Supporting Information

Group 4 metallocene catalysed full dehydrogenation of hydrazine borane

Johannes Thomas,[a] Marcus Klahn,[a] Anke Spannenberg,[a] and Torsten Beweries*[a]

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Experimental Details

General Information. All operations were carried out under argon with standard Schlenk techniques or in a glovebox. All solvents were freshly distilled from sodium/benzophenone, stored under argon and degassed prior to use using standard techniques. Metallocene dichlorides for the preparation of the corresponding metallocene bis(trimethylsilyl)acetylene complexes and titanocene difluorides were purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. Diisobutylaluminum hydride, sodium borohydride and hydrazine sulfate were purchased from Sigma Aldrich and used as received. Hydrazine borane was synthesised according to a the procedure by Goubeau and Ricker[1] and was analysed by ^{1}H NMR as well as IR spectroscopy. Spectra resemble those reported by Demirci et al.[2] All metallocene bis(trimethylsilyl)acetylene complexes,[3] [*rac*-(ebthi)ZrH(μ-H)]$_2$[4] and Cp*$_2$TiH[5] were prepared using literature procedures. The following instruments were used: Mass spectra: MAT 95-XP – NMR spectra: Bruker AV 300. Chemical shifts (^{1}H, ^{13}C) are given in ppm relative to $SiMe_4$ and are referenced to signals of the used solvent: THF-*d8* (δ_H = 1.72, 3.58; δ_C = 25.31, 67.21), benzene-*d$_6$* (δ_H = 7.16, δ_C = 128.0) – Gas chromatography: Agilent Technologies 7890A, Column: 60/80 Carboxen 1000 (Supelco), Detection: TCD and FID – Elemental analyses: ICP-OES 715 (Varian) and Microanalyser TruSpec CHNS (Leco) – IR spectroscopy: Bruker Alpha FT-IR spectrometer – XRD: STOE STADI-P transmission diffractometer with a focusing primary Ge(111) monochromator applying Cu-Kα radiation (λ = 1.54056 Å), with 2Θ angular from 5 to 60 (stepwise: 0.5° per second). Data analysis was performed using the software package Win Xpow. Samples were focused at a 711 hkl silicon waver with vacuum oil (DOW Corning). Volumetric analyses were carried out in a double-walled thermostatically controlled reaction vessel using an automatically operating burette (LIKAT-MesSen Nord GmbH, Stäbelow, Germany).[6]

General procedures for the dehydrogenation of hydrazine borane:

a) With metallocene alkyne complexes and isolated metallocene hydrides

A solution of the catalyst (2 mol%) in 1 mL of THF was added to a solution of hydrazine borane in 6.5 mL of THF (0.034 g, 0.74 mmol), which was stirred at 25 °C or 50 °C, respectively. The reaction vessel was closed, the flow of Argon was stopped and the excess pressure was released. The measurement was started and hydrogen evolution curves were recorded. Gas samples were taken at the end of the experiment and analysed by gas chromatography.

b) With in-situ generated metallocene hydrides

In a double-walled temperature controlled reaction vessel, a mixture of hydrazine borane (0.034 g, 0.74 mmol) and the metallocene difluoride (2 mol%) were dissolved in THF (7.5 mL) and stirred at 25 °C or 50 °C, respectively. Diisobutyl aluminum hydride (4 mol%) was added and the reaction vessel was closed, the flow of Argon was stopped and the excess pressure was released. The measurement was started and hydrogen evolution curves were recorded. Gas samples were taken at the end of the experiment and analysed by gas chromatography.

Preparation of $Cp^*_2Ti(\mu\text{-}H)_2Al\textit{i}Bu_2$ (6):

$Cp^*_2TiF_2$ (0.107 g, 0.3 mmol) was suspended in 10 mL of THF. After addition of a 1M solution of $\textit{i}Bu_2AlH$ in cyclohexane (0.9 mL, 0.9 mmol) at room temperature, the yellow suspension turns blue and formation of hydrogen is observed. Dark blue crystals could be obtained by slow evaporation of the mother liquor. After decantation of the mother liquor, the material was washed with *n*-hexane, and dried in vacuum to give 0.030 g (23 %) of complex **6**. Anal. Calc. for $C_{28}H_{50}AlTi$ (461.32 g/mol): C, 72.86; H, 10.92. Found: C, 67.42; H, 8.49. Despite repeated attemps – including combustion with V_2O_5 – no better results could be obtained. MS (CI, *iso*-butane): *m*/*z* (%) 474 (100), 439 (61).

