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Supporting Information

A Simple Cobalt–Based Catalyst System for the Controlled Dehydropolymerisation of $H_3B{\cdot}NMeH_2$ on the Gram-Scale

Timothy Morgan Boyd,[a] Kori A. Andrea,[a,b] Katherine Baston,[a] Alice Johnson,[a] David E. Ryan,[a] Andrew S. Weller*[a]

[a]Department of Chemistry, Chemistry Research Laboratories, University of Oxford, Oxford, OX1 3TA, UK.
[b]Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada

Corresponding author email address: andrew.weller@chem.ox.ac.uk

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General experimental conditions:

Unless otherwise stated all experimental manipulations were conducted under an argon atmosphere using standard Schlenk and glovebox techniques. Glassware was dried in an oven at 130 °C overnight and flame dried under vacuum prior to use. Pentane, toluene, benzene and tetrahydrofuran were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by three successive freeze-pump-thaw cycles. 1,2-$F_2C_6H_4$ (pretreated with alumina) was dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. C_6D_6 was dried over Na, vacuum distilled and stored over 3 Å molecular sieves. $H_3B{\cdot}NMeH_2$ was purchased from Boron Specialities and recrystallized from Et_2O at -18 °C, except in the case of scale-up experiments where it was used as received. PPh_3 was purchased from Sigma-Aldrich and used as received. $(^iPr_2PCH_2CH_2)_2NH$ 10 wt. % in THF was purchased from Sigma Aldrich and freeze pump thaw degassed prior to use. $(Cy_2PCH_2CH_2)_2NH$ was purchased from Sigma Aldrich and used as received. Methylamine (2 M in THF) was purchased from Sigma Aldrich and used as received. $CoCl_2$ was purchased from Sigma Aldrich and dried under vacuum at 160°C under dynamic vacuum for 48 hours. $CoCl_2(^iPr_2PCH_2CH_2)_2NH$,[1] $CoCl(Cy_2PCH_2CH_2)_2NH$,[2] $CoCl(^iPr_2PCH_2CH_2)_2N$,[1] $CoCl(^iPr_2PCH_2CH_2)_2NH$[3] and $(^iPr_2PCH_2CH_2)_2NMe$[4] were prepared by literature methods.

NMR spectra were recorded on a Bruker AVIIIHD 400 nanobay spectrometer at room temperature unless otherwise stated. Residual protio solvent was used as a reference for ^1H NMR spectra in deuterated solvent samples. For NMR spectrometric samples in 1,2-$F_2C_6H_4$ or protio-THF solvent, ^1H NMR spectra were pre-locked to a sample of C_6D_6 and referenced to the centre of the downfield solvent multiplet, $\delta = 7.07$. ^{11}B NMR spectra were referenced against $BF_3{\cdot}OEt_2$ (external) respectively. Chemical shifts are quoted in ppm and coupling constants (J) in Hz. Magnetic susceptibility measurements were performed in CD_2Cl_2 according to the Evans NMR method.[5] Elemental microanalyses were performed by Stephen Boyer at London Metropolitan University. ICP-MS results were performed at the School of Life Sciences, University of Sussex.

Gel Permeation Chromatography (GPC) was performed on a Malvern Viscotek GPCmax chromatograph fitted with a reference index (RI) detector. The triple-column (plus guard column) setup was contained within an oven (35 °C) and consisted of a porous styrene divinylbenzene copolymer with a maximum pore size of 1,500 Å. THF containing 0.1% w/w $(N^nBu_4)Br$ was used as the eluent at a flow rate of 1.0 mL min^{-1}. Samples were dissolved in the eluent (2.0 mg mL^{-1}), filtered (0.2 μm pore size) and run immediately. The calibration was conducted using a series of monodisperse polystyrene standards (M_n = 474-476,000 $gmol^{-1}$) obtained from Sigma Aldrich.

Synthesis of 3, $CoCl_2(^iPr_2PCH_2CH_2)_2NMe$

Prepared by analogous procedure used for **1** and **2.**[1,2] The product was isolated as a dark blue powder (80 % yield). All attempts of crystallization were unsuccessful. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): silent. δ $^{31}P\{^1H\}$ (162 MHz, CD_2Cl_2, 298 K): silent. Magnetic measurement using Evans method of a CD_2Cl_2 sample: μ_{eff} (200 K) = 4.13 μ_B (μ_{SO} = 3.88 μ_B).

