Electronic Supplementary Information

The direct and reversible hydrogenation of activated aluminium supported by piperidine

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*Structure elucidation of [pip$_2$AlH]$_2$ (**2**) and [pip$_3$Al]$_2$ (**3**) by two-dimensional NMR spectroscopy*

Two-dimensional NMR analyses were carried out using a Bruker Avance Neo 700 MHz spectrometer at 22 °C. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane as the internal standard.

For **2**, 2D ^{1}H–^{1}H COSY spectra (Fig. 1S (left)) were obtained with a phase sensitive pulse program including double quantum filtering (cosygpmfphpp) using the following parameters: 8.5 ppm spectral width, 16 dummy scans, 4 scans, 256 experiments for the indirect dimension and zero filling to 1k data points in F2 and F1, respectively. 2D ^{1}H–^{13}C HSQC spectra of **2** and **3** were collected with a multiplicity edited pulse program (hsqcedetgpsisp2.3) experiment using the following acquisition parameters: sweep width for ^{1}H= 16 ppm, ^{13}C= 160 ppm, 4 scans, 32 dummy scans, 256 experiments for the indirect dimension and zero filling to 1k data points in F2 and F1, respectively.

The two-dimensional ^{1}H spectrum of **2** in benzene-d6 solution showed signals of terminal (higher intensity) and bridging (lower intensity) piperidinyl groups, with corresponding assignments mentioned in the manuscript. Scalar couplings between nuclei are indicated by the cross-peaks in Fig. 1S (left). Thus, the correlation between α-CH$_2$(N) with β-CH$_2$ can be detected and in the same way between β-CH$_2$ with γ-CH$_2$.

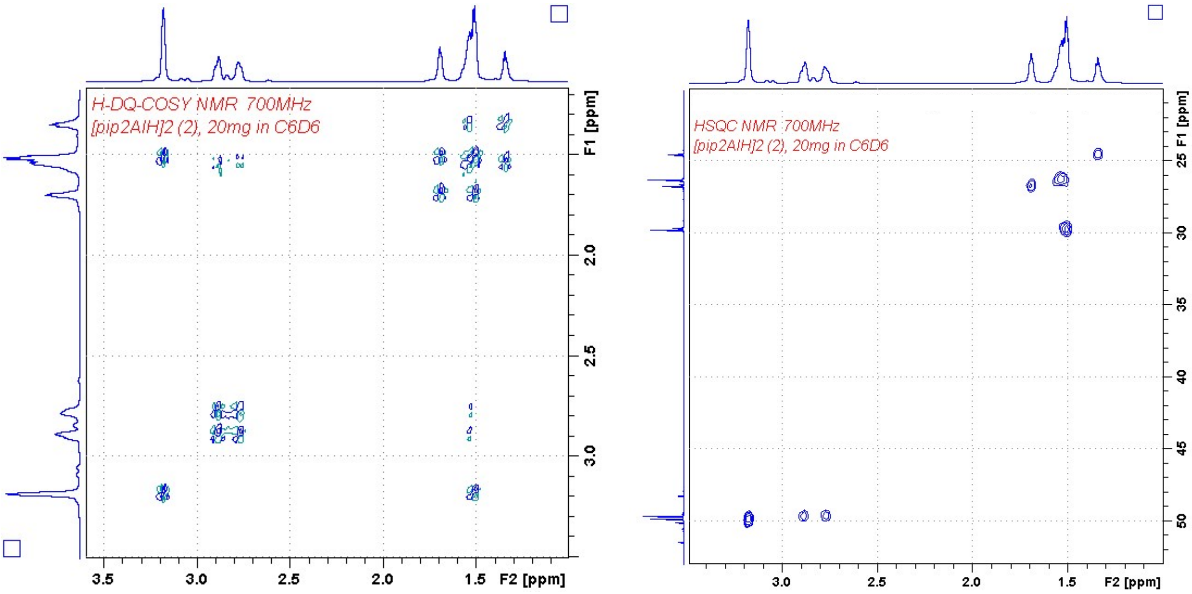


Fig. 1S 2D NMR spectra: ^{1}H–^{1}H COSY (left) and ^{1}H–^{13}C HSQC (right) for [pip$_2$AlH]$_2$ (**2**) in benzene-d6.

