## **Electronic Supplementary Information for:**

## Mechanochemical dehydrocoupling of dimethylamine borane and hydrogenation reactions using Wilkinson's catalyst

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#### **General Information**

All chemicals, unless otherwise stated, were used as received. Borane dimethylamine complex (Me<sub>2</sub>NH·BH<sub>3</sub> 2) and *cis*-stilbene (*cis*-6, 96% by GC) were purchased from Sigma Aldrich. Wilkinson's catalyst (1, RhCl(PPh<sub>3</sub>)<sub>3</sub>, red polymorph) was obtained from JK Scientific. trans-Stilbene (trans-6) was sourced from Merck. Rhodium (III) chloride hydrate w% Rh-content) was purchased from Carbolution.  $(RhCl_3 \cdot xH_2O)$ 39.5 1,3,5-Trimethoxybenzene was obtained from Alfa Aesar. Thin layer chromatography (TLC) was performed using aluminium plates coated with silica gel 60F254 (Merck). Purifications by column chromatography were performed using silica gel 60 and distilled solvents. All reactions were conducted under air. All reactions that were carried out in a ball mill were performed with a RETSCH Mixer Mill MM 400 and standard milling jars. Mechanochemical reactions in which gas transfer was used were performed in custom-made 20 mL stainlesssteel jars with an inner diameter of 2.5 cm and a threaded hole in one half of the jar (Figure S1).



*Figure S1: Custom-made stainless-steel milling jars (20 mL) for gas transfer reactions.* 

*Note*: When conducting mechanochemical reactions involving the use or the generation of gaseous substances, overpressure inside close milling jars can occur. Therefore, the scale of the reaction and the volume of the milling jar have to be considered.

#### Solid-State Nuclear Magnetic Resonance Spectroscopy (SSNMR)

<sup>31</sup>P-MAS-NMR experiments were carried out on a Varian Infinity+ spectrometer equipped with a commercial 2.5 mm MAS double resonance probe (Chemagnetics) operating at 162.532 MHz and were acquired with <sup>1</sup>H decoupling (405.51 MHz). The <sup>31</sup>P-MAS-NMR spectra are the average of up to 256 transients acquired with a repetition delay of up to 1000 s, a 90° pulse duration of 1.9  $\mu$ s and 10 Hz line broadening during data processing. Spin echo pulse sequences were utilised during the measurements. The rotation frequencies were set at 20 kHz.

#### Nuclear Magnetic Resonance Spectroscopy (NMR)

All NMR spectra in solution were recorded either on a Varian V-NMRS 600, Varian V-NMRS 400 or Varian Mercury 300 spectrometer at 25 °C with CDCl<sub>3</sub> as solvent. <sup>11</sup>B and <sup>13</sup>C spectra were recorded broad-band decoupled (<sup>11</sup>B{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}) and will be stated as <sup>11</sup>B and <sup>13</sup>C for simplification. <sup>1</sup>H and <sup>13</sup>C spectra were referenced to the solvent residual signal of CDCl<sub>3</sub> (<sup>1</sup>H:  $\delta$  = 7.26 ppm; <sup>13</sup>C:  $\delta$  = 77.16 ppm).<sup>1</sup> Coupling constants (*J*) are given in Hz. Coupling patterns are given as s = singlet and m = multiplet Data are reported as follows: chemical shift, multiplicity and integration.

#### **PXRD** Measurements and Simulated Patterns

Powder X-ray diffraction (PXRD) spectra were recorded on a Bruker D8 Advance ECO. For samples obtained by milling the measurement was carried out as long scan experiments due to the amorphous character of the ball mill samples. The X-ray source was copper with a wavelength of  $\lambda = 1.5$  Å. The spectra were recorded in a 2 $\Theta$  range of 5 to 50° and with a step size of  $\Delta 2\Theta = 0.018^{\circ}$ .

Simulated PXRD spectra for the red and orange polymorph of Wilkinson's catalyst were obtained from single X-ray crystal data deposited in the Cambridge Structural Database (CSD), <sup>2,3</sup> and calculated using the software Mercury.<sup>4</sup>

#### Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS analysis was done using an Agilent 7890A series GC system equipped with an Agilent 5975C inert XL EI/CI MSD with triple axis detector and an Agilent DB-5 ms column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$ ) with helium as the carrier gas. The standard method of analysis consisted of a 1 µL injection volume at a split ratio of 50:1, having a flow of 1.2 mL·min<sup>-1</sup> with a temperature profile that started at 40 °C with a 3 min isotherm followed by a first

5 °C  $\cdot$  min<sup>-1</sup> ramp finishing at 200 °C. After a hold time of 20 min a second 20 °C  $\cdot$  min<sup>-1</sup> ramp followed, which finished at 280 °C. Finally, this temperature was held for 15 min.

