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Catching the First Oligomerization Event in the Catalytic Formation of Polyaminoboranes: $H_3B\cdot NMeHBH_2\cdot NMeH_2$ Bound to Iridium

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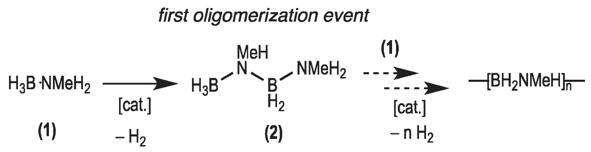
Supporting Information

ABSTRACT: We report the first insertion step at a metal center for the catalytic dehydropolymerization of $H_3B\cdot NMeH_2$ to form the simplest oligomeric species, $H_3B\cdot NMeHBH_2\cdot NMeH_2$, by the addition of 1 equiv of $H_3B\cdot NMeH_2$ to $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMeH_2)][BAr^F{}_4]$ to give $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMeHBH_2\cdot NMeH_2)][BAr^F{}_4]$. This reaction is also catalytic for the formation of the free linear diborazane, but this is best obtained by an alternative stoichiometric synthesis.

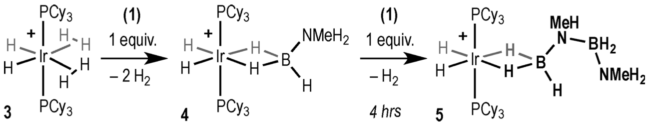
Polyaminoboranes, $[BH_2NHR]_n$, are boron–nitrogen analogues of polyolefins.[1] However, in comparison with the vast area that is encompassed by their ubiquitous carbon analogues,[2] their synthesis and properties have been little studied. Catalytic methods for the synthesis of high-molecular-weight examples of these potentially interesting materials based upon dehydropolymerization of primary amine borane substrates have recently been reported. For example, treatment of $H_3B\cdot NMeH_2$ (**1**) with an appropriate catalyst allows for the preparation of high-molecular-weight poly(methylaminoborane), $[BH_2NMeH]_n$ (Scheme 1).[3]

A variety of catalyst systems have been investigated for the dehydropolymerization of **1**,[3a,4] among the current best being those based upon $Ir(H)_2(POCOP)$ (POCOP = $[\kappa^3\text{-}1,3\text{-}(OP^tBu_2)_2\text{-}C_6H_3]$)[4c] and $[Rh(Ph_2P(CH_2)_xPPh_2)]^+$ ($x = 3-5$),[4b] which produce polyaminoboranes with high molecular weights and reasonable polydispersity indices. However, if fine control over both molecular weight and polymer architecture is to be achieved, knowledge of the mechanistic details of polymer growth is essential, as has been so successfully demonstrated in the synthesis of tailored polyolefins using transition-metal catalysts.[2] In contrast, the key steps in the polymerization of primary amine boranes (e.g., **1**) are yet to be fully resolved.[4c] These would likely be related to coordination/insertion events in olefin polymerization as catalyzed by a transition metal.[5] Herein we report the direct observation of this oligomerization event for **1** by the (catalytic) synthesis of the simplest coupled unit arising from the formal dehydrocoupling of **1** at a metal center to give $H_3B\cdot NMeHBH_2\cdot NMeH_2$ (**2**). The parent inorganic butane $H_3B\cdot NH_2BH_2\cdot NH_3$ has recently been prepared by a noncatalytic route involving the addition of NH_3 to $H_2B(\mu\text{-}H)NH_2BH_2$,[6] and we also report that an analogous procedure using $H_2B(\mu\text{-}H)NHMeBH_2$ produces **2** as a pure material.

Scheme 1. Dehydropolymerization of 1



Scheme 2. Synthesis of Complexes 4 and 5[a]



[a] Anions are not shown. Solvent = 1,2-$C_6H_4F_2$.

