

COMMUNICATION

A Simple Cobalt–Based Catalyst System for the Controlled Dehydropolymerisation of $\text{H}_3\text{B}\cdot\text{NMeH}_2$ on the Gram-Scale

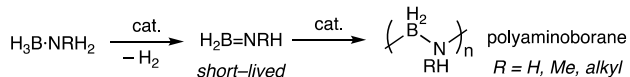
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A simple Co(II)–based amine–borane dehydropolymerisation catalyst system is reported that operates at low loadings, to selectively give $(\text{H}_2\text{BNMeH})_n$ polymer on scale, with catalyst control over M_n , narrow dispersities and low residual metal content.

The dehydropolymerisation of amine–boranes $\text{H}_3\text{B}\cdot\text{NRH}_2$ ($\text{R} = \text{H}$, alkyl) produces a new type of polymer with BN mainchain units: polyaminoboranes, $(\text{H}_2\text{BNRH})_n$.^{1–4} As well as the fundamental interest in their synthesis and structures, polyaminoboranes are precursors to BN–based materials.⁵ While stoichiometric synthetic routes have been reported,⁶ catalysis offers opportunities for precise control over the dehydropolymerisation process.^{2, 3} This is challenging, however, as both the dehydrogenation of the amine–borane, to form a transient aminoborane,⁷ and subsequent polymerisation need to be controlled, Scheme 1. Reflecting this complexity, a holistic mechanism for dehydropolymerisation, that captures the nuances of different catalyst systems, is yet to be articulated. Nevertheless, changes in the degree of polymerisation of $(\text{H}_2\text{BNMeH})_n$ have been reported for $\text{IrH}_2(\text{POCOP})$ ($\text{POCOP} = \kappa^3\text{-}1,3\text{-}(\text{P}^t\text{Bu}_2\text{O})_2\text{C}_6\text{H}_3$),^{8, 9} $\text{Cp}^*\text{TiCl}_2/\text{BuLi}$ ¹⁰ and $(\text{CpZrCl})_2(\text{allenediyl})$ ¹¹ catalysts by variation of catalyst: $\text{H}_3\text{B}\cdot\text{NMeH}_2$ ratio. We have recently reported that for $\{\text{Rh}(\text{L})\}^+$ –based catalysts ($\text{L} =$ chelating diphosphine) similar control is possible, with higher catalyst loadings resulting in lower M_n .^{12, 13} Importantly, added NMeH_2 promotes the formation of the active catalyst,¹² and its role in promoting hydride transfer processes in amine–borane dehydrocoupling



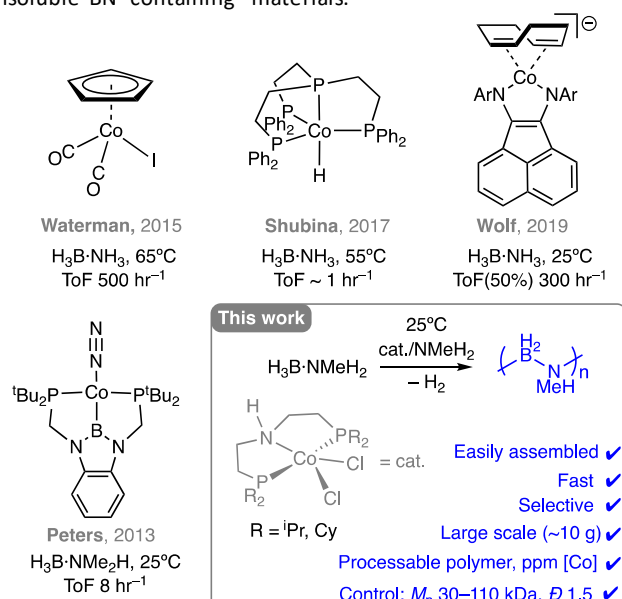
Scheme 1. Amine–borane dehydropolymerisation has been highlighted.^{14, 15}

