Amineborane Dehydrogenation Promoted by Isolable Zirconium Sandwich, Titanium Sandwich and N\textsubscript{2} Complexes.

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Experimental Procedures

**General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.\(^1\) Toluene, benzene, pentane and heptane were further dried by distillation from “titanocene”.\(^2\) Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Argon and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Me\(_2\)NHBH\(_3\) was purchased from Aldrich and sublimed at 30 °C before use. H\(_3\)NBH\(_3\) was prepared according to literature procedure\(^3\) and recrystallized from THF/Et\(_2\)O at low temperature prior to use.

\(^1\)H and \(^13\)C NMR spectra were recorded on a Varian Inova 400 Spectrometer operating at 399.799 MHz (\(^1\)H) and on a Varian Inova 500 Spectrometer operating at 125.704 MHz (\(^13\)C), respectively. \(^{11}\)B NMR spectra were recorded on a Bruker ARX 300 MHz Spectrometer operating at 96.294 MHz (\(^{11}\)B). In some cases, reactions catalytic reactions were monitored in THF solution by \(^{11}\)B NMR spectroscopy. Chemical shifts are reported relative to SiMe\(_4\) using \(^1\)H (residual) or \(^{13}\)C NMR chemical shifts of the solvent as secondary standard or external BF\(_3\)·Et\(_2\)O (\(^{11}\)B). \(1, 4, 2, 5, 3, 6, 4, 7, 6, 8, 7, 9, 8, 10, 9, 10, 11, 10, 11\) and \(11\)\(^{11}\) were all prepared according to literature procedures.
**General Procedure for Catalytic Dehydrogenation of Me₂NHBH₃.** A J. Young NMR tube was charged with 0.018 g (305 μmol) of Me₂NHBH₃ and 0.003 g (6 μmol) of the desired catalyst. Approximately 0.5 mL of benzene-d₆ was added to the tube, sealed with a Teflon valve and heated to 65 °C in a temperature controlled oil bath if necessary. Conversion to [Me₂NBH₂]₂ was monitored as a function of time by ¹¹B NMR and ¹H NMR spectroscopy. ¹¹B NMR (benzene-d₆): δ = 5.0 (t, J_BH = 112 Hz, [Me₂NBH₂]₂); δ = 1.5 (t, J_BH = 113 Hz, [Me₂NBH₂]₃), δ = 37.8 (t, J_BH = 130 Hz, Me₂N=BH₂). A similar procedure was used for the dehydrogenation of NH₃BH₃ with THF as the solvent.

**Quantification of H₂ Gas by Toepler Pump.** A J. Young NMR tube was charged with 0.011 g (187 μmol) of Me₂NHBH₃ and 7 μmol of the desired catalyst. Approximately 0.5 mL of benzene was added either by vacuum transfer or via pipette. The catalytic reaction was stirred until it reached the known time for completion after which time all of the gases were collected by a Toepler pump and quantified. The gases were exposed to combustion conditions by heating to 75 °C under vacuum and the non-condensable gas recollected and the amount of hydrogen liberated determined by difference.

**Preparation of (η⁵-C₈H₁₅-1,3-Pr₂)(η⁵-C₈H₉-1,3-Pr₂)Zr(BH₄)H (13).** A thick walled glass vessel was charged with 0.050 g of (0.102 mmol) of 9 and approximately 5 mL of toluene was added. To the burgundy solution, 0.301 g (5.10 mmol) of Me₂NHBH₃ dissolved in approximately 15 mL of toluene was added, resulting in an immediate color change to yellow. The reaction mixture was stirred and heated to 65 °C for one week, after which time the dihydrogen byproduct, solvent, amineborane product and unreacted
starting material were removed in vacuo. Recrystallization from pentane at 35 °C yielded 0.082 g (79.0%) of a white solid identified as 13. Anal. Calcd. for C_{30}H_{47}ZrB: C, 70.59; H, 9.22. Found: C, 70.59; H, 9.38. ^1H NMR (benzene-d_6): δ = 0.03 (br, 4H, BH_4), 1.02 (d, 8Hz, 3H, THI CHMe_2), 1.06 (d, 4Hz, 3H, THI CHMe_2), 1.13 (d, 7Hz, 3H, Ind CHMe_2), 1.16 (d, 7Hz, 3H, Ind CHMe_2), 1.21 (d, 7Hz, 3H, THI CHMe_2), 1.24 (d, 8Hz, 3H, Ind CHMe_2), 1.37 (m, 1H, THI), 1.41 (m, 1H, THI), 1.51 (d, 7Hz, 3H, Ind CHMe_2), 1.62 (d, 7Hz, 3H, Ind CHMe_2), 1.92 (m, 2H, THI), 2.42 (m, 4H, 2 THI/2 THI CHMe_2), 2.72 (s, 1H, Zr-H), 2.81 (m, 1H, THI), 3.02 (m, 1H, THI), 3.16 (m, 1H, Ind CHMe_2), 3.85 (m, 1H, Ind CHMe_2), 5.16 (s, 1H, CpH), 6.70 (m, 1H, benzo), 6.77 (m, 1H, benzo). ^11B NMR (benzene-d_6): δ = 6.00 (br, Zr-BH_4). ^13C NMR (benzene-d_6): δ = 21.99, 22.22, 22.61, 23.17, 23.37, 24.09, 24.83, 25.49, 25.59, 25.73, 25.96, 25.97, 26.96, 27.41, 28.77, 29.74 (CHMe_2/THI), 108.5, 112.07, 117.34, 117.97, 120.10, 122.04, 123.08, 123.35, 124.20, 124.61, 124.85, 124.94, 126.18, 131.48 (Cp/Benzo). IR (KBr): ν = 2106 (w), 1966 (m), 1634 (w), 1456 (m), 1376 (m), 1142 cm\(^{-1}\) (w).