We recently reported the synthesis of $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMe_2H)][BAr^F{}_4]$ (**A**) [Ar^F = 3,5-$C_6H_3(CF_3)_2$] via addition of $H_3B\cdot NMe_2H$ to $[Ir(PCy_3)_2H_2(H_2)_2][BAr^F{}_4]$ (**3**) along with the observation that this complex slowly ($t_{1/2}$ = 24 h) undergoes dehydrogenation to form the aminoborane complex $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_2B{=}NMe_2)][BAr^F{}_4]$.[7] In the anticipation of similar reactivity for **1**, we prepared $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMeH_2)][BAr^F{}_4]$ (**4**) in an equivalent way (Scheme 2) in quantitative NMR yield. The solid-state structure of **4** (Figure 1) confirms an η^2 binding mode for the amine borane,[7,8] as do the solution NMR spectroscopic data (see the Supporting Information), which are similar to those for **A**. Surprisingly, pure **4** did not undergo dehydrogenation to give an aminoborane (i.e., $H_2B{=}NMeH$)-ligated complex, but instead remained unchanged after 48 h at 298 K; this is also in contrast to related rhodium[9] and neutral ruthenium[10] systems that promote the dehydrogenation of primary amine boranes $H_3B\cdot NRH_2$ (R = Me, ^tBu) to give the corresponding metal-bound aminoboranes.

Although dehydrogenation was not observed for pure **4**, addition of a further equivalent of **1** to a 1,2-$C_6H_4F_2$ solution of **4** resulted in a relatively fast (4 h) reaction to afford H_2 and a new complex identified as $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMeHBH_2\cdot NMeH_2)][BAr^F{}_4]$ (**5**). Crystalline material suitable for an X-ray diffraction experiment was obtained using the $[BAr^{Cl}{}_4]^-$ salt of

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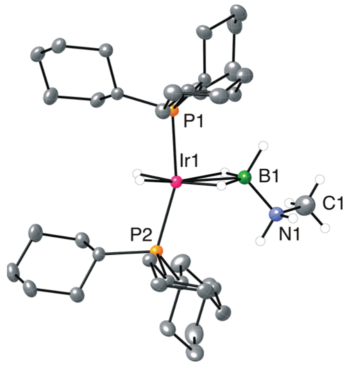


Figure 1. Structure of the cationic portion of **4**,[11] with thermal ellipsoids at the 30% probability level. The minor disordered component is not shown. Selected bond lengths (Å): Ir1−B1, 2.210(7); Ir1−P1, 2.3281(8); Ir1−P2, 2.3347(8); B1−N1, 1.580(8). Selected bond angles (deg): P1−Ir1−P2, 160.76(3); B1−N1−C1, 111.0(6).

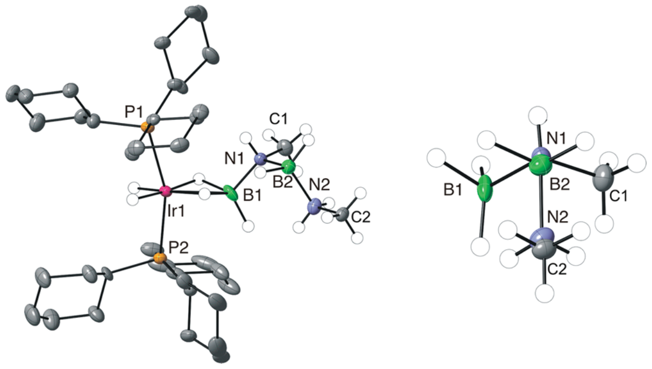
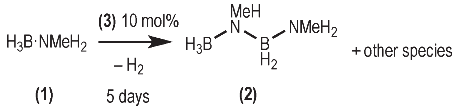


Figure 2. (left) Structure of the cationic portion of **5**,[11] with thermal ellipsoids at the 30% probability level. The $[BAr^{Cl}_4]^-$ anion has been omitted. Selected bond lengths (Å): Ir1−B1, 2.228(5); Ir1−P1, 2.3477(10); Ir1−P2, 2.3308(10); B1−N1, 1.576(5); N1−B2, 1.612(5); B2−N2, 1.607(6). Selected bond angles (deg): P1−Ir1−P2, 159.60(3); B1−N1−B2, 114.5(3); N1−B2−N2, 109.6(3). (right) Newman projection of bound **2**.