Regeneration of the spent HB material:

A sample of spent HB material (20 mg) that was obtained by dehydrogenation of HB with complex **1f** as the catalyst was dispersed in a 1M stock solution of hydrazine in THF (1.6 mL). The mixture was stirred at 50 °C for 24 h, followed by removal of all volatiles in vacuum. The solid, colourless residue was dissolved in THF-d_8 and ^{11}B NMR spectra were recorded to monitor the progress of the reaction. ^{11}B NMR (96 MHz, THF-d_8, 297 K): −17.65 (q, J_{BH} = 96.4 Hz).

Crystallographic details

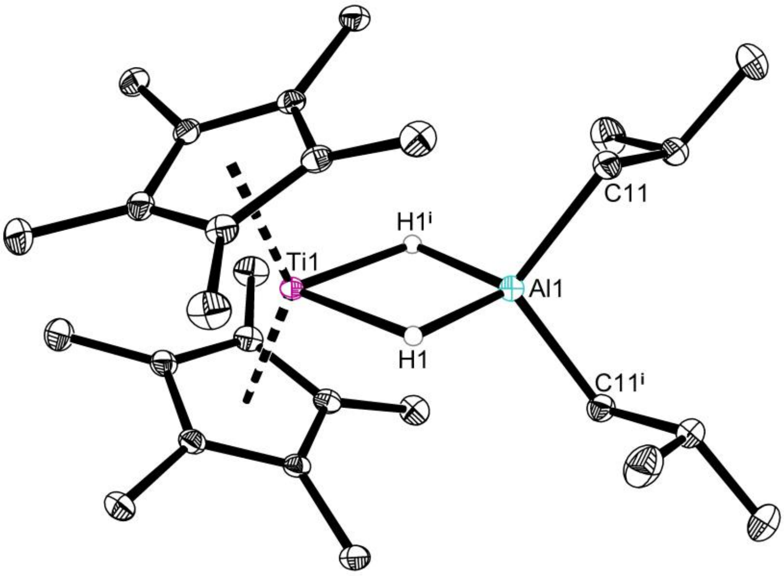

Figure S1. Molecular structure of **6**. Thermal ellipsoids correspond to 30 % probability. Hydrogen atoms (except bridging hydrides) are omitted for clarity. ^{i} Symmetry operator used to generate equivalent atoms: -x+2, y, -z+0.5.

Diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97[7]) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[7]). XP (Bruker AXS) was used for graphical representation.

Crystal data for **6**: $C_{28}H_{50}AlTi$, M = 461.56, monoclinic, space group $C2/c$, a = 15.0433(4), b = 12.0424(3), c = 16.5253(4) Å, β = 110.917(1)°, V = 2796.39(12) Å^3, T = 150(2) K, Z = 4, 32645 reflections collected, 3463 independent reflections (R_{int} = 0.0289), final R values ($I > 2\sigma(I)$): R_1 = 0.0274, wR_2 = 0.0741, final R values (all data): R_1 = 0.0320, wR_2 = 0.0777, 148 parameters.

CCDC 936330 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR investigations

