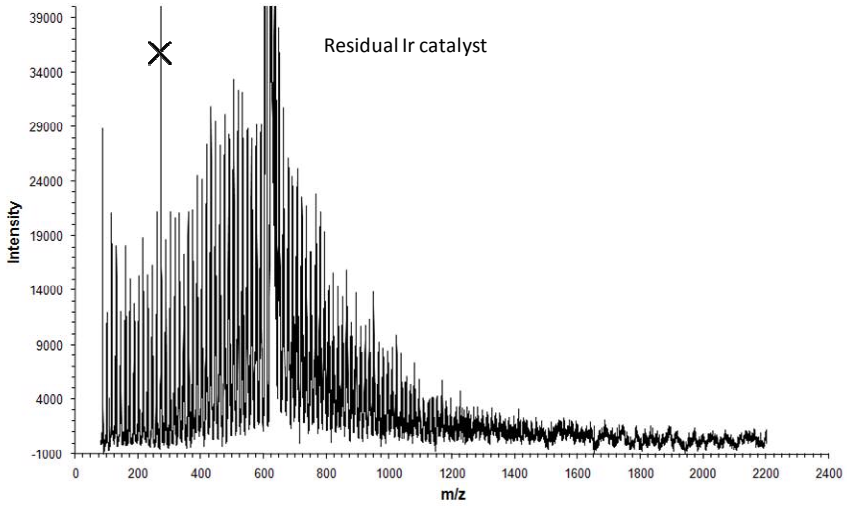

Figure 4. ESI-MS of the soluble portion of the 2:1 mixed AB/MeAB dehydrogenation products. Large peaks in the 600 m/z region represent numerous $[M+H]^+$ ions for various iridium species including **4**, ($^{t\text{Bu}}$POCOP)Ir(H)(OMe), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)$(H)_2$, ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(OH)(H). The crossed out peak shows no isotopic distribution pattern and represents a solvent impurity.

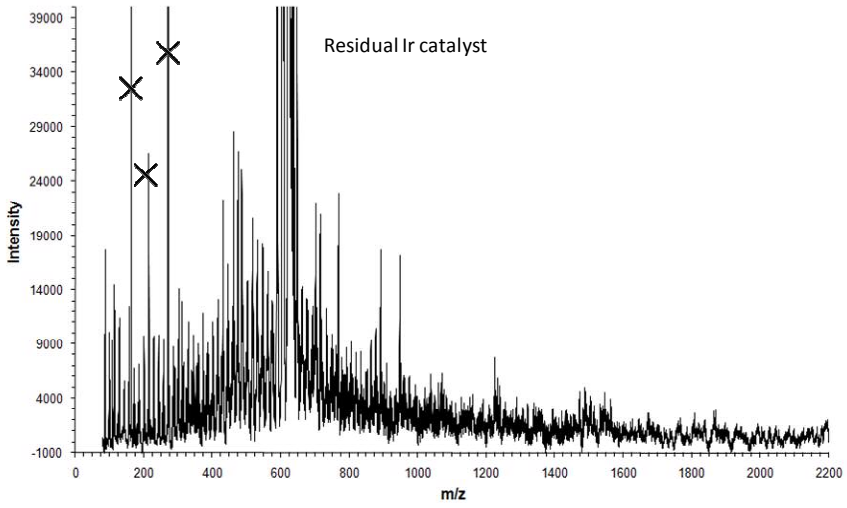

Figure 5. ESI-MS of the soluble portion of the 5:1 mixed AB/MeAB dehydrogenation products. Large peaks in the 600 m/z region represent numerous $[M+H]^+$ ions for various iridium species including **4**, ($^{t\text{Bu}}$POCOP)Ir(H)(OMe), ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)$(H)_2$, ($^{t\text{Bu}}$POCOP)Ir(BH_3)(OMe)(OH)(H). The crossed out peaks show no isotopic distribution patterns and represents impurities in the solvent.

1. Göttker-Schnetmann, P. S. White, M. Brookhart, *Organometallics* **23**, 1766 (2004).