Catalytic Dehydropolymerization of $H_3B{\cdot}NMeH_2$

Dehydropolymerization Under Open Conditions

In a typical experimental set-up (e.g. 0.223 M [$H_3B{\cdot}NMeH_2$], 0.2 mol% catalyst loading), $H_3B{\cdot}NMeH_2$ (25.0 mg, 0.557 mmol) was suspended in 2.0 mL of 1,2-$F_2C_6H_4$. Double the desired amount of catalyst was weighed into a separate flask and dissolved in 1.0 mL of 1,2-$F_2C_6H_4$. The $H_3B{\cdot}NMeH_2$ containing flask was flushed with argon through an exit needle and 0.5 mL of the catalyst solution was added to the reaction mixture quickly followed by 2 equiv. of $NMeH_2$. The resultant solution was stirred for the desired reaction time at 400 rpm at room temperature. 0.5 mL of the reaction mixture was removed for NMR spectroscopy. The remaining reaction mixture was transferred to 40 mL of rapidly stirred pentane to give an off-white suspension which was isolated by filtration. The off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis.

Dehydropolymerization Under Hydrogen Evolution Measurement Conditions

In a typical experimental set-up (e.g. 0.223 M [$H_3B{\cdot}NMeH_2$], 0.4 mol% catalyst loading), $H_3B{\cdot}NMeH_2$ (25.0 mg, 0.557 mmol) was suspended in 4.0 mL of 1,2-$F_2C_6H_4$ in a jacketed two-neck Schlenk flask connected to a recirculating cooler and the temperature set at 25 °C. Double the desired amount of catalyst was weighed into a separate flask and dissolved in 2.0 mL of 1,2-$F_2C_6H_4$. The $H_3B{\cdot}NMeH_2$-containing flask was sealed off from the Ar supply and connected to a water-filled gas burette. The pre-catalyst solution was added to the reaction mixture followed by 2 equiv. of $NMeH_2$ and the resultant solution was decanted into 40 mL of rapidly stirred pentane to give an off-white suspension which was isolated by filtration. The off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis.

Scale-up Dehydropolymerization and Metal-Removal Procedure

In a typical experimental set-up $H_3B{\cdot}NMeH_2$ (e.g. 5 M [$H_3B{\cdot}NMeH_2$] in THF) was dissolved in THF. Double the desired amount of catalyst was weighed into a separate flask and dissolved in 1.0 mL of THF. The $H_3B{\cdot}NMeH_2$ containing flask was flushed with argon through an exit needle and 0.5 mL of the catalyst solution was added to the reaction mixture followed by 2 equiv. of $NMeH_2$. The resultant solution was stirred for the desired reaction time at 400 rpm. 0.5 mL of the reaction mixture was removed for analysis by NMR spectroscopy. The remaining reaction mixture was transferred to 40 mL of rapidly stirred pentane to give an off-white suspension which was isolated by filtration. The off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis. To remove residual metal catalyst from the isolated polymer, a sample of polymer (500 mg) was dissolved in THF (50 mL) and flash filtered through a silica plug. The solution of polymer was reduced to 5 mL and transferred to rapidly stirring pentane to give an off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis.

In THF at lower absolute concentration of catalyst (e.g. 0.223 M [$H_3B{\cdot}NMeH_2$], 0.4 mol% catalyst loading) results in no reaction. This is explained by impurities in the THF (~10 ppm H_2O) titrating out the active catalyst, resulting in reaction only at higher absolute catalysts concentrations.

Ten Gram Scale Dehydropolymerization of $H_3B{\cdot}NMeH_2$ catalysed by 1

$H_3B{\cdot}NMeH_2$ (10 g, 0.22 mol) was dissolved in THF (40 ml) under nitrogen. **1** (20 mg, 46 mmol) was separately dissolved in 5 mL of THF and transferred to the flask containing $H_3B{\cdot}NMeH_2$, followed by the addition of 2 equiv. of $NMeH_2$ (50 μL). The resultant solution was stirred for 2 h under a high nitrogen flow to remove the large volume of hydrogen produced (5 L). The remaining reaction mixture was transferred to 500 mL of rapidly stirred pentane to give an off-white suspension which was isolated by filtration. The off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis.

Table S1. $H_3B{\cdot}NMeH_2$ dehydropolymerization conditions and polymer characterisation data using catalyst **2** in 1, 2-$F_2C_6H_4$

Entry[a]	mol%	M_n/gmol^{-1} [b]	Đ[b]	Yield/mg (%)[c]
1	0.2	71, 000	1.5	30 (60)
2	0.4	51, 100	1.7	30 (60)
3	0.8	22, 400	1.5	30 (60)

[a]General reaction conditions: 0.05 g $H_3B{\cdot}NMeH_2$ in 1,2-$F_2C_6H_4$ (0.224 M), 5 min. [b]Relative to polystyrene standards. [c]Approximate due to transfer losses from reaction flask