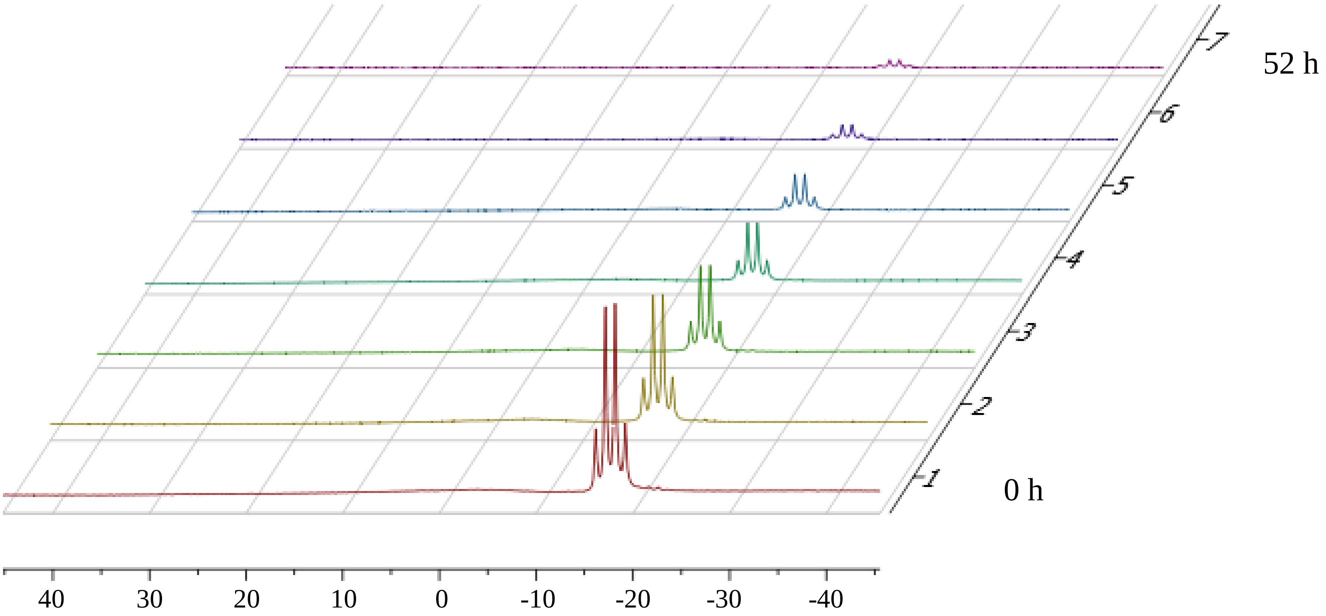

Figure S2. ^{11}B NMR spectra (96 MHz, THF-*d8*, 24 °C) of the dehydrogenation of HB using **1a** as the catalyst.