5 (Ar^{Cl} = 3,5-$C_6H_3Cl_2$).[11,12] The solid-state structure of the cation (Figure 2) shows **2** η^2-bound to the $\{Ir(PCy_3)_2(H)_2\}^+$ fragment. Although the preformed cyclic oligomer $[H_2BNMeH]_3$ has been shown to coordinate with Rh fragments,[13] as have the related species $H_3B\cdot NMe_2BH_2\cdot NMe_2H$[8b,13] and $[H_2BNMe_2]_2$,[8b,14] this is the first report of both the synthesis of **2** and its coordination to a metal center. The bond lengths and angles are unremarkable compared to those of related Ir(III) complexes (e.g., **4** and $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMe_3)][BAr^F_4]$[7]). Interestingly, bound **2** adopts a gauche conformation similar to that found for $H_3B\cdot NH_2BH_2\cdot NH_3$[6] but different from that expected for 2-methylpentane. Two quadrupolar-broadened integral 1 H Ir−H−B signals were observed in the ^1H NMR spectrum (500 MHz) at δ −6.15 and −6.32, thus showing that BH exchange at the Ir center does not occur, similar to **A**.[7] Three NH environments (δ 4.13, 4.02, 2.99) and a complex Ir−H signal (2 H) suggestive of inequivalent hydride environments were also observed. In the $^1H\{^{11}B\}$ NMR spectrum, as well as signals due to the BH_3 group, two environments were observed for the central BH_2 unit (δ 2.48, 2.37). The stereogenic nitrogen center, N1, thus confers C_1 symmetry to the molecule. A pair of tightly coupled AB doublets [J(PP) = 287 Hz] were observed in the $^{31}P\{^1H\}$ NMR spectrum. The ^{11}B NMR spectrum showed two broad signals at δ +17.1 and −5.8, the former shifted to high frequency relative to free **2** (see below), consistent with coordination to a metal center. Electrospray ionization mass spectrometry showed a clear parent ion for the cation (m/z 843.58 obsvd, 843.58 calcd) that also demonstrated the correct isotopic pattern. The free oligomer **2** can be released from the metal center by addition of excess MeCN to a C_6H_5F solution of **5** [$\delta(^{11}B)$: −5.3 (t, 108 Hz), −17.8 (q, 92 Hz)]. However, under these conditions, **2** is not stable and reacts to give further products, including $[H_2BNMeH]_3$. We speculate that the adduct complex $[Ir(PCy_3)_2H_2(NCMe)_2][BAr^F_4]$ promotes this reaction.[7]

Scheme 3. Catalytic Production of 2



Under 10 mol % (0.025 M) loading at 298 K, **3** or **4** slowly promoted catalytic dehydrogenation of **1** to give free **2** (Scheme 3). However, this reaction was not clean, and other species were observed (~10% concentration relative to **2** over the course of catalysis), with $H_2B(\mu\text{-}H)NHMeBH_2$ as the principal component (~5%) alongside smaller amounts of $[H_2BNMeH]_3$ and $[HBNMe]_3$. During catalysis the resting state (^{31}P NMR) is **5**, alongside a minor unidentified species. **5** is also a competent precatalyst for the formation of **2** from **1** (10 mol %), while in the absence of catalyst no reaction was observed. We did not observe a growing oligomeric chain on the metal upon addition of excess **1** to **5**, although $[HBNMe]_3$ formed upon heating (40 °C, 3 days). It thus appears that **3** is selective for the single oligomerization event of **1**, in contrast to other catalyst systems that promote rapid dehydropolymerization,[3a,4a−4c] although interestingly these systems also yield $[HBNMe]_3$ as the final thermodynamic product.

