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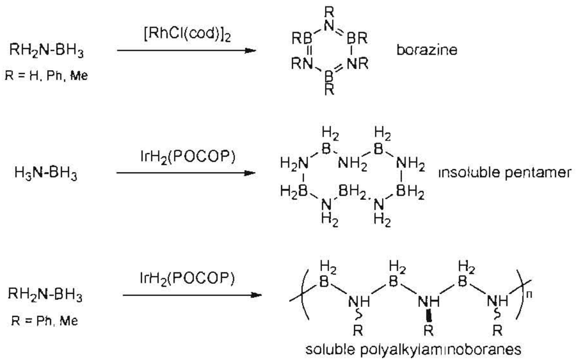
Soluble B-N Polymers: Poly(α-olefin) Analogs via Metal Complex-Catalyzed Amine Borane Dehydrogenation**

*Vincent Pons and R. Tom Baker**

Dedicated to the memory of Clinton F. Lane, great friend of boron chemistry

Over the last few decades, catalytic dehydrocoupling has evolved from a mechanistically interesting chemical transformation[1,2] to a practical route to inorganic polymers that have shown utility as new materials and processable ceramic precursors.[3] In attempting to make new B-P and B-N inorganic polymers, Manners *et al.* studied the heteronuclear dehydrocoupling of phosphine boranes and amine boranes.[1] While the former gave high polymers such as $(PhHP\text{-}BH_2)_n$,[4] evaluation of a variety of catalysts with primary and secondary amine boranes or even ammonia borane lead only to B-N cyclic oligomers.[5] However, using an iridium phosphinito pincer complex originally employed by Goldberg and Heinekey[6] for dehydrogenation of ammonia borane (AB, $H_3N\text{-}BH_3$), Manners now reports formation of soluble aminoborane polymers and copolymers derived from primary amine boranes (Scheme 1).[7] With this report, an analogy is made between primary amine boranes and α-olefins. The prospects of tuning metal complex catalysts for control of B-N polymer microstructure are exciting for synthesis of new B-N materials. In addition, variation of the N substituent offers promise for processable precursors to carbon-free B-N ceramics.



Scheme 1. Diverse products derived from metal catalyzed amine borane dehydrogenation (POCOP = 2,6-$(^tBu_2POCH_2)C_6H_3$, cod = 1,5-cyclooctadiene).

The chemistry of amine boranes which began in earnest in the mid twentieth century[8] continues to attract chemists and materials scientists. Organic chemists have exploited the reducing and hydroborating properties of amine boranes as convenient alternatives to air- and moisture-sensitive borane-THF adduct or borohydride salts. Although amine boranes are usually less reactive, mild reaction conditions are permitted by use of metal amidoboranes[9] or transition metal catalysts[10] for reactions such as the reduction of olefins, amides or epoxides. For example, while hydroboration of alkenes using $^tBuH_2N\text{-}BH_3$ proceeds only at higher temperature, Couturier and coworkers demonstrated transfer hydrogenation at 25 °C using 10 mol% Pd/C.[11] More recently, Jiang and Berke proposed a mechanism for the dehydrocoupling of dimethylamineborane (DMAB, $Me_2HN\text{-}BH_3$) and subsequent olefin transfer hydrogenation by homogeneous rhenium catalysts.[12]

In materials science applications, Stucky showed that changing the amine group of the amine borane, could be used to control both nucleation and growth rate of dodecanethiol-capped gold nanoparticles.[13] This work takes advantage of a tunable borane reducing agent for nanoparticle growth control that will certainly generate further investigation.

In pursuit of processable B-N ceramic precursors, Blum and Laine described the first example of transition metal catalyzed dehydrogenation of amine boranes.[14] Heating a benzene solution of $Me_3N\text{-}BH_3$ and methylamine (1:1.1) at 60 °C for 85 hours, for example, with 0.07 mol% $Ru_3(CO)_{12}$ afforded hydrogen, several volatile products including trimethylborazine and non-volatile B-N-linked borazines (polyborazylene), a colorless solid that gave a ceramic yield of 60% upon heating to 850 °C under nitrogen. Later work by Sneddon,[15] Paine[3] and others used clever combinations of inorganic and polymer chemistry to develop processable precursors that address application needs for fibers, coatings, and porous-body boron nitride forms.