XRD studies

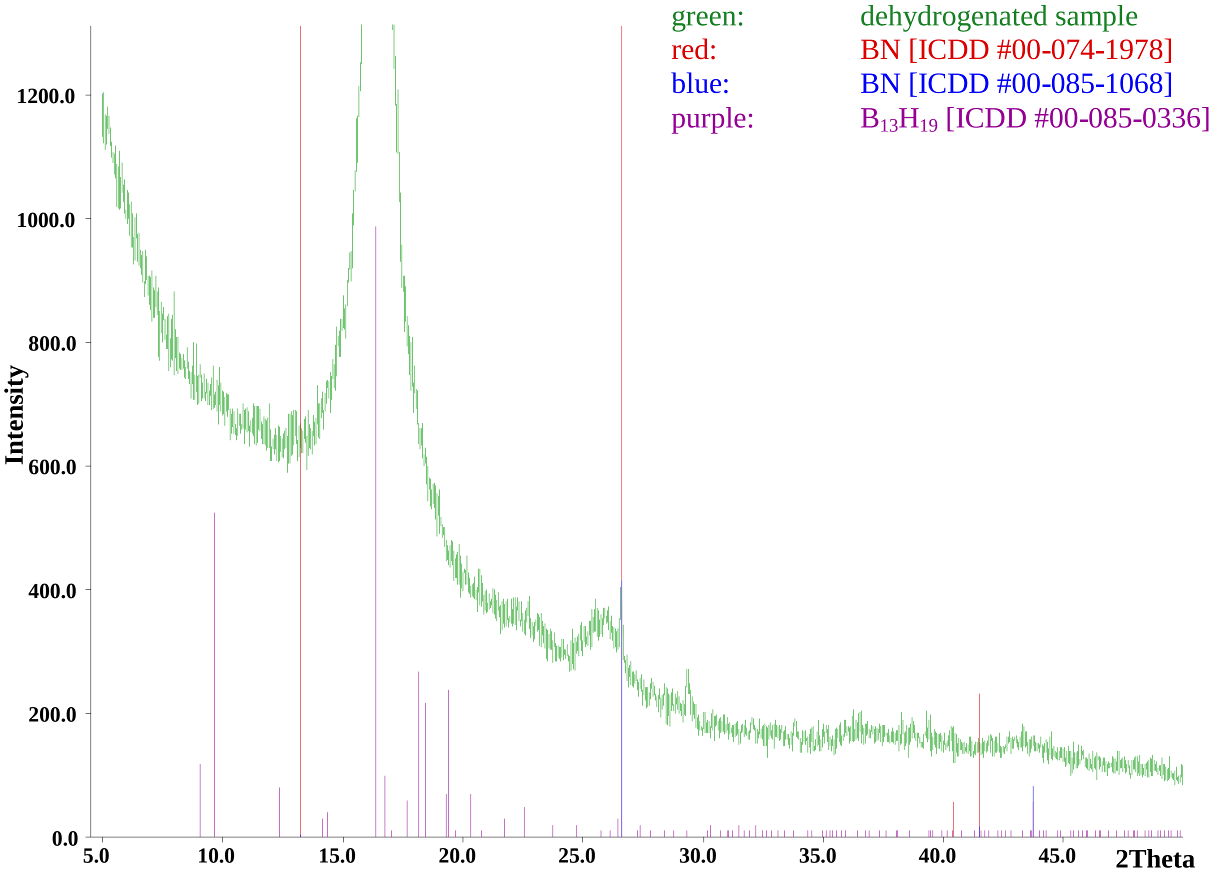

Figure S3. XRD analysis of the HB decomposition product. Reference samples from ICDD are given for comparison.

