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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### THE AGGREGATION OF LITHIUM IMIDO BORATES

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Online publication date: 12 August 2010

**To cite this Article** Slattery, John M. and Russell, Christopher A.(2004) 'THE AGGREGATION OF LITHIUM IMIDO BORATES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 179: 4, 931 — 932

**To link to this Article:** DOI: 10.1080/10426500490428924

**URL:** <http://dx.doi.org/10.1080/10426500490428924>

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## THE AGGREGATION OF LITHIUM IMIDO BORATES

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(Received August 17, 2003; accepted October 3, 2003)

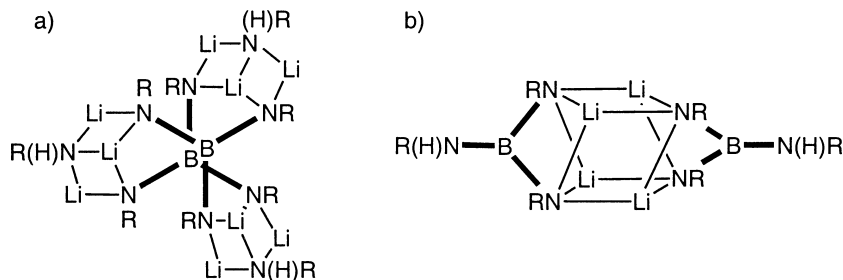
*Keywords:* Anions; boron; imido; lithium; solid-state structures

Recent studies concerning p-block imido anion chemistry have tended to focus on imido compounds where the central atom is from groups 15 or 16. The imido anions of group 13 are less well investigated. Imido anions of boron have been synthesised by the deprotonation of triamidoboranes by alkyl lithium bases. It was observed in this study and in those of Chivers<sup>1</sup> and Nöth<sup>2</sup> that alkyl lithium reagents not only act as a base, deprotonating the N–H protons to form imido anions but also as a nucleophile, attacking the electron deficient group 13 atom to form various addition and substitution products.

Reaction of  $B\{N(H)Ph\}_3$  with  $Bu^nLi$  (3 equiv.) in toluene leads to the formation of a lithium salt containing triimidoborate trianions  $Li_9[\{B(NPh)_3\}_2\{N(H)Ph\}_3]$  **1** (Figure 1a). This crystallizes with a cage structure where two  $Li_3B(NPh)_3$  units sandwich three molecules of  $LiN(H)Ph$ , formed by the nucleophilic substitution of  $B\{N(H)Ph\}_3$  by  $Bu^nLi$ . Reaction of  $B\{N(H)Ph\}_3$  with  $PhLi$  (3 equiv.) in THF leads to the formation of the lithium salt of an amidobisimidoborate dianion  $Li_4[B\{N(H)Ph\}(NPh)_2]_2$  **2** (Figure 1b). This crystallizes as an ion-contacted dimeric structure where the imido arms of two dianions coordinate four lithium ions to form a cage that contains  $Li_2N_2$  rhombohedral motifs.

Examination of these structures and those of previously reported complexes leads to an insight into the aggregation behavior of lithium imido borates. Planar imido dianions such as  $[B\{N(H)Ph\}(NPh)_2]^{2-}$  **2** and  $[RB(NBu^t)_2]^{2-}$  <sup>1</sup> are able to satisfy the coordination requirements of their lithium counterions using their imido arms. Planar trianions

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**FIGURE 1** Schematic representations of the core structures of complexes **1** and **2**.

such as  $[\text{B}(\text{NPh})_3]^{3-}$  **1** and those seen by Nöth<sup>2</sup> find it difficult to satisfy the coordination requirements of the  $\text{Li}^+$  cations with their imido arms and hence find it difficult to form stable structures. Aggregation with other anionic fragments from the reaction mixture that additionally coordinate  $\text{Li}^+$  ions helps to overcome this problem.

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