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Improved Synthesis of Bis(borano)hypophosphite Salts

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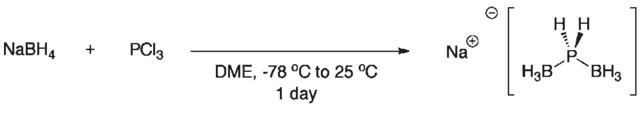
A synthesis of the bis(borano)hypophosphite anion with various counterions has been developed to make use of more benign and commercially available reagents. This method avoids the use of potentially dangerous reagents used by previous methods and gives the final products in good yield. Details of the crystal structure determination of the sodium salt in space group *Ama*2 are given using a novel computational technique combined with Rietveld refinement.

The bis(borano)hypophosphite ion $[PH_2(BH_3)_2]^-$, or [PB], was first synthesized by Gamble and Gilmont in 1940[1] but was not accurately characterized until 1967.[2] Since then, few studies have improved upon the synthesis or expanded the chemistry of this ion despite the fact that similar compounds have found wide applicability in energy storage,[3] reduction chemistry,[4] and transition-metal catalysis.[5]

Currently, borohydrides are receiving a large amount of interest for their high weight percentage of hydrogen.[3b,6] However, problems associated with slow kinetics and reversibility plague these complex anionic materials.[6c] It is thought that the strong B−H bonds formed in *closo*-boron-containing products prevent facile reversibility. Disruption of the lattice energy of boron-containing products through the introduction of more polarizable atoms with diffuse orbitals, such as phosphorus, may facilitate the reversibility of hydrogen release. Related to this idea is the work of Stephan and co-workers, which demonstrates the ability of phosphorus−boron compounds to reversibly activate dihydrogen via frustrated Lewis acid−base chemistry.[3c−f]

Scheme 1. Synthesis of Na[PB] (**1**)



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Phosphorus−boron compounds have also been the focus of transition-metal-mediated transformations. Livinghouse,[7] Imamoto,[8] Börner,[9] and Bergman[10] have used boron species to facilitate the synthesis of various chiral and achiral phosphorus-based ligands. Manners and co-workers are well-known for their investigations into inorganic heterocycles and polymers made from phosphorus and boron compounds.[5]

Simple [PB] salts containing mostly hydrogen, phosphorus, and boron have the potential to make an impact as precursors to more advanced inorganic materials in the aforementioned areas of research. Toward this goal, a more efficient and safer route to several salts of the [PB] anion has been developed.

Syntheses of the various salts of $[PH_2(BH_3)_2]^-$ are known;[1,2,11] however, most methods use phosphine, ammonia, and diborane, are performed at temperatures as low as −196 °C, and take upward of 7 days to complete. Even the most recently published method from Mayer and co-workers still necessitates the low-temperature synthesis and isolation of H_3P-BH_3.[12] To avoid these hazards, a new method was developed from commercially available starting materials (Scheme 1).

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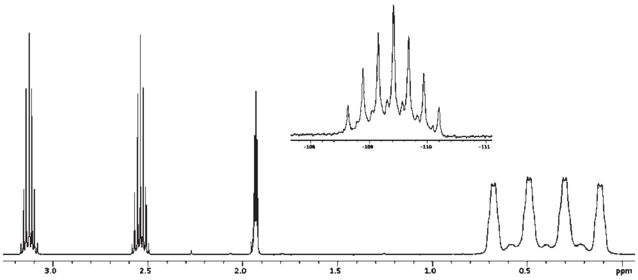

Figure 1. ^{1}H NMR of **1** in CD_3CN with the ^{31}P NMR spectrum in the inset.

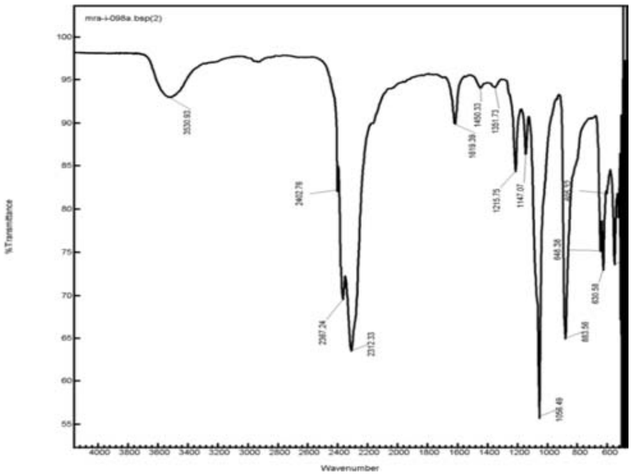

Figure 2. IR spectrum of **1**. The PH_2 and BH_3 symmetric stretching modes are at roughly 2350 cm^{-1}.