Volumetric data

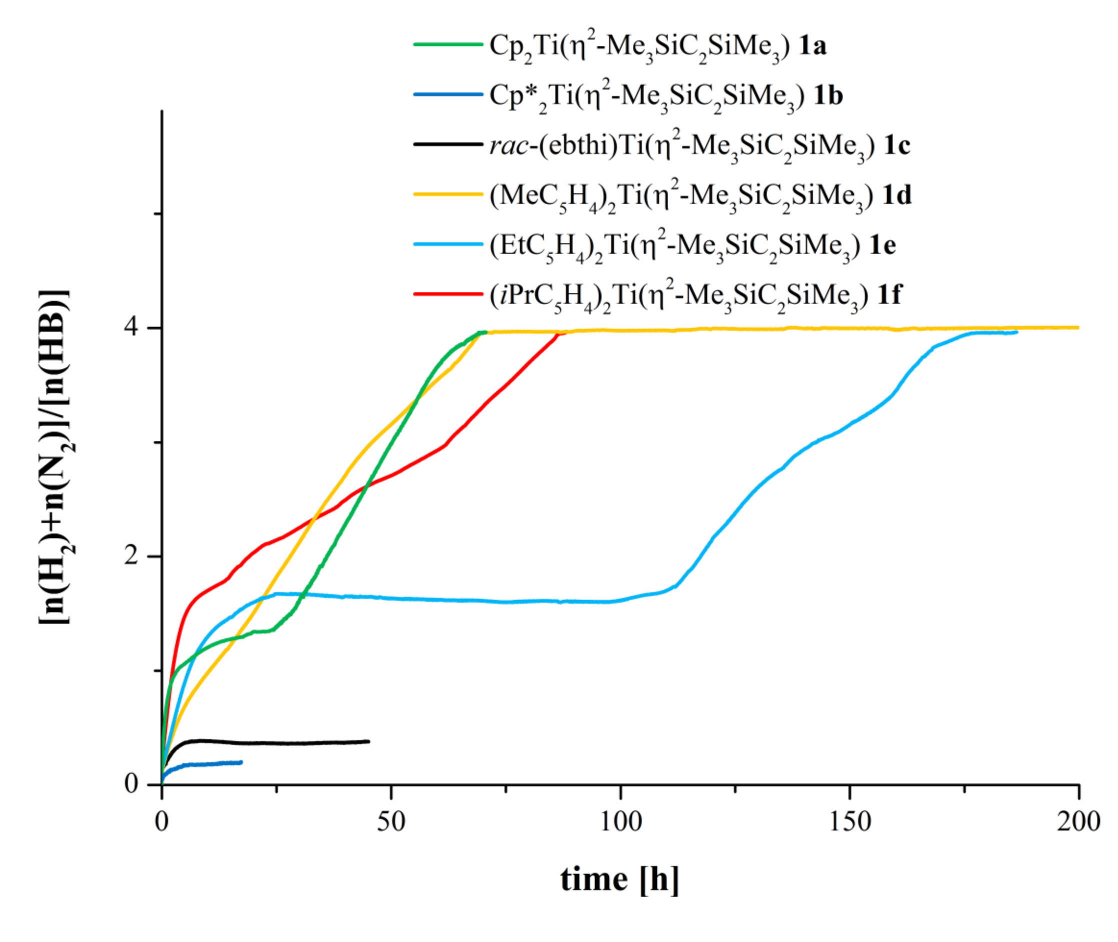

Figure S4. Volumetric data of HB dehydrogenation using titanocene catalysts **1a-1f** at *T* = 25 °C in THF.

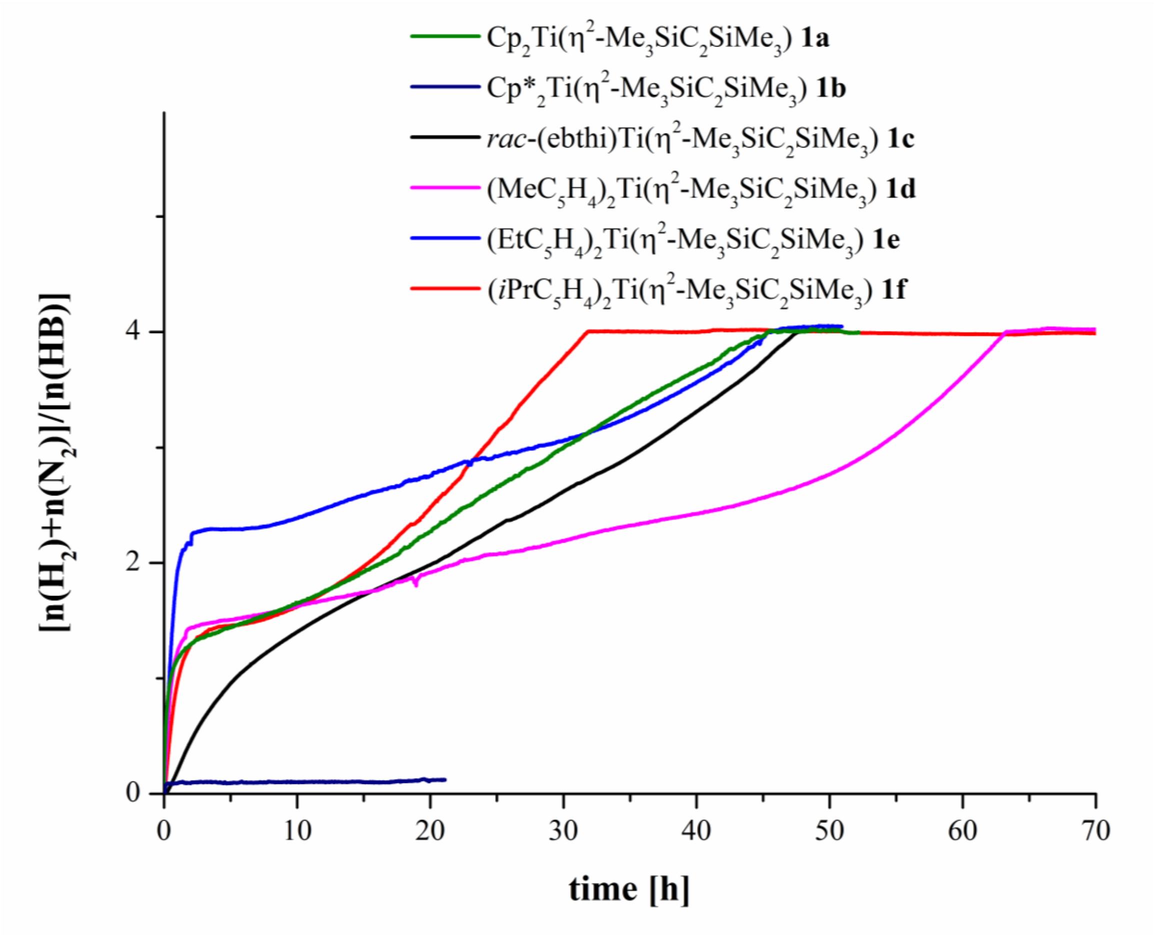

Figure S5. Volumetric data of HB dehydrogenation using titanocene catalysts **1a**-**1f** at $T = 50$ °C in THF.