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Informed by these studies on Rh–based systems, and inspired by the reports of Schneider¹⁶ and Beweries¹⁷ on $\{\text{Fe}(\text{iPr}_2\text{PCH}_2\text{CH}_2)_2\text{NH}\}$ –based catalysts for amine–borane dehydropolymerisation, we now report that similar Co(II)–precatalysts, first reported by Arnold,¹⁸ are remarkably efficient for the dehydropolymerisation of $\text{H}_3\text{B}\cdot\text{NMeH}_2$ to give $(\text{H}_2\text{BNMeH})_n$, when a NMeH_2 promoter is used. These $\text{CoCl}_2(\text{R}_2\text{PCH}_2\text{CH}_2)_2\text{NH}/\text{NMeH}_2$ systems ($\text{R} = \text{iPr}$, Cy) are easily assembled from cheap, commercially available, starting materials. They operate at low catalyst loadings, to selectively give processable (drop castable) polymer on scale (up to 10 g), with catalyst control over M_n , reasonably narrow dispersity and low residual metal content in the polymer. While Co–based catalysts have been reported for amine–borane dehydrocoupling more generally (Scheme 2),¹⁹ they can be rather unselective for the formation of soluble polyaminoboranes over other products, e.g. borazine or insoluble BN–containing materials.



Scheme 2. Cobalt–based catalysts for amine–borane dehydrocoupling.

Table 1. H₃B·NMeH₂ dehydropolymerisation conditions and polymer characterisation data, using catalysts **1**–**5** and in situ formed catalyst

Entry	catalyst ^a	mol%	solvent	[H ₃ B·NMeH ₂]/M ^b	time/mins	M _n /g mol ⁻¹ ^c	Đ	Yield/g (%)
1	1	0.2	1,2-F ₂ C ₆ H ₄	0.223	10	66,900	1.4	~0.03 (~60) ^f
2	1	0.4	1,2-F ₂ C ₆ H ₄	0.223	10	48,000	1.4	~0.03 (~60) ^f
3	1	0.8	1,2-F ₂ C ₆ H ₄	0.223	10	33,100	1.4	~0.03 (~60) ^f
4	1	0.02	THF	5	90	98,800	1.6	0.792 (74)
5	1	0.1	THF	5	60	85,800	1.6	0.837 (78)
6	1	0.8	THF	5	10	48,000	1.7	0.904 (84)
7	2	0.02	THF	5	90	112,400	1.5	0.913 (85)
8	2	0.1	THF	5	60	81,900	1.5	0.865 (81)
9	2	0.8	THF	5	10	47,500	1.6	0.835 (78)
10 ^e	2	0.02	THF	5	120	74,200	1.6	8.12 (85)
11	L1/CoCl₂ ^d	0.1	THF	5	60	62,500	1.6	0.831 (78)
12 ^e	4	0.4	1,2-F ₂ C ₆ H ₄	0.223	10	76,100	1.4	~0.03 (~60) ^f
13	5	0.4	1,2-F ₂ C ₆ H ₄	0.223	10	42,900	1.5	~0.03 (~60) ^f

a) + 2 equiv. NMeH₂, 298 K open to Ar flow. b) in 5 cm³ solvent ≡ 1.12 g H₃B·NMeH₂ in THF; ≡ 0.05 g H₃B·NMeH₂ in 1,2-F₂C₆H₄. c) Relative to polystyrene standards; d) Stirred for 1hr before addition of H₃B·NMeH₂/NMeH₂. e) No NMeH₂ added. f) approximate due to transfer losses from reaction flask. g) 10 g H₃B·NMeH₂