# **Single Crystal X-Ray Structure of Red and Orange Polymorphs of Wilkinson's Catalyst** Figure S2 shows the single crystal structure of both polymorphic forms of Wilkinson's catalyst. The single crystal data was obtained from the Cambridge Crystallographic Data Centre and were produced with the software Mercury.<sup>2-4</sup>



Figure S2: Single crystal structure for both polymorphic forms of Wilkinson's catalyst. Hydrogen atoms are omitted for clarity. Left side: Red polymorph; Right side: Orange polymorph.

#### Synthesis of the Orange Polymorph of Wilkinson's Catalyst in Solution<sup>5</sup>

In a screw cap tube RhCl<sub>3</sub>·xH<sub>2</sub>O (100.0 mg, 0.38 mmol, 1.00 equiv.) was dissolved in 1.7 mL EtOH. In a second tube, freshly recrystallised PPh<sub>3</sub> (398.7 mg, 1.52 mmol, 4.00 equiv.) was dissolved in 5.5 mL of hot EtOH. This solution was added to ethanolic solution of rhodium and the tube was closed. The mixture was stirred for 5 min in an oil bath at 80 °C. Then, the reaction mixture was cooled in an ice bath for 1 min. The cold reaction mixture was filtered and the solid washed with a minimum amount of Et<sub>2</sub>O to remove remaining PPh<sub>3</sub> and formed Ph<sub>3</sub>PO. The product was dried under vacuum to afford 263.0 mg (0.28 mmol, 75%) of an orange solid.

#### Mechanosynthesis of Wilkinson's Catalyst; Neat Conditions

RhCl<sub>3</sub>·xH<sub>2</sub>O (50.0 mg, 0.19 mmol Rh, 1.00 equiv.) and freshly recrystallised PPh<sub>3</sub> (249.2 mg 0.95 mmol, 5.00 equiv.) were added to a 10 mL ZrO<sub>2</sub> milling jar with one ball (7 mm in diameter) made of the same material. The reaction mixture was milled for 90 min at 25 Hz. The resulting residue was washed with a minimum amount of Et<sub>2</sub>O to remove remaining PPh<sub>3</sub> and formed Ph<sub>3</sub>PO to afford Wilkinson's catalyst in 68% yield.

The obtained solid was dried in high vacuum and was then analysed by SSNMR. Low crystallinity of the neat-synthesised material prevented its analysis by PXRD.

#### Mechanosynthesis of Wilkinson's Catalyst; LAG Conditions

RhCl<sub>3</sub>·xH<sub>2</sub>O (50.0 mg, 0.19 mmol Rh, 1.00 equiv.) and freshly recrystallised PPh<sub>3</sub> (249.2 mg 0.95 mmol, 5.00 equiv.) were added to a 10 mL ZrO<sub>2</sub> milling jar with one ball (7 mm in diameter) made of the same material. All LAG experiments were carried out with a  $\eta$ -value of 0.25. The reaction mixture was milled for 90 min at 25 Hz. The resulting residue was washed with a minimum amount of Et<sub>2</sub>O to remove remaining PPh<sub>3</sub> and formed Ph<sub>3</sub>PO. The obtained solid was dried in high vacuum and was then analysed by PXRD and SSNMR. LAG using ethanol gave Wilkinson's catalyst in quantitative yield.





Figure S3: Experimental and simulated PXRD patterns of various samples of Wilkinson's catalyst in the  $2\Theta$ -range from 5 to 25 °. a) Solution-made orange polymorph of Wilkinson's catalyst; b) Simulated PXRD of orange polymorph of Wilkinson's catalyst. LAG samples of Wilkinson's catalyst c) MeOH; d) EtOH; e) 1-PrOH; f) 2-PrOH; g) 1-BuOH; h) rac-2-BuOH; i) Commercially available red polymorph of Wilkinson's catalyst; j) Simulated PXRD of red polymorph of Wilkinson's catalyst.

#### Stability Test of Me<sub>2</sub>NH·BH<sub>3</sub> 2 Under Ball Milling Conditions

Me<sub>2</sub>NH·BH<sub>3</sub> (202 mg, 3.43 mmol, **2**) was added into a stainless-steel milling jar (20 mL) equipped with one ball of the same material (10 mm in diameter). The substrate was milled for 60 min at 30 Hz. <sup>1</sup>H and <sup>11</sup>B NMR spectra were recorded before and after milling (Figure S4 and S5). The resulting NMR spectra showed the stability of the borane dimethylamine complex under ball milling conditions.