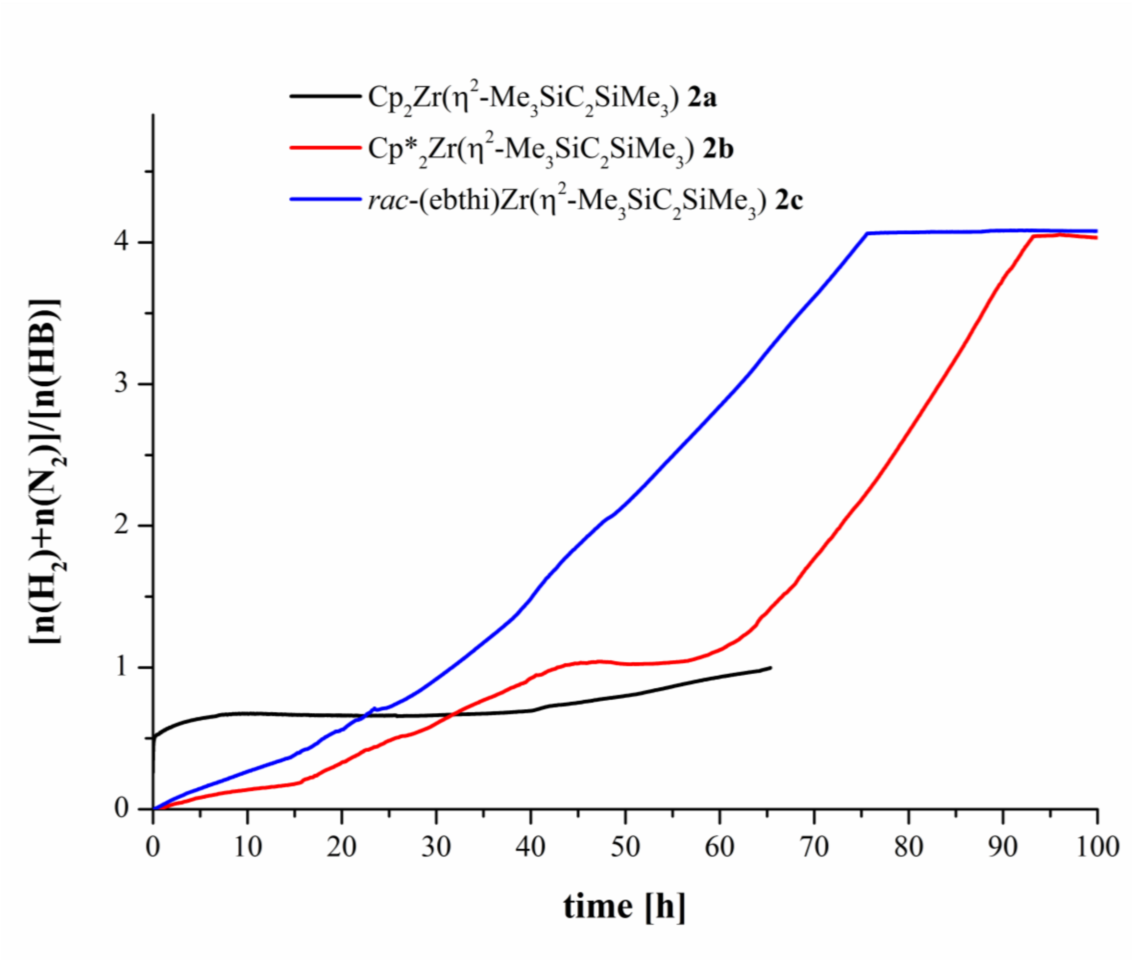

Figure S6. Volumetric data of HB dehydrogenation using zirconocene catalysts **2a**-**2c** at T = 25 °C in THF.