Addition of CoCl₂ to (R₂PCH₂CH₂)₂NH (R = ⁱPr, **L1**; Cy, **L2**) results in the known complexes CoCl₂(R₂PCH₂CH₂)₂NH (**1**, **L1**;¹⁸ **2**, **L2**²⁰) isolated as purple microcrystalline solids. Screening precatalysts **1** or **2** (0.4 mol%, 25°C, 1,2-F₂C₆H₄) for the dehydropolymerisation of H₃B·NMeH₂ resulted in no H₂ evolution or colour change and the return of unreacted H₃B·NMeH₂. By contrast, addition of 2 equivalents of an amine relative to [Co] (NMeH₂, 2 M in THF), a known promoter in amine–borane dehydrocoupling,^{12, 14–16} resulted in a clear, tan coloured, solution and immediate H₂ production as measured by eudiometer (Fig. 1 and ESI). At the end of catalysis (20 mins for catalyst **1**) ~1 equivalent of H₂ per H₃B·NMeH₂ had been evolved. ¹¹B NMR spectroscopy showed a broad single resonance at δ –6.83 characteristic of linear (H₂BNMeH)_n,^{2, 8} with no borazine or residual H₃B·NMeH₂ observed. Turnover is rapid for complex **1** (ToF ~800 hr⁻¹), with complex **2** even faster (~6000 hr⁻¹, see ESI).²¹ Precipitation of the polymer formed into pentanes gave the off–white powder (H₂BNMeH)_n in ~60% yield, on a 30 mg scale. Analysis by GPC (RI detector, relative to polystyrene standards) shows that medium² molecular weight polymer is formed: e.g., **1** M_n = 47,600 g mol⁻¹ (Đ = 1.5). However, recent studies comparing RI/polystyrene standards with dynamic light scattering/DOSY techniques show that the former may significantly overestimate M_n for (H₂BNMeH)_n.^{4, 11}

When open to a flow of Ar catalysis, is faster (10 mins for

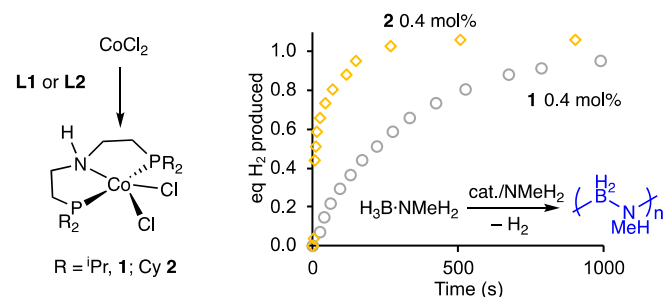


Figure 1. Synthesis of precatalysts **1** and **2** and time course plot for H₂ evolution (0.4 mol%, + 2 equiv. NMeH₂, 298 K, 5 cm³ solvent, eudiometer, first 1000 s).

completion using complex **1**). Changing the catalyst loading (Table 1, entries 1–3) changed the degree of polymerisation in the resulting polymer, with low loadings resulting in significantly higher molecular weights, while Đ remains unchanged. Combined, the NMR and GPC data show that this is a rather controlled²² polymerisation. There is no significant change in the isolated polymer (M_n, Đ or yield, ESI) if catalysis is performed under an H₂ atmosphere (eudiometer) or in a system under an Ar flow. H₂ has been shown to modify the degree of polymerisation for some systems,¹² but not others.²³

The scale of reaction is limited by the low solubility (~0.22 M) of H₃B·NMeH₂ in 1,2-F₂C₆H₄.²³ THF is a significantly better solvent, and has been used previously in the IrH₂(PONOP) system to obtain high substrate concentrations, i.e. 10 M.⁸ For catalysts **1** and **2** THF is also a suitable solvent, although catalysis takes longer compared with 1,2-F₂C₆H₄ (~1 hour). Operating at 5 M [H₃B·NMeH₂], high molecular weight polymer can be isolated on ~1-gram scale: i.e. 0.02 mol% **2**, M_n = 112,400 g mol⁻¹. As for 1,2-F₂C₆H₄ solvent, there is control over M_n with catalyst loading (entries 4–9, Fig. 2A shows data for **2**), Đ does not vary considerably (1.5–1.7) and ¹¹B NMR spectroscopy shows selective conversion to polymer (Fig. 2B). The isolated off–white polymer can be drop casted from concentrated THF solutions (1 g/cm³) to form brittle films of (H₂BNMeH)_n, Fig. 2C. Analysis for residual Co–content in the isolated polymer using ICP–MS shows that most is retained, although the low catalyst loadings mean that this is still at the ppm level, e.g. 830 ppm for a 0.4 mol% loading of complex **2**. Passing (H₂BNMeH)_n rapidly through a short silica plug significantly reduces the Co–content (138 ppm) without degradation, as measured by GPC and ¹¹B NMR spectroscopy (ESI). The polymer produced is bench stable for at least 1 month (unoptimised, see ESI).