A solution of phosphorus trichloride in dimethyl ether (DME) was added to a rapidly stirring solution of sodium borohydride in DME at −78 °C to give the sodium bis(borano)hypophosphite salt (**1**) after the solution was allowed to warm to room temperature. When the reaction was monitored by both ^{1}H and ^{31}P NMR spectroscopy, it was evident that PH_3 was generated quickly from the reduction of PCl_3. Ultimately, PH_3 was consumed to form the hypophosphite moiety. The yield for this reaction ranged from 60 to 80%.

NMR spectra of **1** show signals consistent with the proposed structures and the reported literature data (Figure 1).[2,11−13] IR spectroscopy data show bands consistent with those previously reported and assigned for the [PB] anion (Figure 2). The powder X-ray diffraction (XRD) pattern of **1** reveals a new crystalline material (the Na[PB] diffraction pattern pictured in Figure 3).

When this method was applied to lithium, calcium, or potassium borohydride, a yellow insoluble, water-sensitive mass was isolated. No signals in the ^{1}H and ^{31}P NMR spectra of either the supernatant or the solid material were indicative of the [PB] anion. The same yellow mass was also isolated in the preparation of **1** when the solvent was changed from DME to tetrahydrofuran (THF). This curious solvent effect has not been investigated further, but it is possible that a difference in the solubility of the intermediates generated during the reduction of PCl_3 is responsible for the lack of product formation. Reactive intermediates that are poorly stabilized might form an amorphous boron- or phosphorus-containing polymeric material. This phenomenon would account for the insoluble yellow precipitate, but no tests have been done at this time to identify the decomposition products.

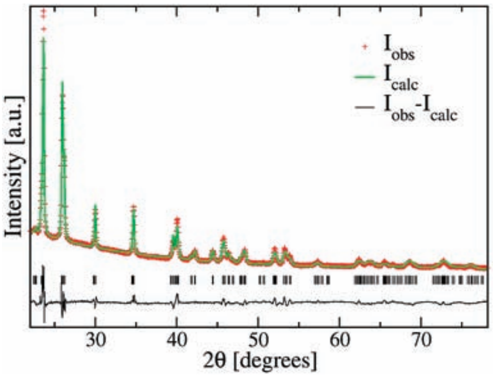

Figure 3. Rietveld-refined powder XRD pattern of **1** in space group *Ama*2. The difference curve (black trace) is below the observed data (red +) and spectra of the predicted structure (green trace).

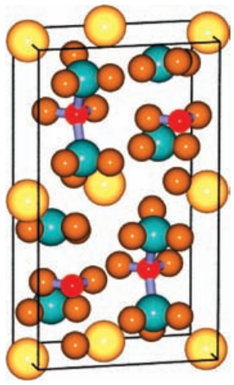

Figure 4. Predicted crystal structure of **1**, in space group *Ama*2. The [PB] anions are shown in red, green, and brown, corresponding to the P, B, and H atoms, respectively. The yellow atoms are Na.

The sodium salt crystallizes in the orthorhombic space group *Ama*2 with lattice parameters a = 13.77 Å, b = 7.91 Å, and c = 4.50 Å. The structure was predicted using the method of prototype electrostatic ground states, which combines a simplified electrostatic Hamiltonian and Monte Carlo simulated annealing to find prototype structures that are further refined using state-of-the-art first-principles techniques.[14] Briefly, the complex [PB] anion was modeled using rigid BH_3 and PH_2 moieties. Charges for boron- and phosphorus-bound H atoms were −0.25e and +0.25e, respectively, with a radius of R_H = 1.5 Å. The charge and radius of sodium were taken as +1e and 0.97 Å. Rotation and canting of the P−B bond was allowed for flexibility. The Rietveld-refined structure is shown in Figure 3 and indicates excellent agreement with the measured powder XRD patterns. Figure 4 shows the predicted unit cell in *Ama*2. Wyckoff positions of the atoms within the unit cell may be found in the Supporting Information.