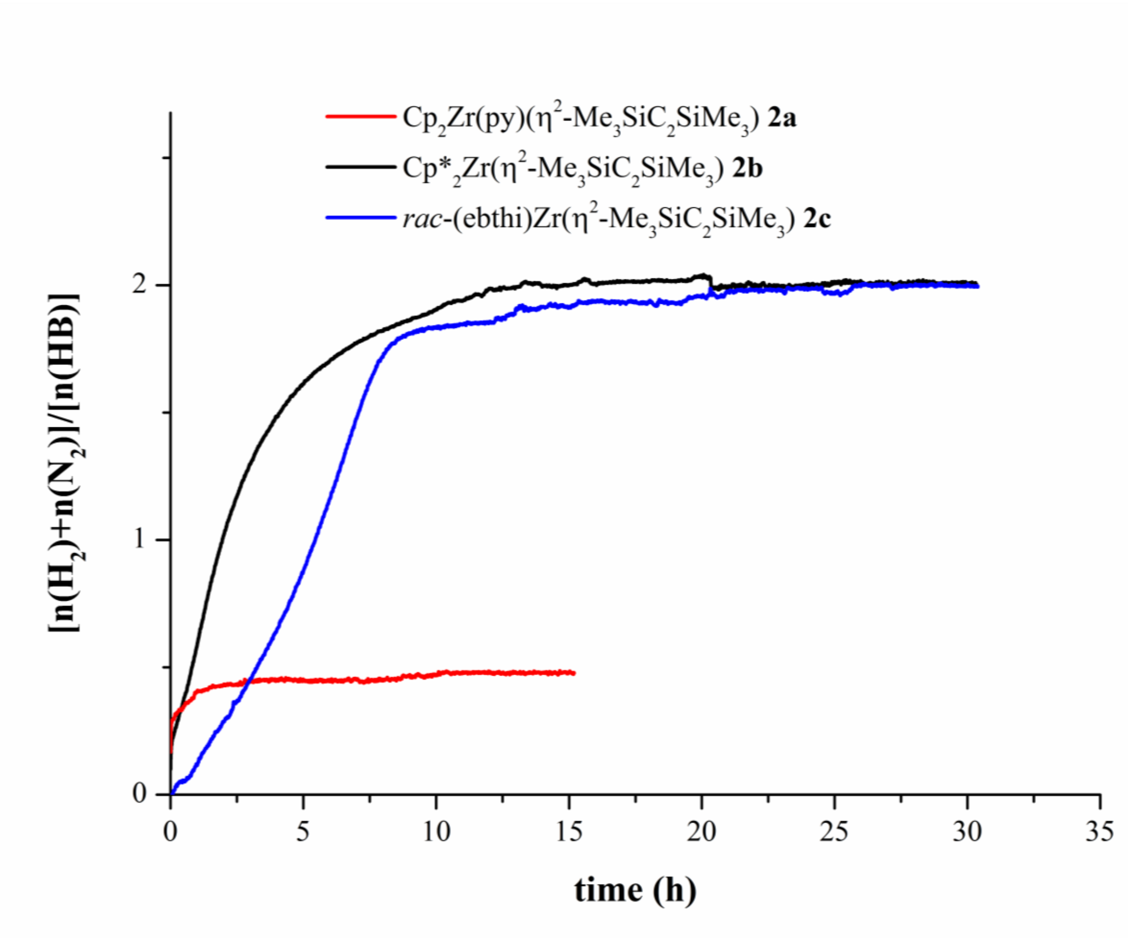

Figure S7. Volumetric data of HB dehydrogenation using zirconocene catalysts **2a**-**2c** at *T* = 50 °C in THF.