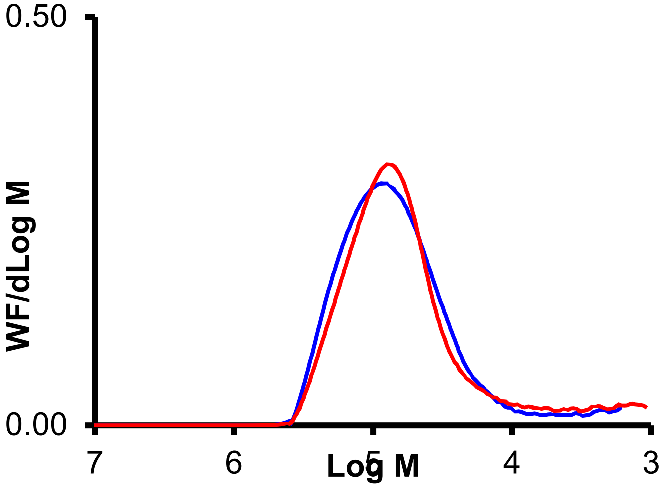

Figure S1. Overlaid GPC traces of $(H_2BNMeH)_n$ obtained using **2** in 1,2-$F_2C_6H_4$ at 0.4 mol% under open (red) and H_2 evolution (blue) conditions. Red trace: M_n = 51, 100 gmol^{-1}; $Đ$ = 1.7. Blue trace: M_n = 51, 100 gmol^{-1}; $Đ$ = 1.7

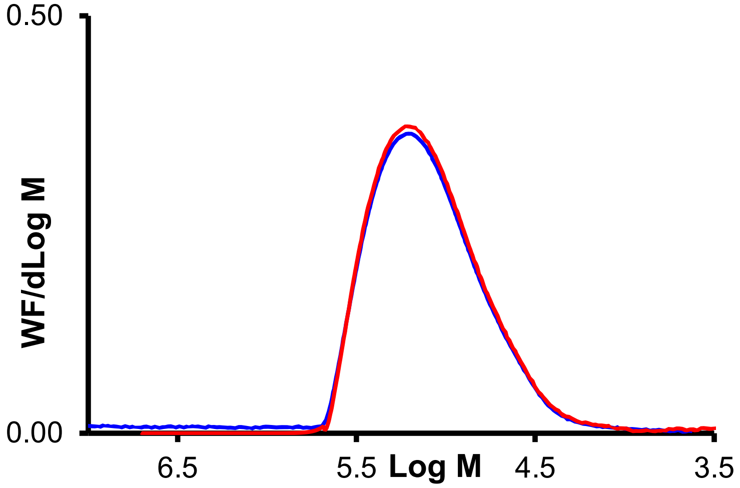

Figure S2. Overlaid GPC traces of $(H_2BNMeH)_n$ (Table 1, entry 4) immediately after purification (blue) and after storage under air for 1 month (red). Red trace: M_n = 98, 250 gmol^{-1}; $Đ$ = 1.6. Blue trace: M_n = 98, 800 gmol^{-1}; $Đ$ = 1.6

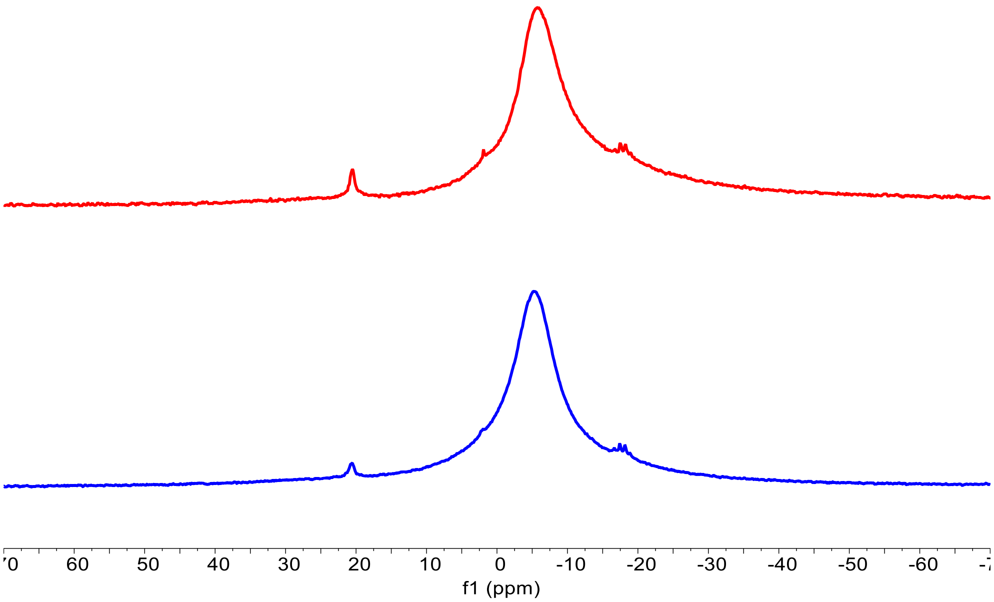

Figure S3. Overlaid ^{11}B NMR spectrum of isolated polyaminoboranes immediately after purification (blue) and after storage under air for 1 month (red).