Since the catalytic production of **2** produced compositionally impure material, **2** was independently prepared via modification of the method recently reported by Shore and Zhao for the preparation of the linear diborazane $H_3B\cdot NH_2BH_2\cdot NH_3$.[6] A solution of $H_3B\cdot THF$ and $H_3B\cdot NH_2Me$ heated to 60 °C over 70 h produced $H_2B(\mu\text{-}H)NHMeBH_2$. Subsequent ring opening by addition of a methylamine solution at −78 °C furnished **2**, which was isolated in 72% yield as a white solid upon removal of the solvent. Recrystallization from CH_2Cl_2/hexane at −40 °C produced X-ray-quality crystals, and **2** was shown to crystallize with a single molecule in the asymmetric unit. Interestingly, **2** crystallizes in the antiperiplanar conformation (see Figure 3), in contrast to the gauche arrangement observed upon metal coordination in **5** (viz. dihedral B1−N1−B2−N2: 59.9° in **5**, 179.9° in **2**). In comparison with **5**, the B−N distances are all slightly shorter in free **2**, with the greatest difference found for B1−N1, as might be expected. Multinuclear NMR characterization in solution was consistent with the structure revealed by X-ray analysis and the observations made for **5** (and liberated **2**). Three signals attributed to B−H groups in a 1:1:3 ratio (δ 2.05, 1.76, 1.31, respectively) were observed in the $^1H\{^{11}B\}$ spectrum (CD_2Cl_2), with the BH_3 signals shifting considerably to lower frequency upon coordination to the metal in **5**, as expected. The ^{11}B NMR

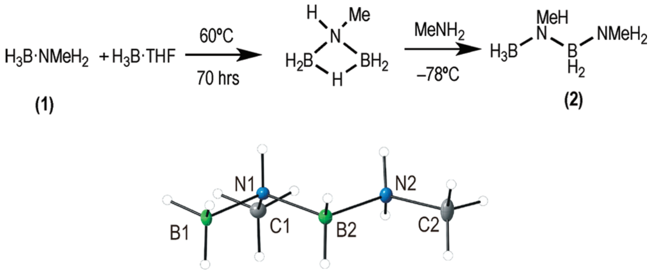
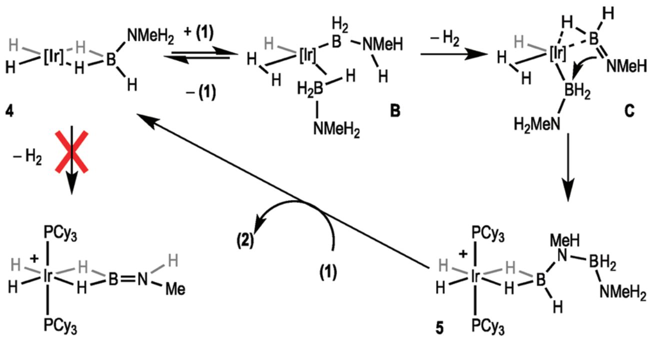


Figure 3. Solid-state structure of isolated **2**, with thermal ellipsoids at the 30% probability level.[11] Selected bond lengths (Å): N1–B1, 1.4887(19); N1–B2, 1.5730(19); N1–C1, 1.5906(19); N2–C2, 1.4822(19); N2–B2, 1.5864(19). Selected bond angles (deg): B1–N1–B2, 108.73(11); B1–N1–C1, 110.89(11); B2–N1–C1, 115.71(11); C2–N2–B2, 112.62(11); N1–B2–N2, 109.14(10).

Scheme 4. Suggested Mechanism for the Formation of 5[a]



[a] [Ir] = $[Ir(PCy_3)_2]^+$.

spectrum of **2** matched that liberated from **5**.[15] Addition of preformed **2** (see below) to **3** generated **5** cleanly.