Regeneration of spent HB material

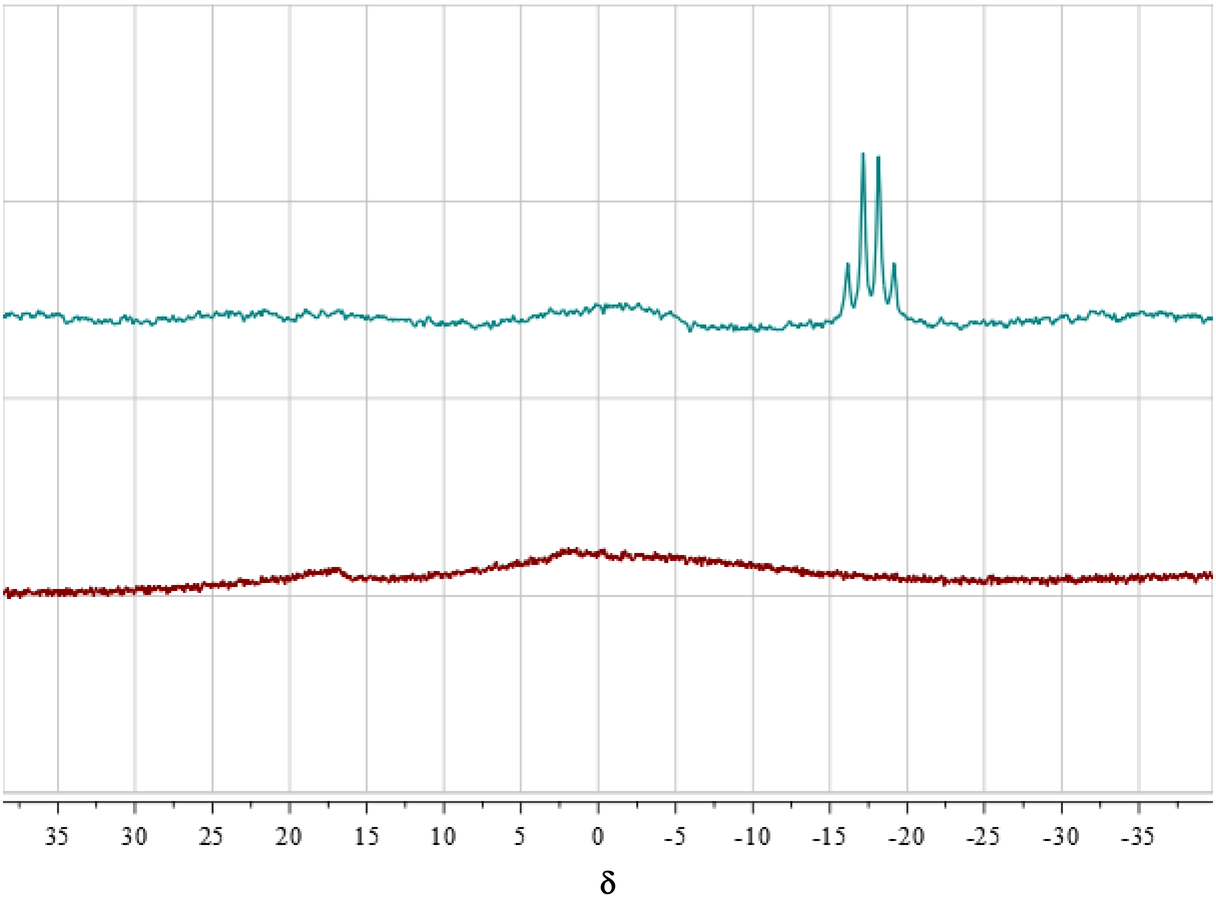

Figure S8. ^{11}B NMR (96 MHz, THF-d_8, 297 K) of the regenerated HB dehydrogenation product (green) as well as of the slurry of the spent HB fuel (red). The single resonance at −17.65 (q, J_{BH} = 96.4 Hz) ppm indicates the formation of HB after regeneration with hydrazine.

References

1 J. Goubeau and E. Ricker, *Z. Anorg. Allg. Chem.*, 1961, **310**, 123.

2 R. Moury, G. Moussa, U. B. Demirci, J. Hannauer, S. Bernard, E. Petit, A. van der Lee and P. Miele, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1768.

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4 R. B. Grossmann, R. A. Doyle and S. L. Buchwald, *Organometallics*, 1991, **10**, 1501.

5 W. W. Lukens, P. T. Matsunaga and R. A. Andersen, *Organometallics*, 1998, **17**, 5240.

6 Details referring to the experimental setup were described before in: T. Beweries, J. Thomas, M. Klahn, A. Schulz, D. Heller and U. Rosenthal, *ChemCatChem*, 2011, **3**, 1865.

7 G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112.