Figure S4: <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of Me<sub>2</sub>NH·BH<sub>3</sub>. (1) Before milling. (2) After milling.



Figure S5:  ${}^{11}B{}^{1}H{}$  NMR spectra (CDCl<sub>3</sub>) of Me<sub>2</sub>NH·BH<sub>3</sub>. (1) Before and (2) after milling.

## General Procedure for the Rh-Catalysed Dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub> 2 by Ball Milling

Me<sub>2</sub>NH·BH<sub>3</sub> (100.0 mg, 1.70 mmol, 1.00 equiv., **2**) and RhCl(PPh<sub>3</sub>)<sub>3</sub> (8.0 mg, 8.5  $\mu$ mol, 0.5 mol %, **1**) were added to a stainless-steel jar (20 mL) equipped with one milling ball of the same material (10 mm in diameter). The jar was provided with a gas outlet tube, which went into a CDCl<sub>3</sub> filled vial. The reaction mixture was milled for 30 min at 25 Hz. The reaction mixture and the CDCl<sub>3</sub> solution were analysed by NMR.

## Analysis of the Rh-Catalysed Dehydrocoupling by <sup>11</sup>B NMR, <sup>11</sup>B{<sup>1</sup>H} NMR and <sup>1</sup>H NMR Spectroscopy

The residue obtained after the mechanochemical reaction was analysed by <sup>11</sup>B NMR spectroscopy (Figure S6). Alongside dimer **3**,<sup>6</sup> formation of additional unidentified boron-containing species was observed.



Figure S6: NMR analysis in CDCl<sub>3</sub> of the mechanochemical dehydrocoupling reaction of **2** catalysed by Wilkinson's catalyst. a)  ${}^{11}B_{\{}^{1}H_{\}}$  NMR spectrum of Me<sub>2</sub>NH·BH<sub>3</sub> **2**. b)  ${}^{11}B_{\{}^{1}H_{\}}$  NMR spectrum of the reaction mixture after milling. c) Close-up of the  ${}^{11}B$  NMR spectrum of the reaction mixture after milling.



4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 f1 (ppm)

Figure S7: <sup>1</sup>H NMR analysis in CDCl<sub>3</sub> of the mechanochemical dehydrocoupling reaction of **2** catalysed by Wilkinson's catalyst. a) <sup>1</sup>H NMR spectrum of  $Me_2NH\cdot BH_3$  **2**. b) <sup>1</sup>H NMR spectrum of the reaction mixture after milling. c) Close-up of the <sup>1</sup>H NMR spectrum of the reaction mixture after milling.

### General Procedure for Gas Volume Measurement by Water Displacement in the Rh-Catalysed Dehydrocoupling of Me<sub>2</sub>NH·BH<sub>3</sub> 2

Me<sub>2</sub>NH·BH<sub>3</sub> (50 mg, 0.85 mmol, 1.00 equiv., **2**) and RhCl(PPh<sub>3</sub>)<sub>3</sub> (3.9 mg, 4.2  $\mu$ mol, 0.5 mol %) were added to a stainless-steel jar (20 mL) equipped with one milling ball of the same material (10 mm in diameter). The milling jar was provided with a gas outlet tube. The content was milled for 30 min at 25 Hz while measuring the formation of H<sub>2</sub> (Figure S8).





Figure S8: (a) General reaction set-up for gas volume measurement by water displacement. (b) Water level before the reaction. (c) Water level after the reaction. (Bottom)  $H_2$  evolution over time.

#### General Procedure for the Hydrogenation of trans-Stilbene (trans-6) in the Ball Mill

*trans*-Stilbene (36.1 mg, 0.20 mmol, 1.00 equiv., *trans*-6), RhCl(PPh<sub>3</sub>)<sub>3</sub> (1.9 mg, 2.1  $\mu$ mol, 1 mol %) and Me<sub>2</sub>NH·BH<sub>3</sub> (13.0 mg, 0.22 mmol, 1.10 equiv., **2**) were added into a 10 mL stainless-steel jar with one ball (10 mm in diameter) made of the same material. The jar was closed and parafilm wrapped around it. The reaction mixture was milled for 90 min at 25 Hz. Then, the reaction mixture was analysed by NMR and GC-MS. Purification of product **7** was carried out by column chromatography with *n*-hexane as eluent. Hydrogenation of *trans*-6 using the commercial available Wilkinson catalyst afforded 28.3 mg of a white solid (0.155 mmol, yield = 78%).

