(Fig. 1)Received 00th January 20xx,

1. Department of Chemistry, Chemistry Research Laboratories, University of Oxford, Oxford, OX1 3TA, UK.
2. Department of Chemistry, Memorial University of Newfoundland, St. John’s, Newfoundland A1B 3X7, Canada

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

A Simple Cobalt–Based Catalyst System for the Controlled Dehydropolymerisation of H3B·NMeH2 on the Gram-Scale

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

A simple Co(II)–based amine–borane dehydropolymerisation catalyst system is reported that operates at low loadings, to selectively give (H2BNMeH)n polymer on scale, with catalyst control over *M*n, narrow dispersities and low residual metal content.

The dehydropolymerisation of amine–boranes H3B·NRH2 (R = H, alkyl) produces a new type of polymer with BN mainchain units: polyaminoboranes, (H2BNRH)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 (H2BNMeH)n have been reported for IrH2(POCOP) (POCOP = 3-1,3-(PtBu2O)2C6H3),8, 9 Cp\*2TiCl2/BuLi10 and (CpZrCl)2(allenediyl)11 catalysts by variation of catalyst:H3B·NMeH2 ratio. We have recently reported that for {Rh(L)}+–based catalysts (L = chelating diphosphine) similar control is possible, with higher catalyst loadings resulting in lower *M*n.12, 13 Importantly, added NMeH2 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

Informed by these studies on Rh–based systems, and inspired by the reports of Schneider16 and Beweries17 on {Fe(iPr2PCH2CH2)2NH}–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 H3B·NMeH2 to give (H2BNMeH2)n, when a NMeH2 promoter is used. These CoCl2(R2PCH2CH2)2NH/NMeH2 systems (R = 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 | catalysta | mol% | solvent | [H3B·NMeH2]/Mb | time/mins | *M*n/g mol–1 c | *Đ* | Yield/g (%) |
| 1 | **1** | 0.2 | 1,2–F2C6H4 | 0.223 | 10 | 66, 900 | 1.4 | ~0.03 (~60)f |
| 2 | **1** | 0.4 | 1,2–F2C6H4 | 0.223 | 10 | 48, 000 | 1.4 | ~0.03 (~60)f |
| 3 | **1** | 0.8 | 1,2–F2C6H4 | 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) |
| 10g | **2** | 0.02 | THF | 5 | 120 | 74, 200 | 1.6 | 8.12 (85) |
| 11 | **L1**/CoCl2d | 0.1 | THF | 5 | 60 | 62,500 | 1.6 | 0.831 (78) |
| 12e | **4** | 0.4 | 1,2–F2C6H4 | 0.223 | 10 | 76, 100 | 1.4 | ~0.03 (~60)f |
| 13 | **5** | 0.4 | 1,2–F2C6H4 | 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 loses 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%, 25ºC, 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  –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 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 rapidlythrough 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, Ð = 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.** Dehydropolymerization 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 N*Me* unit rather than N*H*, 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 –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 dehydropolymerisation. 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)}31 systems – remains to be determined. Noteworthy is that non–catalytic routes to (H2BNMeH)n result in polymer with very high dispersity6 orlow 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

Acknowledgments

The EPRSC (EP/M024210/1), the University of Oxford. A NESRC Vanier Canada Graduate Scholarship and Michael Smith Foreign Study Supplement (KAA).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. E. M. Leitao, T. Jurca and I. Manners, *Nature Chem.*, 2013, **5**, 817-829.

2. A. L. Colebatch and A. S. Weller, *Chem. Eur. J.*, 2019, **25**, 1379-1390.

3. D. Han, F. Anke, M. Trose and T. Beweries, *Coord. Chem. Rev.*, 2019, **380**, 260-286.

4. D. A. Resendiz-Lara, G. R. Whittell, E. M. Leitao and I. Manners, *Macromolecules*, 2019, **52**, 7052-7064.

5. V. A. Du, T. Jurca, G. R. Whittell and I. Manners, *Dalton Trans.*, 2016, **45**, 1055-1062; X. Wang, T. N. Hooper, A. Kumar, I. K. Priest, Y. Sheng, T. O. M. Samuels, S. Wang, A. W. Robertson, M. Pacios, H. Bhaskaran, A. S. Weller and J. H. Warner, *CrystEngComm*, 2017, **19**, 285-294.

6. C. A. De Albuquerque Pinheiro, C. Roiland, P. Jehan and G. Alcaraz, *Angew. Chem. Int. Ed.*, 2018, **57**, 1519-1522.

7. O. J. Metters, A. M. Chapman, A. P. M. Robertson, C. H. Woodall, P. J. Gates, D. F. Wass and I. Manners, *Chem. Commun.*, 2014, **50**, 12146-12149.

8. A. Staubitz, A. Presa Soto and I. Manners, *Angew. Chem. Int. Ed.*, 2008, **47**, 6212-6215.

9. A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332-13345.

10. T. Jurca, T. Dellermann, N. E. Stubbs, D. A. Resendiz-Lara, G. R. Whittell and I. Manners, *Chem. Sci.*, 2018, **9**, 3360-3366.