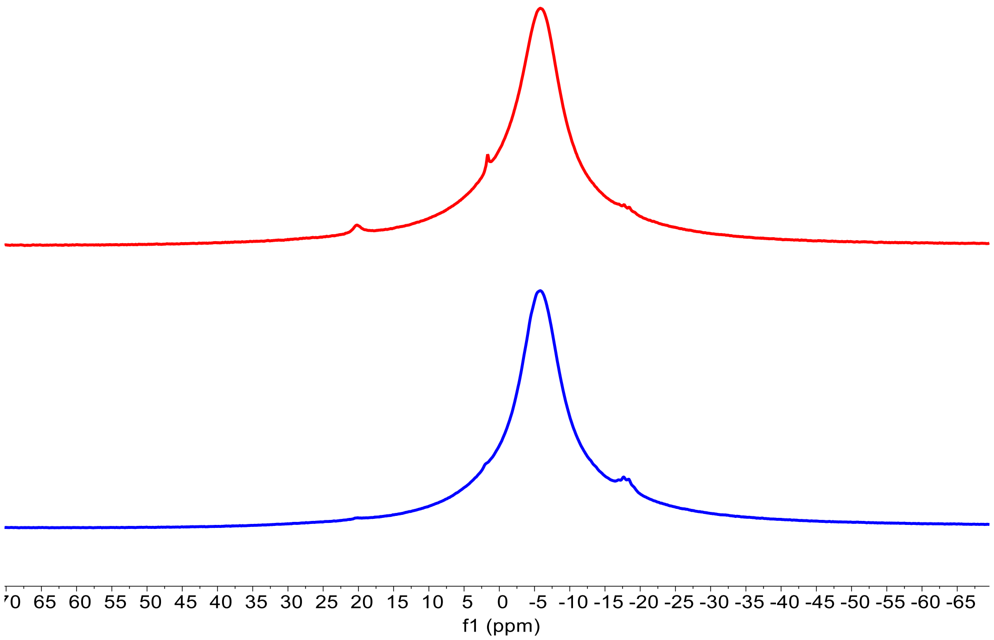

Figure S4. Overlaid ^{11}B NMR spectrum of isolated polyaminoboranes immediately after purification (blue) and after passing through silica to remove residual cobalt (red).

Synthesis of Key Reaction intermediates

In situ formation of complex 1 for the catalytic dehydropolymerization of $H_3B{\cdot}NMeH_2$

$CoCl_2$ (3 mg) was dissolved in THF (1 ml) to which ($^iPrPCH_2CH_2)_2NH$ (10 wt% in THF , 7 mg, 62 μL) was added and left to stir at room temperature for 1 hour. In the catalytic flask $H_3B{\cdot}NMeH_2$ was dissolved in THF (4 ml) the flask was flushed with argon through an exit needle and the catalyst solution was added to the reaction mixture followed by 2 equiv. of $NMeH_2$ (2 M, 25 μL). The reaction mixture was left to stir for 90 minutes. Following this the remaining reaction mixture was transferred to 40 mL of rapidly stirring pentane to give an off-white suspension which was isolated by filtration. The off-white solid $(H_2BNMeH)_n$ was dried under vacuum overnight prior to GPC analysis

In situ formation of colloidal cobalt nanoparticles for the dehydropolymerization of $H_3B{\cdot}NMeH_2$

1.12 g of $H_3B{\cdot}NMeH_2$ in 4 mL of THF and 3 mg of $CoCl_2$ in 1 mL of THF were combined in a flask resulting in a light blue solution. 2 equiv. of $NMeH_2$ (2 M, 25 μL) was then added to the flask resulting in an immediate colour change and black precipitate. No significant turnover was observed after 1 h. After the allotted time, ($^iPrPCH_2CH_2)_2NH$ (10 wt% in THF, 7 mg, 62 μL) was added to the reaction mixture and allowed to react for a further 2 hours upon which no further turnover was observed.

Video 1 Explanation

Hydrogen eudiometer measurement from Figure 1 using pre-catalyst **2** (0.223 M [$H_3B{\cdot}NMeH_2$], 0.4 mol% catalyst loading, 1,2–$F_2C_6H_4$).

Video 2 Explanation

$CoCl_2$ + 2 $NMeH_2$ + $H_3B{\cdot}NMeH_2$ (5 M [$H_3B{\cdot}NMeH_2$], 0.1 mol% catalyst, THF).
Left: time = 0
Right: time = 5 mins.

Final scene: sample of reaction mixture after 1 hour showing magnetic behavior of nanaoparticles.

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