Aust. J. Chem. http://dx.doi.org/10.1071/CH13198

Communication

B-Methyl Amine Borane Derivatives: Synthesis, Characterization, and Hydrogen Release

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We describe the synthesis of MeH₂N–BH₂Me (**3**) and H₃N–BH₂Me (**4**) as potential hydrogen storage materials with 6.8 wt-% and 8.9 wt-% capacity, respectively. Compounds **3** and **4** readily release 2 equivalents of H₂ at 80°C in the presence of a CoCl₂ catalyst to furnish the corresponding trimerized borazine derivatives. Regeneration of **3** from its spent fuel material can be accomplished using a simple two-step process: activation with formic acid followed by reduction with LiAlH₄.

Manuscript received: 23 April 2013. Manuscript accepted: 26 May 2013. Published online: 24 June 2013.

Boron-nitrogen containing chemical hydride compounds have recently received considerable attention as possible hydrogen storage materials due to their high gravimetric density and favourable kinetics of hydrogen release.^[1] Ammonia borane (AB, H₃N–BH₃, 19.6 wt-% H₂) and *N*-substituted derivatives of AB have been the focus of numerous literature reports detailing hydrogen release conditions^[2] and regeneration^[3] of spent-fuel material. Additionally, solution-phase mechanistic studies have been published,^[4] for both thermal^[5] and catalytic^[6] dehydrogenation of amine-boranes, providing insights that have led to catalyst and product optimization in subsequent work.

Research in our group centres on developing the fundamental chemistry and applications of boron-nitrogen heterocycles.^[7,8] We recently reported the synthesis of 1,2-BN-cyclohexane 1,^[9] a cyclic amine-borane, and noted that it cleanly releases hydrogen to form a trimer **1T** when thermally activated (Scheme 1). Invigorated by this discovery, we developed the BN-methylcyclopentane material **2**,^[10] which is liquid at room temperature. Compound **2** also cleanly releases hydrogen (two equiv. H₂ per molecule of **2**) both thermally and catalytically using cheap, first-row transition metal halide catalysts such as CoCl₂, NiCl₂, and FeCl₂ at moderate temperature (50–80°C). Under both thermal and catalytic conditions the exclusive product is trimer **2T**.

Compounds 1 and 2 can be considered cyclic substituted derivatives of AB, analogous to the widely studied *N*-alkyl AB derivatives,^[11] but with additional substitution at the boron position. While surveying the literature in the course of developing materials 1 and 2, we were surprised to discover that, in contrast to the multitude of studies detailing the synthesis and properties of AB and *N*-alkyl AB derivatives, reports of linear, *B*-alkyl-substituted AB derivatives, such as compounds 3 and 4 (Scheme 2), are scarce.^[12] In fact, to the best of our knowledge there are no published synthetic routes to the *B*-Me AB derivatives 3 and 4. Spurred on by this gap in the literature, we describe here the synthesis and characterization of these novel AB

derivatives. We also present a preliminary investigation into their hydrogen release properties using catalytic $CoCl_2$, which promotes the rapid release of two equivalents of H_2 from both compounds.

Scheme 2 illustrates our synthetic route to *B*-Me AB derivatives 3 and 4. Salt metathesis of NaBH₄ and NH₄Cl has been used to synthesize ammonia borane in very high yield.^[13] Using an analogous synthetic strategy, we were pleased to find that treating Li[MeBH₃]^[14] with the appropriate commercially available amine-hydrochloride salt led to the loss of one equivalent of H₂ and generated compounds 3 and 4 in 88 % and 75 % isolated yield, respectively.

The melting point of compound **3** is 47°C and it can undergo repeated melt and freeze cycles without apparent decomposition. Compound **3** is stable in THF solution for >48 h at 55°C before minor degradation is apparent by ¹¹B NMR. The melting point of compound **4** is 58°C, at which point the material begins to decompose, releasing H₂. Compound **4** is likewise unstable in THF solution at 55°C; the starting material is consumed within 18 h.



Scheme 1. Hydrogen storage by boron-nitrogen heterocycles.



Scheme 2. Synthesis of novel B-substituted AB derivatives 3 and 4.



Fig. 1. Auotmated burette measurement of dehydrogenation of compounds 2, 3, and 4 (conditions: CoCl₂ 5 mol-%, diglyme, 80°C).