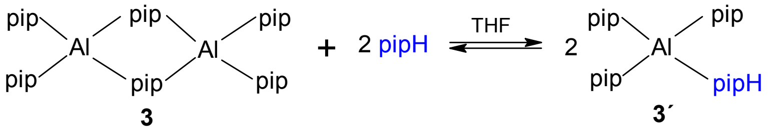
The signals between 2.77–2.89 ppm for **2** (Fig. 1S, left) correspond to α-CH$_2$ protons of bridging piperidinyl groups, the presence of axial and equatorial protons was confirmed by scalar coupling between dissimilar nuclei ^1H–^{13}C which indicated one signal at 48.2 ppm in proton/carbon cross-peak (Fig. 1S, right). The complex multiplets between 1.45 and 1.60 ppm originate from β-CH_2 of terminal and bridging piperidinyl groups. However, severe signal overlap in ^1H NMR spectra hinders accurate assignment. Extension of ^1H to ^1H–^{13}C HSQC leads to the dispersion of peaks along the ^{13}C dimension and greatly alleviates peak overlapping, thus terminal (at 1.50 ppm) and bridging (at 1.53 ppm) proton piperidinyl group resonances by the different carbon resonances (at 29.7 and 26.3 ppm, respectively) can be well distinguished.

*Formation of pip$_3$AlpipH (**3´**) with the piperidine excess*

The synthesis with Y-activated aluminium supported by piperidine revealed the complex **3´**, which differs from **3** formed by the reaction of piperidine with aluminium hydride. ^1H NMR of **3´** spectra clearly showed two different piperidine moieties surrounding the aluminium centre (Fig. 2S). After integration of the spectrum, the composition of **3´** - pip$_3$AlpipH, was suggested. The signal at 0.68 ppm was assigned to the N-H group of **3´**. The more precise investigation of this complex was hindered by its instability.

(**3´**) **^{1}H NMR** (500.13 MHz, C_6D_6): δ = 0.68 (1 H, m, N-H, pipH), 1.11 (4 H, m, β-CH_2, pipH), 1.20 (2 H, m, γ-CH_2, pipH), 1.60 (12 H, m, β-CH_2, pip), 1.78 (6 H, m, γ-CH_2, pip), 2.40 (4 H, m, α-CH_2, pipH), 3.19 (12 H, m, α-CH_2(N), pip) ppm. **^{13}C NMR** (125.76 MHz, C_6D_6): δ = 24.5 (γ-CH_2, pipH), 26.0 (β-CH_2, pipH), 27.2 (γ-CH_2, pip), 30.0 (β-CH_2, pip), 47.1(α-CH_2(N), pipH), 50.4 (α-CH_2(N), pip) ppm. **^{27}Al NMR** (130.3 MHz, C_6D_6): δ = 107 ppm.

It was concluded that complex **3´** was formed due to the presence of extra piperidine in the reaction mixture. In order to confirm this suggestion the measurements with **3** and piperidine addition were performed. The solution of piperidine (pipH, 0.1 or 0.2 mL) in 0.5 mL benzene-d6 was added to pure **3** dissolved in 0.7 mL benzene-d6. With increasing pipH concentration the bridging piperidinyl groups disappeared, however terminal ligands were not influenced (Fig. 2S). The observed effect is possibly due to the rapid exchange of piperidine with the piperidinyl ligand in molecules **3** and **3’**, the latter formed by reaction of **3** with piperidine:



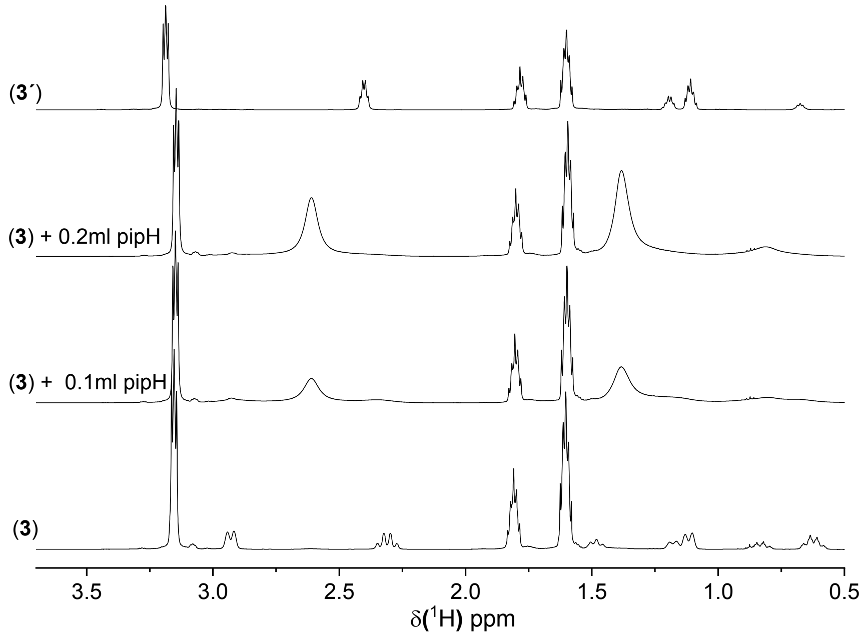


Fig. 2S ^1H NMR spectra of pure **3**, and with addition of piperidine (in 0.5 mL benzene-d6).