With the recent interest in high capacity hydrogen storage, attention to amine borane dehydrogenation has increased greatly.[16] Although promising hydrogen release results have been obtained for ammonia borane in the solid state[17] and in ionic liquids,[18] metal-catalyzed dehydrogenation of amine-boranes offers the potential for additional control over both extent and rate of hydrogen production. As an example, while thermal dehydrogenation of DMAB requires heating at 150 °C, this is one of the better substrates for metal-catalyzed dehydrogenation as evidenced by reports of effective catalysts ranging from titanocene to CuCl(IMes) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene).[19]

In the first detailed studies, precious metal catalyst precursors such as $[RhCl(cod)]_2$ were effective for dehydrogenation of both primary and secondary amine boranes, although less so for ammonia-borane.[5] Typical products were cyclic amino- and iminoborane oligomers. In a subsequent report Goldberg, Heinekey and coworkers[6] reported that dehydrogenation of AB in THF by

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IrH_2(POCOP) yields fast release of a single equivalent of hydrogen and an insoluble colorless solid identified as $(H_2N\text{-}BH_2)_5$ [POCOP = 2,6-($^tBu_2POCH_2$)C_6H_3].[20] Later studies demonstrated similar rates for methylamine borane ($MeH_2N\text{-}BH_3$, MeAB) but DMAB reacted only at higher temperature.[21] While the latter afforded the expected cyclic aminoborane dimer, MeAB dehydrogenation in dilute THF solutions was unique in yielding soluble aminoborane products even when combined with an equivalent amount of AB.

Thermolysis of MeAB has been shown to proceed via ionic intermediate, $[BH_2(NH_2Me)_2][BH_4]$. [22] Subsequent addition of MeAB affords acyclic aminoborane chains that then undergo dehydro-cyclisation to mixtures of soluble amino- and iminoborane cyclic oligomers. In contrast, Brown and Heseltine reported a highly insoluble methylaminoborane polymer, $(HMeN\text{-}BH_2)_n$, obtained by transamination of dimethylaminoborane, $Me_2N\text{-}BH_2$, with methylamine in the vapour phase.[23] In the latest advance, Manners *et al.* employed the IrH_2(POCOP) catalyst with a suspension of MeAB in THF to afford *soluble* high polymers.

The simplicity of the NMR spectra (^{13}C, ^{11}B and ^1H) of Manners' $(MeHN\text{-}BH_2)_n$ polymers suggests a high degree of linearity and gel permeation chromatography results show M_w = 160,000 with a fairly high polydispersity index (PDI = 2.9). Analogous reactions using neat liquid *n*-$BuH_2N\text{-}BH_3$ gave very soluble polymers with M_w = 400,000 (PDI = 1.6). Copolymers prepared from MeAB and *n*-$BuH_2N\text{-}BH_3$ showed decreasing molecular weight and increasing PDI with greater incorporation of MeAB. This trend was even more noticeable for MeAB/AB copolymers for which the 1:1 mixture affords M_w = 47,000 with a PDI of 3.9. The insolubility of the material derived from AB itself does not allow for distinction between an analogous polymeric structure and cyclic oligomers; further characterization of this microcrystalline solid is needed.[17d,24]

The mechanism of metal complex-catalyzed dehydrocoupling has been studied in some detail for homocouplings such as Si-Si.[2] Dehydrocoupling of polar amine boranes, on the other hand, involves reactions of protic NH bonds and hydridic BH bonds. Although a number of different mechanisms have been proposed, the unique role of the iridium hydride in IrH_2(POCOP) in deprotonating the N-H bond as the first step in AB activation was described in computational work by Paul and Musgrave. [25] Moreover, the importance of aminoborane, $H_2N\text{-}BH_2$, binding to the metal center in determining product selectivity has recently been identified. [26] However, since chain propagation is necessarily accompanied by additional hydrogen loss and formation of heteronuclear B-N bonds, much more work needs to be done to further understand mechanistic details of cyclic oligomer vs. polymer formation.

This exciting exploitation of metal catalyzed dehydrocoupling for the synthesis of a new family of B-N α-olefin analogues presents new opportunities for both fundamental mechanistic understanding and applications in materials science.

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