We performed our dehydrogenation experiments using an automated gas burette apparatus,^[15] which enabled us to determine both the rate and amount of hydrogen released. We chose to use CoCl₂ as the catalyst for our studies, as it was found in our previous work^[10a] to be the most active catalyst screened for the dehydrogenation of compound 2. The results of our burette experiment are depicted in Fig. 1. Under identical dehydrogenation conditions previously established for compound 2 (5 mol-% catalyst loading, 80°C, diglyme solvent), the B-methyl substituted linear AB derivatives 3 and 4 displayed a rapid rate of hydrogen release that is similar to the release of the equivalent amount of H_2 from 2. Interestingly, under these conditions, hydrogen release from AB is relatively slow. Less than 0.75 equivalents of H₂ from AB is released in 45 min (see Supplementary Material). These results indicate that the novel B-substituted AB derivatives 3 and 4 could potentially be useful as hydrogen storage materials, with gravimetric capacities of 6.8 wt-% and 8.9 wt-% hydrogen, respectively.

We noticed bubbling immediately upon addition of $CoCl_2$ to THF solutions of **3** and **4**, at room temperature, before we could begin data collection (reaction mixtures were prepared in a glovebox). We attribute the release of less than 2 equivalents H_2 from compounds **3** and **4** to the loss of hydrogen before we could begin our burette experiment. We have tested this theory in a qualitative way and found that we can account for the full 2 equivalents of H_2 when we keep the catalyst and the substrate separated until data collection has been initiated (see Supplementary Material for details). We also noticed a temperature dependence of the rate of hydrogen release. At 60°C the release of two equivalents of H_2 from compound **4** took >40 min (see Supplementary Material for details).

Facile recharging of spent material with hydrogen equivalents is critical for the widespread adoption of any chemical platform for hydrogen storage. In the case of ammonia borane, researchers have recently developed methods for the regeneration of a model AB spent fuel material, polyborazylene (PB), using digestion strategies based on benzenedithiol/Sn-H or hydrazine/NH₃.^[3] However, PB is only one of several potential products that can result from AB dehydrogenation. In contrast, the cyclic AB derivatives 1 and 2 each cleanly form one trimeric product upon hydrogen release (1T and 2T, Scheme 1).^[9,10a] We found that under both thermal and catalytic conditions, 3 and 4 initially form a mixture of dehydrogenated compounds (based on the observation of multiple peaks in the ¹¹B NMR spectrum, which were not isolated or characterized). Extended heating of the mixture (36 h) causes the intermediate species to converge to a single product, which we have identified as the trimeric species hexamethylborazine 5 in the case of 3, and 2,4,6-trimethylborazine 6 in the case of 4, on the basis of their 11 B NMR chemical shifts (Scheme 3). After catalytic dehydrogenation of 3 in refluxing THF using our standard catalyst and loading (5 mol-% CoCl₂), we were able to isolate 5 in 71 % yield using column chromatography.

Scheme 4 shows the regeneration of the fully charged compound **3** from the spent material **5**. Activation of **5** with 3 equivalents formic acid generates the BN-cyclohexane analogue **7**. We isolated a crystal of **7** suitable for single crystal X-ray diffraction, which unambiguously confirms our structural assignment. Interestingly, additional equivalents of formic acid do not add to boron or break the central BN ring, even in 10-fold excess. However, addition of LiAlH₄ to **7** does break apart the trimer and cleaves the B–O bonds to install the B(H)₂



Scheme 3. Observation/isolation of borazine products in the dehydrogenation of 3 and 4.



Scheme 4. Regeneration of spent fuel trimer 5 to fully charged compound 3.

moieties.^[16] Workup using wet THF as a proton source gives **3**, which was isolated in 46 % yield. While we acknowledge that the use of energetic reagents such as LiAlH₄ and the modest yield afforded by this proposed regeneration pathway are not ideal for use on a large scale, further optimization may enable us to take advantage of the well defined nature of the spent-fuel products to devise a lower energy, higher yielding regeneration protocol.

In summary, we synthesized two novel *B*-Me substituted AB derivatives **3** and **4**, and investigated their hydrogen release properties. We found that $CoCl_2$ catalyzed rapid release of two equivalents H_2 from each compound. We also demonstrated that the isolated product of the dehydrogenation of compound **3**, hexamethylborazine **5**, can be converted back to **3** in a two-step process, which makes possible a potential hydrogen storage fuel cycle based on this material.

Supplementary Material

Experimental procedures, compound characterization data for all new compounds, and the CIF file for structure 7 are available on the Journal's website.

Acknowledgements

We gratefully acknowledge the USA Department of Energy (DE-EE-0005658) for financial support. Funding for the University of Oregon Chemistry Research and Instrumentation Services was furnished in part by the NSF (CHE-0923589).

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