All piperidinoalanes are extremely sensitive to traces of moisture or hydroxyl groups of other origin (e.g. remaining Si-OH groups at the glass surface) resulting in the formation of pipH. As could be shown by 2D EXSY

NMR, already small amounts of pipH are in fast exchange on the NMR timescale with the pip ligands of the alanes. This gives rise to interesting exchange reactions but is beyond the scope of this work and will therefore not be discussed in detail here.

The existence of **3´** was confirmed by the addition of piperidine to the product formed by the direct hydrogenation of Al*(Zr) (**1** and **2**). After the hydrogenation reaction in the autoclave reactor was completed, 0.5 mL of piperidine was added to 1 mL of the filtered reaction mixture. The NMR spectra recorded for both samples detected the change from **1** and **2** to **3´** in the sample with piperidine addition, the ^{27}Al NMR spectra are shown exemplarily in Fig. 3S.

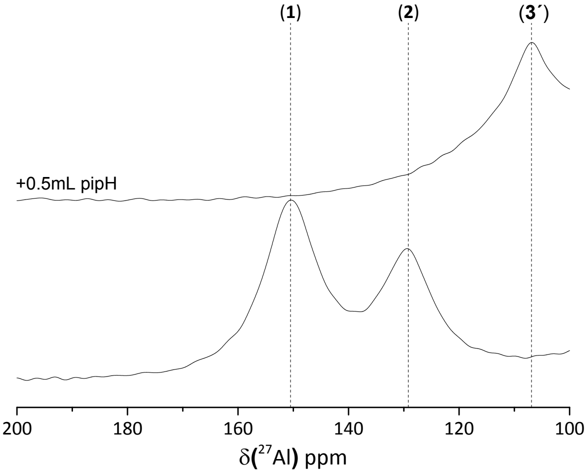


Fig. 3S ^{27}Al NMR spectra of the products formed by direct hydrogenation of Al*(Zr) supported by piperidine (bottom) and with further addition of 0.5 mL of piperidine (top).

Formation of piperidinoalanes without hydrogen pressure

In the glove box, the reactants (0.55 g (20.3 mmol) of Al*(Zr), 2 mL (20.2 mmol) of piperidine) were weighed and dissolved in 25 mL of THF in an autoclave reactor. The reactor was sealed, removed from the glove box and connected to the pressure sensor and thermocouple. The reaction mixture was stirred for ~24 h. The pressure increase up to 7.5 bar was observed until ~21 h (Fig. 4S, left). After ~24 h the reactor was transferred into the glove box and the sample was taken for NMR analysis. Conversion of Al*(Zr) was 55%. The ^{27}Al NMR analysis of the formed product shown in Fig. 4S (right) revealed the formation of **2** and **3**.