Limited insight into the mechanism of oligomerization can be gleaned from labeling and crossover experiments. Addition of D_2 to **4** resulted in H/D exchange at boron and iridium only (with the concomitant observation of H_2 and HD), while addition of 1 equiv of $H_3B\cdot NMeD_2$ to **3** resulted in the formation of $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMeD_2)][BAr^F{}_4]$ (**4-*N*-D$_2$**), which showed no evidence for incorporation of D into the Ir hydrides over 4 h. This suggests that B–H activation in **4** is a low-energy process relative to N–H activation, consistent with calculations on related $H_3B\cdot NMe_2H$ systems.[7,8b] Spin-saturation-transfer experiments on **4** that showed chemical exchange between Ir–*H* and Ir–*H*–B only, consistent with this. These observations, alongside the requirement of an excess of **1** to promote oligomerization and the lack of dehydrogenation of **4** to form an aminoborane species, point to the tentative mechanism suggested in Scheme 4. B–H activation[7] in **4** and σ coordination of additional **1** gives intermediate **B**, which then loses H_2, possibly promoted by BH$(\delta-)\cdots(+\delta)$HN dihydrogen interactions,[8a,16] to form the aminoborane/base-stabilized boryl[17] complex **C**.[18] B–N coupling followed by B–H bond formation leads to complex **5**. The coupling of two $H_3B\cdot NMe_2H$ ligands at a $TiCp_2$ center to form the corresponding linear diborazane was recently proposed on the basis of kinetic studies,[19] while for the $Ir(H)_2(POCOP)$ system, polymer-growth kinetics suggested a chain-growth mechanism invoking both metal-mediated dehydrogenation of **1** (to form an aminoborane) and B–N coupling.[4c] Similar conclusions were drawn from the study of the dehydrocoupling of $H_3B\cdot NMe_2H$ to form dimeric aminoboranes, which suggested that the metal is involved in both dehydrogenation and oligomerization steps,[7,20] with the corresponding linear diborazane $H_3B\cdot NMe_2BH_2\cdot NMe_2H$ (or a close relative[21]) observed as an intermediate during dehydrocoupling.[8b,19,20,22] Addition of $H_3B\cdot NMe_3$ (which contains no NH functional group) to **4** did not give a mixed linear diborazane but instead afforded $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_3B\cdot NMe_3)][BAr^F{}_4]$[7] and $[HBNMe]_3$ after 24 h. We suggest that this might occur because the bulky $H_3B\cdot NMe_3$ hinders the B–N coupling step in the relatively crowded $\{Ir(PCy_3)_2(H)_2\}^+$ fragment in **C**; instead, aminoborane is liberated and trimerizes[7,22] to give $[H_2BNMeH]_3$, which then undergoes dehydrogenation to afford $[HBNMe]_3$.[13,22] Support for this scenario comes from the addition of one equivalent of $[H_2BNMeH]_3$[13] to **3**, which rapidly (<1 h) gave $[HBNMe]_3$ and **3**. Addition of **1** to **4-*N*-D$_2$** resulted in the eventual formation of **5** with deuterium incorporated at both N positions of bound **2**, presumably as a result of initial exchange of amine boranes bound to the metal center. H_2, HD, and D_2 were also observed. However, as D was also incorporated into the hydrides (possibly via exchange of bound H_2 with D_2/HD) as well as into the PCy_3 ligands, we cannot rule out alternative mechanisms for the oligomerization step, potentially involving intermolecular N–H proton transfer from **1** to the metal[21] or the involvement of cyclometalated phosphines.

The outlined mechanism also accounts for the lack of further oligomerization events, as the terminal N–H group in **5** is distant from the metal center and thus less likely to participate in H_2 elimination. This leads us to suggest that the isolation of **5** is a rather specific case and might not be directly applicable to the mechanism of formation of polyaminoboranes at other metal centers,[4a–c] although is it likely that some mechanistic steps are common. Importantly, it is this selectivity for the synthesis of **2**, the product of the first oligomerization event in the formation of polyaminoboranes, that no doubt allows for its isolation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full experimental data for the syntheses; crystallographic data for **2**, **4**, and **5**, including atomic positional and thermal parameters (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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