Replacing THF with DME as the reaction solvent allows for isolation of the lithium bis(borano)hypophosphite salt (**2**) in good yield. The reaction is similar to the preparation of **1**, but once the crude Li[PB] is obtained, it is then extracted in air with Et_2O, which has not been dried or sparged with

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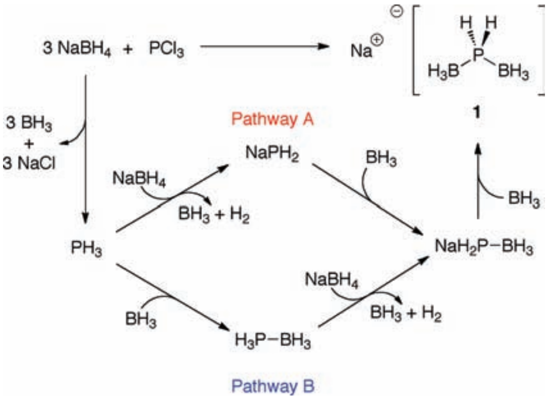

Figure 5. Proposed mechanism for Na[PB] formation.

nitrogen. The residual water present in Et_2O is necessary to hydrolyze excess $LiBH_4$, which is difficult to separate from Li[PB] because of similar solubility properties. Compound **2** is stable to this residual water, and hydrolyzed salts can be filtered away from the product. Li[PB] is obtained as a white solid from the filtrate after removal of the volatile materials.

The calcium bis(borano)hypophosphite salt (**3**) has been synthesized, but additional changes to the method had to be made in order to obtain product. THF replaced DME as in the method for **2**, but this change simply avoids the formation of the yellow insoluble precipitate and gives no product. By ^1H and ^{31}P NMR, it is evident that PCl_3 has been reduced to PH_3, but PH_3 has not reacted further to form the [PB] anion. Heating the reaction mixture to 70 °C for 12 h in a sealed vessel achieves some product formation, but the addition of excess BH_3 in a solution of THF was also necessary to increase the yield to 80%, as determined by ^1H NMR. Because of solubility issues, the salt has not been isolated free of $Ca(BH_4)_2$.

To understand the formation of the [PB] anion, a mechanism has been proposed that accounts for the experimental observations made when using various borohydrides. In all cases except potassium, it was found that PCl_3 is reduced to form PH_3 quantitatively within minutes. However, yields of [PB] vary depending on the borohydride salt, leading us to believe that further conversion of PH_3 must be based on the availability and reactivity of the borohydride in question. A potential mechanism shows phosphine reacting with excess borohydride to form a metal phosphide (Figure 5, pathway A). If the borohydride is poorly solubilized or not reactive with phosphine, product formation will be impacted. Therefore, when it was found that the calcium borohydride was not generating sufficient amounts of $Ca[PB]_2$ at room temperature, the reaction mixture was heated in a sealed vessel. These new conditions allowed the borohydride and phosphine to react, and the yield was improved.

On the basis of literature precedent,[15] another mechanism has been proposed to address the potential phosphine–borane adduct formation (Figure 5, pathway B). However, we believe pathway A is more likely due to the reported dissociation of this adduct at −30 °C.

A new method for the preparation of the [PB] anion has been devised. This method improves upon the previous literature procedures by using a one-step process with commercially available and relatively safe starting materials in place of a multistep procedure with gaseous or explosive reagents such as ammonia, phosphine, and diborane.

The [PB] anion is an interesting molecule with many current and potential applications. Its high hydrogen content, along with a relative tolerance to air and water, makes this compound well suited for future studies in hydrogen storage. Businesses and research groups in need of new inorganic polymers may also take advantage of this [PB] anion as a building block toward materials with interesting properties. The improved procedure detailed above should make for a safer and more convenient avenue to further investigation.

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Supporting Information Available: Details of the syntheses described above, X-ray crystallographic data, NMR, and elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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