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>): δ (ppm) 7.29 (m, 4H), 7.21 (m, 6H), 2.94 (s, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>): δ (ppm) 141.9, 128.6, 128.5, 126.1, 38.1.

Data is in accordance with the literature.<sup>7</sup>

#### General Procedure for the Hydrogenation of cis-Stilbene (cis-6) in the Ball Mill

*cis*-Stilbene (36.1 mg, 35.7  $\mu$ L ( $\rho = 1.011 \text{ mg}\cdot\mu\text{L}^{-1}$ ), 0.20 mmol, 1.00 equiv., *cis*-6), RhCl(PPh<sub>3</sub>)<sub>3</sub> (1.9 mg, 2.1  $\mu$ mol, 1 mol %) and Me<sub>2</sub>NH·BH<sub>3</sub> (13.0 mg, 0.22 mmol, 1.10 equiv., **2**) were added into a 10 mL stainless-steel jar with one ball (10 mm in diameter) made of the same material. The jar was immediately closed and parafilm wrapped around it. The reaction mixture was milled for 90 min at 25 Hz. The reaction mixture was milled for 90 min at 25 Hz. Thereaction mixture was milled for 90 min at 25 Hz.

#### General Procedure for Hydrogenation of Diphenylacetylene (8) in the Ball Mill



Diphenylacetylene (35.6 mg, 0.20 mmol, 1.00 equiv., **8**), RhCl(PPh<sub>3</sub>)<sub>3</sub> (1.9 mg, 2.0  $\mu$ mol, 1 mol %, red polymorph of **1**) and Me<sub>2</sub>NH·BH<sub>3</sub> (1.10-2.20 equiv., **2**) were added in the given order into a 10 mL stainless-steel milling jar with one ball (10 mm in diameter) made of the same material. The jar was closed and parafilm wrapped around it. The reaction mixture was milled for 90 min to 2 h at 25 Hz. Then, the reaction mixture was analysed by NMR and GC-MS.

#### GC-MS and NMR analysis of reaction mixtures



Figure S9: GC-MS analysis of the Rh-catalysed hydrogenation of cis-stilbene (cis-6) after 30 min. IS = Internal Standard (1,3,5-trimethoxybenzene).



Figure S10: GC-MS analysis of the Rh-catalysed hydrogenation of cis-stilbene (cis-6) after 90 min. IS = Internal Standard (1,3,5-trimethoxybenzene).



Figure S11: GC-MS analysis of the Rh-catalysed hydrogenation of diphenylacetylene (8) after 90 min with 2.20 equiv. of 2. IS = Internal Standard (1,3,5-trimethoxybenzene).



Figure S12: Analysis by <sup>1</sup>H NMR spectroscopy of the Rh-catalysed hydrogenation of cis-6 using Wilkinson's catalyst. And determination of the amount of trans-7 formed by rhodium catalysed isomerisation of cis-6 after 90 min with 2.20 equiv. of 2. IS = Internal Standard (1,3,5-trimethoxybenzene). Top: <sup>1</sup>H NMR of cis-6; Middle: Reaction mixture using red Wilkinson's catalyst; Bottom: Reaction mixture using LAG made Wilkinson's catalyst.





Figure S13: Monitoring of the mechanochemically made dehydrocoupling products by NMR spectroscopy. a)  ${}^{11}B_1^{(1)}H_1^{(1)}$  NMR spectrum in CDCl<sub>3</sub> immediately after the milling reaction was halted; the presence of the potential oligomers of the type  $[Me_2N-BH_2]n$  at -1.12 ppm is shown by the arrow. b)  ${}^{11}B_1^{(1)}H_1^{(1)}$  NMR spectrum in CDCl<sub>3</sub> of the crude mixture after two weeks; the broad signal at -1.12 ppm is not longer observed. c)  ${}^{11}B$  NMR spectrum in CDCl<sub>3</sub> immediately after the milling reaction was halted; the presence of the potential oligomers of the type  $[Me_2N-BH_2]n$  as a triple at -1.12 ppm is shown by the arrow. d)  ${}^{11}B$  NMR spectrum in CDCl<sub>3</sub> of the crude mixture after two weeks; the broad signal at -1.12 ppm is shown by the arrow. d)  ${}^{11}B$  NMR spectrum in CDCl<sub>3</sub> of the crude mixture after two weeks; the presence of the potential oligomers of the type  $[Me_2N-BH_2]n$  as a triple at -1.12 ppm is shown by the arrow. d)  ${}^{11}B$  NMR spectrum in CDCl<sub>3</sub> of the crude mixture after two weeks; the broad triplet at -1.12 ppm is not longer observed.

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