Supporting Information

Group 4 metalloocene catalysed full dehydrogenation of hydrazine borane

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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 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, \([rac-\text{(ebthi)ZrH(µ-H)})]_2\)\(^4\) and \(\text{Cp}^*\text{TiH}^5\) 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-d\(_8\) (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 (Superco), 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 ºC or 50 ºC, 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 ºC or 50 ºC, 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(µ-H)2AliBu2 (6):
Cp*2TiF2 (0.107 g, 0.3 mmol) was suspended in 10 mL of THF. After addition of a 1M solution of iBu2AlH 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 C28H50AlTi (461.32 g/mol): C, 72.86; H, 10.92. Found: C, 67.42; H, 8.49. Despite repeated attempts – including combustion with V2O5 – 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-d8 and 11B NMR spectra were recorded to monitor the progress of the reaction. 11B NMR (96 MHz, THF-d8, 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. 1 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\textsuperscript{7}) and refined by full-matrix least-squares techniques on $F^2$ (SHELXL-97\textsuperscript{7}). XP (Bruker AXS) was used for graphical representation.

Crystal data for 6: C\textsubscript{28}H\textsubscript{50}AlTi, $M = 461.56$, monoclinic, space group $C2/c$, $a = 15.0433(4)$, $b = 12.0424(3)$, $c = 16.5253(4)$ Å, $\beta = 110.917(1)^\circ$, $V = 2796.39(12)$ Å\textsuperscript{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](http://www.ccdc.cam.ac.uk/data_request/cif).

**NMR investigations**

![NMR spectra](image)

**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.

- **green:** dehydrogenated sample
- **red:** BN [ICDD #00-074-1978]
- **blue:** BN [ICDD #00-085-1068]
- **purple:** B$_3$H$_{19}$ [ICDD #00-085-0336]
Volumetric data

Figure S4. Volumetric data of HB dehydrogenation using titanocene catalysts 1a-1f at $T = 25\, ^\circ\text{C}$ in THF.
Figure S5. Volumetric data of HB dehydrogenation using titanocene catalysts 1a-1f at $T = 50 \, ^\circ\text{C}$ in THF.
Figure S6. Volumetric data of HB dehydrogenation using zirconocene catalysts 2a-2c at $T = 25 \, ^{\circ}\text{C}$ in THF.
**Figure S7.** Volumetric data of HB dehydrogenation using zirconocene catalysts 2a-2c at $T = 50 \, ^\circ\text{C}$ 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