This dehydropolymerisation can be repeated on a 10 g scale using precatalyst **2** (entry 10) to give an off–white polymer of M_n = 74,200 g mol⁻¹, Đ = 1.6.²⁴ No special precautions were used: catalysis was performed in a round–bottomed flask under a N₂ flow (to dilute/remove H₂) using THF from a drying column

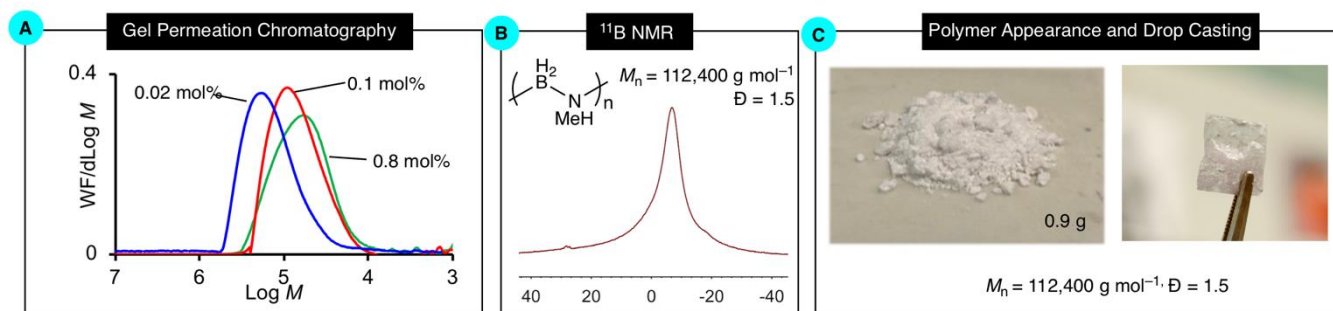


Figure 2. Dehydrogenation using catalyst **2**/H₃B-NMeH₂ (5 m) in THF **A**) GPC data for different catalyst loadings, versus polystyrene standards. **B**) ¹¹B NMR spectrum of the reaction mixture post polymerization using **2** at 0.02 mol%. **C**) Polymer isolated from pentane precipitation and an example of a drop-cast film (Table 1, entry 7).

(~10 ppm H₂O) and polymer was worked up open to air. The versatility of this catalyst system is further demonstrated by the in situ assembly straight from commercially sourced CoCl₂ and **L1**, before (*vide infra*) adding H₃B-NMeH₂/NMeH₂ (entry 11).

The paramagnetic Co(II) centre and low catalyst loadings make catalyst speciation studies challenging. However, a preliminary mechanistic study using complexes based upon **L1** (iPr) points to possible catalytic pathways. Use of a ligand with an NMe unit rather than NH, CoCl₂(iPr₂PCH₂CH₂)₂NMe **3**,²⁵ resulted in no reaction. The independently prepared Co(II) complex CoCl(iPr₂PCH₂CH₂)₂N, **4**,¹⁸ is – in contrast – an effective catalyst in the *absence* of NMeH₂ (entry 12). These observations point to a possible cooperative ligand, constant oxidation-state, cycle for dehydrogenation (Scheme 3). Such mechanisms have been proposed by Schneider for (Fe**L1**)–based amine–borane dehydrocoupling catalysts,¹⁶ and Beller – using complex **1** for the reduction of carboxylic acids to alcohols.²⁵ We propose the role of NMeH₂ is to bring the pre-catalyst, **1**, onto cycle by promoting hydride transfer from H₃B-NMeH₂, with concomitant elimination of Cl[–], to form CoClH(iPr₂PCH₂CH₂)₂NH. This could occur through formation of [NMeH₃]Cl via deprotonation of a σ–bound amine–borane intermediate and elimination of H₂B=NMeH, Scheme 3 inset. An alternative is hydride transfer with formation of boronium [H₂B(NMeH₂)₂]Cl, as suggested for other systems.^{14, 23} We favour the former, based on recent computational studies.¹⁵

A Co(I)/Co(III) catalytic dehydrogenation pathway cannot be discounted, as hydride sources are established to react with CoCl₂(ligand) precursors to form Co(I) complexes,^{25, 26} such as CoCl(iPr₂PCH₂CH₂)₂NH, **5**.^{18, 25} Complex **5** undergoes reversible oxidative addition of H₂ and silanes,^{18, 27} which supports an inner sphere BH/NH activation mechanism with H₃B-NMeH₂. When starting from complex **5**, (H₂BNMeH)₂ is produced in a similar timescale and *M_n* compared with **1** (Entry 13). The attenuation of turnover under H₂ measurement conditions implicate reversible H₂ addition in the catalytic cycle. Beller has