**Preparation of (η^5-C_{9}H_{9}-1,3-iPr_2)_2Zr(BH_4)H (14).** This compound was prepared in a similar manner to 13 with 0.070 g of (0.140 mmol) of 11 and 0.160 g (2.71 mmol) of Me_2NHBH_3 with heating at 70 °C for three weeks. ^1H NMR (benzene-d_6): δ = -0.02 (br, 4H, BH_4), 1.16 (d, 3H, THI CHMe_2), 1.17 (d, 3H, THI CHMe_2), 1.20 (d, 3H, THI CHMe_2), 1.21 (d, 3H, THI CHMe_2), 1.48 (m, 2H, THI), 1.65 (m, 2H, THI), 1.98 (m, 2H, THI), 2.10 (m, 2H, THI), 2.49 (m, 2H, THI), 2.60 (m, 2H, THI), 2.80 (m, 2H, THI CHMe_2), 2.98 (m, 2H, THI), 3.02 (m, 2H, THI CHMe_2), 5.16 (s, 2H, CpH), 5.44 (s, 1H,
ZrH). $^{11}$B NMR (benzene-$d_6$): $\delta = 7.90$ (br, Zr-BH$_4$). $^{13}$C NMR (benzene-$d_6$): $\delta = 23.33, 23.35, 24.08, 24.12, 24.38, 24.54, 25.89, 28.55, 28.77$ (CHMe$_2$/THI), 98.35, 123.29, 123.45 (Cp). One CHMe$_2$/THI and two Cp resonances not located. IR (KBr): $\nu = 1965$ (m), 1624 (w), 1450 (m), 1362 (m), 1143 cm$^{-1}$ (w).

**Preparation of (η$^5$-C$_5$Me$_4$H)$_2$Zr(BH$_4$)H (12).** Prepared in a similar manner as 13 using 0.003 g of (.009 mmol) of 7 and 0.026 g (1.53 mmol) of Me$_2$NHBH$_3$, heating at 65 ºC for one week. $^1$H NMR (benzene-$d_6$): $\delta = -0.03$ (br , 4H, BH$_4$), 1.85 (s, 6H, CpMe), 1.93 (s, 6H, CpMe), 2.02 (s, 6H, CpMe), 2.07 (s, 6H, CpMe), 4.89 (s, 2H, CpH), 5.34 (s, 1H, Zr-H). $^{11}$B NMR (benzene-$d_6$): $\delta = 3.11$ (br, Zr-BH$_4$). $^{13}$C NMR (benzene-$d_6$): $\delta = 12.55, 12.69, 13.39, 14.77$ (CpMe), 107.07, 114.38, 116.91, 121.85, 122.51 (Cp). IR (KBr): $\nu = 2453$ (m), 2413 (m), 2087 (w), 1973 (w), 1578 (w), 1453 (w), 1366 (m), 1138 (m), 1026 cm$^{-1}$ (w), 841 (m).

**Preparation of (η$^5$-C$_5$H$_3$-1-Me-3-Pr)$_2$TiCl.** A 250 mL round bottomed flask was charged with 1.495 g (11.67 mmol) of Li[C$_5$H$_3$-1-Me-3-Pr] and 2.14 g (5.84 mmol) of TiCl$_3$(THF)$_3$. Approximately 100 mL of THF was added by vacuum transfer. The solution was heated to reflux overnight after which the solvent was removed in vacuo. The resulting solid was dissolved in pentane and filtered through Celite. Removal of the pentane in vacuo yielded a brown solid, which was recrystallized from pentane at –35 ºC. Anal. Calcd. for C$_{18}$H$_{26}$TiCl: C, 66.37; H, 8.05. Found: C, 65.97; H, 8.22.
Preparation of \([(\eta^5\text{-C}_5\text{H}_3\text{-1-Me,3-}^{\text{i}}\text{Pr})_2\text{Ti}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)\) (5). A 100 mL round bottom flask was charged with 28.10 g of mercury and approximately 5 mL of toluene was added. To the stirring solution, 0.141 g (6.13 mmol) of sodium was added and the mixture was stirred for 20 minutes. 0.387 g (1.19 mmol) of \((\eta^5\text{-C}_5\text{H}_3\text{-1-Me,3-}^{\text{i}}\text{Pr})_2\text{TiCl}\) dissolved in 20 mL of toluene was added and the reaction was stirred vigorously for three days. Filtration of the blue solution through Celite followed by solvent removal \textit{in vacuo} produced a blue oil. Recrystallization from pentane at −35 °C yielded 0.10 g (13.8 %) of a blue solid identified as 5. Anal. Calcd. for \(\text{C}_{36}\text{H}_{52}\text{Ti}_2\text{N}_2\): C, 71.05; H, 8.61; N, 4.60. Found: C, 70.85; H, 9.06; N, 4.34.
Using 1 mol % $[\text{Cp}^\text{Me}_4\text{TiN}]_2$

$y = -0.000287x - 1.038372$

$R^2 = 0.993115$

Figure S1: Plot of $\ln([\text{Me}_2\text{NHBH}_3])$ vs time (sec) for catalytic dehydrogenation of $\text{Me}_2\text{NHBH}_3$ at 22 °C using 2 mol % cat. loading.
Figure S2: $^1$H-coupled $^{11}$B NMR spectra of 1 mol % 3 and Me$_2$NHBH$_3$ in C$_6$D$_6$ at 23 ºC with time.

Figure S3. $^1$H-coupled $^{11}$B NMR spectra of 1 mol % 4 and NH$_3$BH$_3$ in THF at 65 ºC with time. Initially there is some undissolved NH$_3$BH$_3$ but upon conversion, all products and starting materials are dissolved.
References