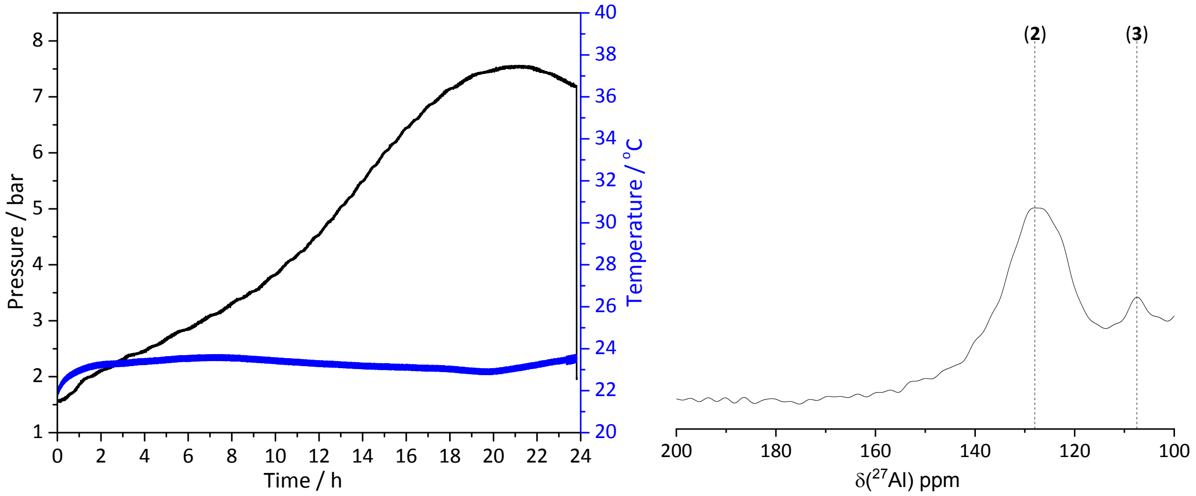


Fig. 4S Reactor pressure during reaction of Al*(Zr) with piperidine in THF (left), ^{27}Al NMR spectra of the formed product after ~24 h (right).

*Decomposition properties of [pipAlH$_2$]$_2$ (**1**) and [pip$_2$AlH]$_2$ (**2**)*

Decomposition of **1** was performed in steps of 20 °C from 100 °C until 200 °C. After 2 h at the desired temperature, the sample was cooled and a part of the solid was taken for NMR analysis, afterwards the sample was heated until the next desired temperature. Starting from 160 °C, partial sublimation was observed on the cold part of the flask and a grey precipitate on the bottom.

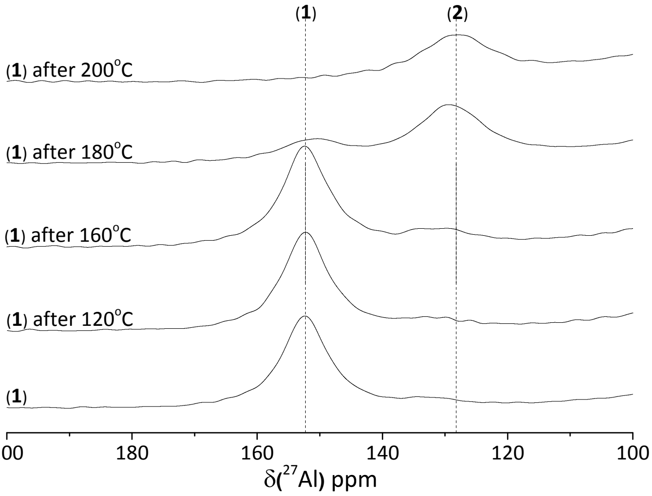


Fig. 5S Stepwise thermal decomposition of [pipAlH$_2$]$_2$ (**1**).

NMR analysis of the sample after 200 °C revealed the presence of only **2**. Fig. 5S shows that the decomposition of **1** to **2** commences at around 160 °C, with increasing temperature the **1** : **2** ratio decreases.

Thermal decomposition behaviour of **2** was investigated using TG/DSC/MS analysis (Fig. 6S). Compound **2** showed the small and weak endothermic signal at 121 °C, corresponding to the melting point, reproduced by several measurements. The second event starts at 275 °C and is assigned to the decomposition of **2** followed by the vigorous release of piperidine and hydrogen, which caused the fluctuations of the heat flow signal. The endothermic event finished at 306 °C with a mass loss of 68.8 %. The same event was observed for compound **1** confirming the suggestion about the decomposition of **1** via **2**.

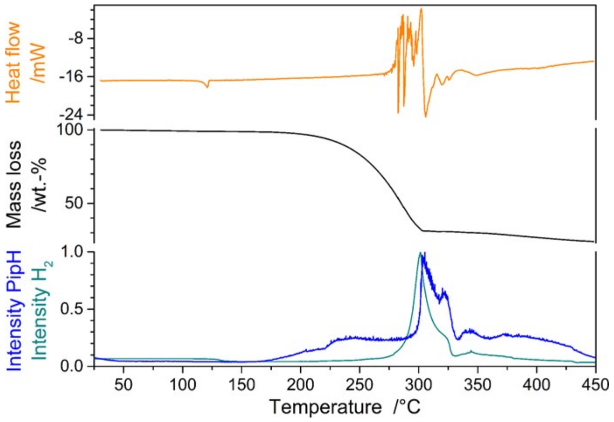


Fig. 6S DSC (top), TGA (middle), and MS (bottom) data of [pip$_2$AlH]$_2$ (**2**).