Soluble B–N Polymers

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Soluble Boron–Nitrogen High Polymers from Metal-Complex-Catalyzed Amine Borane Dehydrogenation**

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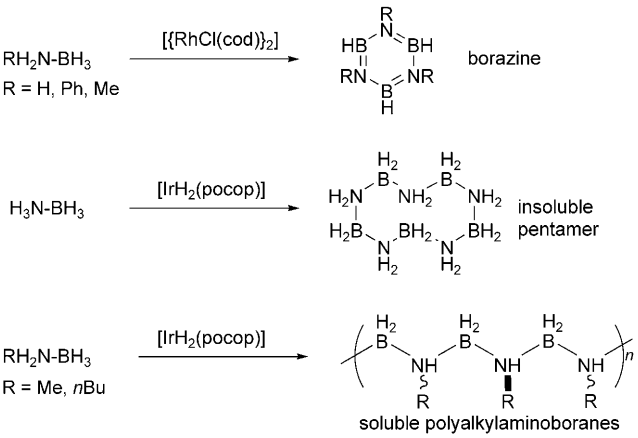
In memory of Clinton F. Lane

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 boron–phosphorous and boron–nitrogen inorganic polymers, Manners and co-workers studied the heteronuclear dehydrocoupling of phosphine boranes and amine boranes. While the former gave high-molecular-weight polymers such as $(PhHP–BH_2)_n$,[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, Heinekey, and co-workers[6] for dehydrogenation of ammonia borane (AB, $H_3N–BH_3$), Manners and co-workers now report formation of soluble aminoborane polymers and copolymers derived from primary amine boranes (Scheme 1).[7] With this report, an analogy is made between primary aminoboranes, $RHNBH_2$, and α-olefins. The high selectivity obtained by the authors contrasts with that found in previous reports on thermal and metal-catalyzed amine borane dehydrogenation.[8] The prospects of tuning metal complex catalysts for control of B–N polymer microstructure are exciting for synthesis of new B–N materials. Moreover, variation of the substituents at the nitrogen atom of the primary amine borane offers promise for processable precursors to carbon-free B–N ceramics.

The chemistry of amine boranes, which began in earnest in the mid twentieth century,[9] continues to attract chemists and materials scientists. Organic chemists have exploited the reducing and hydroborating properties of amine boranes as convenient alternatives to the air- and moisture-sensitive borane–THF adduct and borohydride salts. Although amine boranes are usually less reactive, mild reaction conditions are permitted by use of metal amidoboranes[10] or transition-metal catalysts[11] for reactions such as the reduction of olefins, amides, or epoxides. For example, while hydroboration of alkenes using $tBuH_2N–BH_3$ proceeds only at higher temperature, Couturier and co-workers demonstrated transfer hydrogenation at 25 °C using 10 mol % Pd/C.[12] More recently, Jiang and Berke proposed a mechanism for the dehydrocoupling of dimethylamine borane (DMAB, $Me_2HN–BH_3$) and subsequent olefin transfer hydrogenation by homogeneous rhenium catalysts.[13]



Scheme 1. Diverse products derived from metal-catalyzed amine borane dehydrogenation. cod = 1,5-cyclooctadiene, pocop = κ^3-1,3-$(OPt\text{-}Bu_2)_2C_6H_3$.

In materials science applications, Stucky and co-workers 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.[14] This work takes advantage of a tunable borane reducing agent for nanoparticle growth control that will certainly see more application.

Initial studies of AB thermolysis detailed the preparation of $(H_2N–BH_2)_n$ for which a linear structure was first proposed primarily on the basis of X-ray powder diffraction data.[15] While early reports of insoluble aminoborane polymers date from 1938,[16] later application of a battery of modern techniques (X-ray diffraction, IR, XPS, and MAS NMR spectroscopy as well as mass spectrometry) has not yet been able to distinguish between linear and large cyclic oligomers.[17,18]

In pursuit of processable B–N ceramic precursors, Blum et al. described the first example of transition-metal-catalyzed dehydrogenation of amine boranes.[19] Heating a benzene

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solution of $Me_3N{-}BH_3$ and methylamine (1:1.1) at 60 °C for 85 h, for example, with 0.07 mol % $[Ru_3(CO)_{12}]$ afforded hydrogen, several volatile products (including trimethylborazine), and nonvolatile 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,[20] 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.[8] Although promising hydrogen release results have been obtained for ammonia borane in the solid state[21] and in ionic liquids,[22] 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, it 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).[5,23]

In the first detailed studies, precious-metal catalyst precursors such as $[\{RhCl(cod)\}_2]$ (cod = 1,5-cycloocatdiene) were effective for dehydrogenation of both primary and secondary amine boranes, although less so for ammonia borane.[5] Ammonia borane and primary amine boranes were converted to borazine as well as other side products (Scheme 1). In a subsequent report, Goldberg, Heinekey, and co-workers[6] reported that dehydrogenation of AB in THF by $[IrH_2(pocop)]$ yields fast release of a single equivalent of hydrogen and an insoluble colorless solid identified as $(H_2N{-}BH_2)_5$.[18] Later studies demonstrated similar rates for methylamine borane ($MeH_2N{-}BH_3$, MeAB), but DMAB reacted only at higher temperature.[24] While DMAB 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 the ionic intermediate $[BH_2(NH_2Me)_2](BH_4)$[25] that initiates formation of acyclic methylaminoborane chains. These chains then undergo dehydrocyclization to mixtures of soluble amino- and iminoborane cyclic oligomers. In contrast, Brown and Heseltine reported a highly insoluble methylaminoborane polymer, $(HMeN{-}BH_2)_n$, obtained by transamination of dimethylaminoborane, $Me_2N{-}BH_2$, with methylamine in the vapor phase.[26] In the latest advance, Manners and co-workers employed the $[IrH_2(pocop)]$ catalyst with a suspension of MeAB in THF to afford soluble high polymers in good yields.[7]

The simplicity of the NMR spectra (^{13}C, ^{11}B and ^{1}H; THF) of Manners' $(MeHN{-}BH_2)_n$ polymers suggests a high degree of linearity, and gel permeation chromatography results show molecular weights (M_w) of 160000 with a fairly high polydispersity index (PDI = 2.9). Analogous reactions using neat liquid nBuH$_2$N–BH$_3$ gave very soluble polymers with $M_w = 400000$ (PDI = 1.6). Copolymers prepared from MeAB and nBuH$_2$N–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 product with $M_w = 47000$ and 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.[17e,27]

The mechanism of metal-complex-catalyzed dehydrocoupling has been studied in some detail for homocoupling reactions, such as those between silicon atoms.[2] Dehydrocoupling of polar amine boranes, on the other hand, likely proceeds by a different mechanism as it involves reactions of protic N–H bonds and hydridic B–H 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.[28] Moreover, the importance of aminoborane ($H_2N{-}BH_2$) binding to the metal center in determining product selectivity has recently been identified.[29] 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 versus polymer formation.

In spite of the complex chemistry associated with dehydrogenation of amine boranes, the current work of the Manners group demonstrates the power of transition-metal catalysis in allowing the reaction to take "the high road". 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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