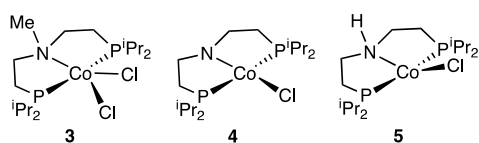
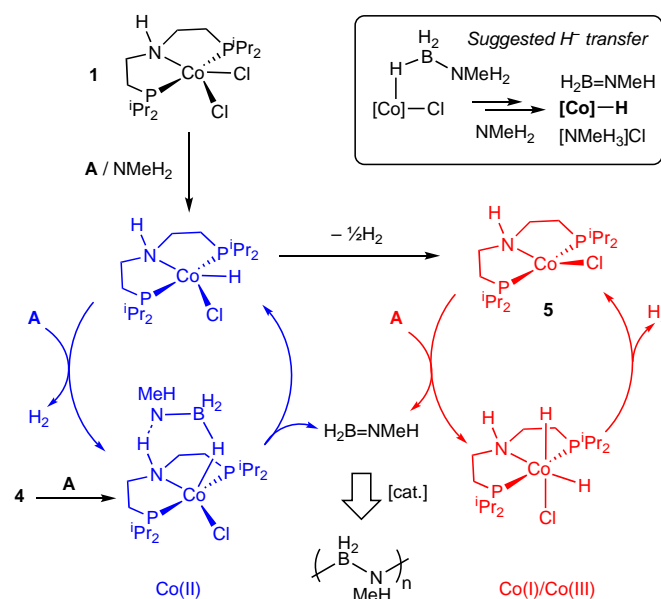


Chart 1. Complexes **3**, **4** and **5**.



Scheme 3. Possible mechanisms for dehydrogenation. Blue = ligand cooperative Co(II) constant oxidation state cycle, Red = inner sphere Co(I)/Co(III) cycle. **A** = H₃B-NMeH₂. The relative contributions from each cycle are undetermined.

recently discussed a similar ambiguity in mechanism using **1** for the reduction of carboxylic acids.²⁵

We discount the formation of a colloidal catalyst as addition of sub-stoichiometric PPh₃ (1,2-F₂C₆H₄, **1**, 0.4 mol%) did not retard catalysis or change the polymer recovered, while no darkening of the solution is observed.²⁸ In contrast when 2 x NMeH₂ is added to CoCl₂/H₃B-NMeH₂,²⁹ in the absence of **L1**, the solution turns black, rather than the tan colour when using preformed complex **2**. There is no significant turnover after 1 hour and a magnetic precipitate (colloidal Co) is formed (ESI).

Whichever homogeneous pathway is operating for dehydrogenation, subsequent head-to-tail propagation of the formed aminoborane, H₂B=NMeH, leads to the formation of well-defined (H₂BNMeH)_n. Whether this is under catalyst (initiator) control – as suggested for IrH₂(PNONP),³⁰ {Rh(Xantphos)}²³ or {Fe(Cy₂PCH₂CH₂PCy₂)₃}³¹ systems – remains to be determined. Noteworthy is that non-catalytic routes to (H₂BNMeH)_n result in polymer with very high dispersity⁶ or low molecular weight⁷ – very different from that observed here.

Conclusions

The development of polyaminoboranes as useful precursors for materials science and electronics applications rests upon their controlled, scalable, practical and efficient synthesis. The simple Co(II)-based system we report here offers one such solution to this. The key to such efficient catalysis is the use of NMeH₂, which we propose acts to promote the formation of hydride intermediates on the catalytic cycle. While significant challenges remain in determining, and then controlling, the precise mechanism of dehydropolymerisation (i.e., initiation, propagation, termination), highlighting the role of amine-borane/NMeH₂ as a promoter for {CoCl₂} precatalyst systems more generally may be useful to the wider community.³²

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Conflicts of interest

There are no conflicts to declare.

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