11. M. Trose, M. Reiß, F. Reiß, F. Anke, A. Spannenberg, S. Boye, A. Lederer, P. Arndt and T. Beweries, *Dalton Trans.*, 2018, **47**, 12858-12862.

12. G. M. Adams, D. E. Ryan, N. A. Beattie, A. I. McKay, G. C. Lloyd-Jones and A. S. Weller, *ACS Catalysis*, 2019, **9**, 3657-3666.

13. A. L. Colebatch, B. W. Hawkey-Gilder, G. R. Whittell, N. L. Oldroyd, I. Manners and A. S. Weller, *Chem. Eur. J.*, 2018, **24**, 5450-5455; H. C. Johnson, E. M. Leitao, G. R. Whittell, I. Manners, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.*, 2014, **136**, 9078-9093.

14. M. Roselló-Merino, J. López-Serrano and S. Conejero, *J. Am. Chem. Soc.*, 2013, **135**, 10910-10913.

15. E. A. K. Spearing-Ewyn, N. A. Beattie, A. L. Colebatch, A. J. Martinez-Martinez, A. Docker, T. M. Boyd, G. Baillie, R. Reed, S. A. Macgregor and A. S. Weller, *Dalton Trans.*, 2019, **48**, 14724-14736.

16. A. Glüer, M. Förster, V. R. Celinski, J. Schmedt auf der Günne, M. C. Holthausen and S. Schneider, *ACS Catalysis*, 2015, **5**, 7214-7217.

17. F. Anke, D. Han, M. Klahn, A. Spannenberg and T. Beweries, *Dalton Trans.*, 2017, **46**, 6843-6847.

18. S. S. Rozenel, R. Padilla and J. Arnold, *Inorg. Chem.*, 2013, **52**, 11544-11550.

19. T. M. Maier, S. Sandl, I. G. Shenderovich, A. Jacobi von Wangelin, J. J. Weigand and R. Wolf, *Chem. Eur. J.*, 2019, **25**, 238-245; S. Todisco, L. Luconi, G. Giambastiani, A. Rossin, M. Peruzzini, I. E. Golub, O. A. Filippov, N. V. Belkova and E. S. Shubina, *Inorg. Chem.*, 2017, **56**, 4296-4307; J. K. Pagano, J. P. W. Stelmach and R. Waterman, *Dalton Trans.*, 2015, **44**, 12074-12077; T.-P. Lin and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 15310-15313; A. St. John, K. I. Goldberg and D. M. Heinekey, *Top. Organomet. Chem.*, 2013, **40**, 271-287.

20. G. Zhang, Z. Yin and S. Zheng, *Org. Lett.*, 2016, **18**, 300-303.

21. Although the gross temporal profile was repeatable, variations between independent catalytic runs meant that a kinetic analysis was not appropriate.

22. E. Y. X. Chen, *Chem. Rev.*, 2009, **109**, 5157-5214.

23. G. M. Adams, A. L. Colebatch, J. T. Skornia, A. I. McKay, H. C. Johnson, G. C. Lloyd−Jones, S. A. Macgregor, N. A. Beattie and A. S. Weller, *J. Am. Chem. Soc.*, 2018, **140**, 1481-1495.

24. At this scale and concentration the reaction mixture becomes viscous during catalysis, meaning the mass transport effects may influence the final polymer characteristics

25. K. Junge, B. Wendt, A. Cingolani, A. Spannenberg, Z. Wei, H. Jiao and M. Beller, *Chem. Eur. J.*, 2018, **24**, 1046-1052.

26. S. P. Semproni, C. C. Hojilla Atienza and P. J. Chirik, *Chem. Sci.*, 2014, **5**, 1956-1960.

27. S. S. Rozenel, R. Padilla, C. Camp and J. Arnold, *Chem. Commun.*, 2014, **50**, 2612-2614.

28. P. Büschelberger, E. Reyes-Rodriguez, C. Schöttle, J. Treptow, C. Feldmann, A. Jacobi von Wangelin and R. Wolf, *Cat. Sci. Tech.*, 2018, **8**, 2648-2653.

29. H. Dai and H. Guan, *ACS Catalysis*, 2018, **8**, 9125-9130.

30. S. Bhunya, T. Malakar and A. Paul, *Chem. Commun.*, 2014, **50**, 5919-5922.

31. R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott and N. C. Smythe, *J. Am. Chem. Soc.*, 2012, **134**, 5598-5609.

32. A. Mukherjee and D. Milstein, *ACS Catalysis*, 2018, **8**, 11435-11469; K. Junge, V. Papa and M. Beller, *Chem. Eur. J.*, 2019, **25**, 122-143; X. Liu, W. Zhang, Y. Wang, Z.-X. Zhang, L. Jiao and Q. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 6873-6882.