

# Borane–Ammonia Complexes Stabilized by Hydrogen Bonding

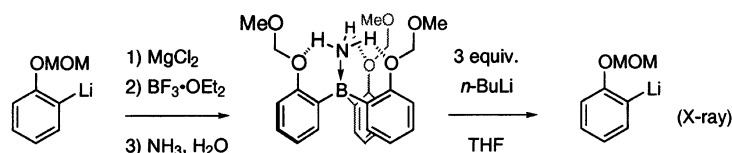
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## ABSTRACT

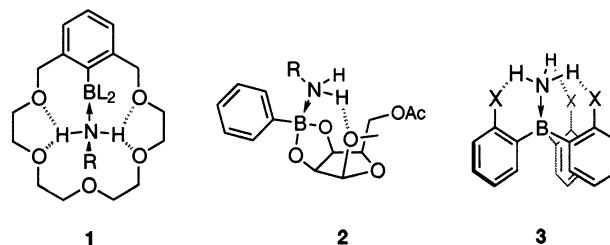


Novel borane–ammonia complexes, wherein an  $\text{NH}_3$  molecule is tightly bound through all four of its atoms, have been prepared and studied. The solid-state structure of ortho MOM-phenyllithium is reported.

The molecular recognition of neutral compounds remains an important part of supramolecular chemistry.<sup>1</sup> Though numerous receptors for charged species, including ammonium ions, have been found, few examples of guest molecules that recognize amines or ammonia have been reported. In 1992, Reetz et al. described borane–amine complexes of type **1**.<sup>2</sup> Their stability was traced to a three-point binding of the  $\text{RNH}_2$  group involving a dative BN bond and two hydrogen bonds to the crown ether moiety. Ammonia itself was found to form a highly stable adduct **1** ( $\text{R} = \text{H}$ ) as well, in which a four-point binding may be operative. However, no crystallographic evidence was obtained to further support this claim. In a subsequent communication, carbohydrate-derived complexes (**2**) that feature similar interactions were reported.<sup>3</sup>

We now present a new class of borane–ammonia complexes, wherein an ammonia molecule is tightly bound to a ligand through all four of its atoms.<sup>4</sup> This *symmetric four-point interaction* represents a unique bonding situation of considerable theoretical interest. The triarylborane ammonia complexes have the general architecture **3**, with X being a group able to engage in hydrogen bonding. In combination

with the electron-deficient boron center, these coordinating groups hold the  $\text{NH}_3$  molecule firmly in place. Complexes of type **3** are not only structurally intriguing but also show some unique reactivity (vide infra).



The synthesis of these compounds is straightforward and typically involves ortho-metalation chemistry, also facilitated by the coordinating group X (Scheme 1).<sup>5</sup> Lithiation of anisole, transmetalation with  $\text{MgCl}_2$ , subsequent addition of  $\text{BF}_3 \cdot \text{OEt}_3$ , and quenching with  $\text{NH}_4\text{OH}$  furnished compound **3a**. Alternatively, **3a** could be prepared using the Grignard

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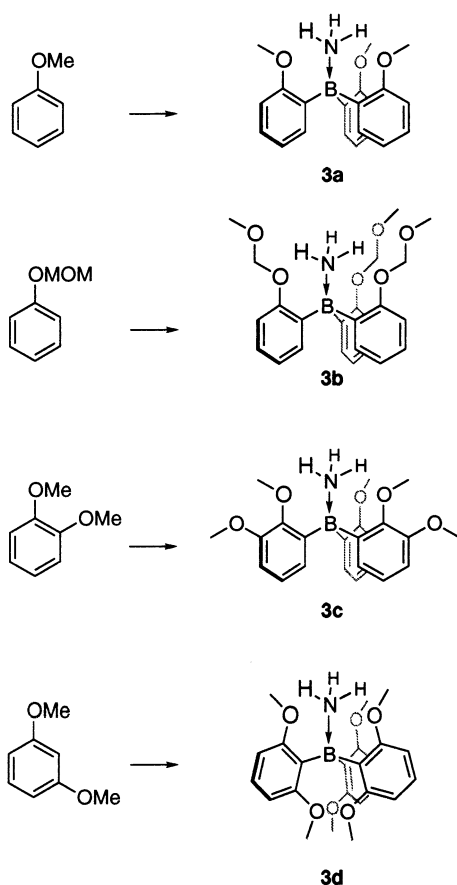
(1) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, UK, 2000; see also references therein.

(2) Reetz, M. T.; Niemeyer, C. M.; Hermes, M.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 1017.

(3) Reetz, M. T.; Huff, J.; Goddard, R. *Tetrahedron Lett.* **1994**, *35*, 2521.

(4) For a recent review of amine–borane chemistry, see: (a) Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197. See also: (b) Huskens, J.; Goddard, R.; Reetz, M. T. *J. Am. Chem. Soc.* **1998**, *120*, 6617. (c) Nozaki, K.; Tsutsumi, T.; Takaya, H. *J. Org. Chem.* **1995**, *60*, 6668.

(5) For a review of directed ortho-metalation, see: (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. See also: (b) Ronald, R. C.; Winkle, M. R. *Tetrahedron* **1983**, *39*, 2031. (c) McMurry, J. E.; Farina, V.; Scott, W. J.; Davidson, A. H.; Summers, D. R.; Shenvi, A. *J. Org. Chem.* **1984**, *49*, 3803.

Scheme 1<sup>a</sup>

<sup>a</sup> Reaction conditions: (1) *n*-BuLi, Et<sub>2</sub>O; (2) MgCl<sub>2</sub>; (3) BF<sub>3</sub>·OEt<sub>2</sub>; (4) NH<sub>4</sub>OH, H<sub>2</sub>O. **3a**, 41%; **3b**, 44%; **3c**, 50%.

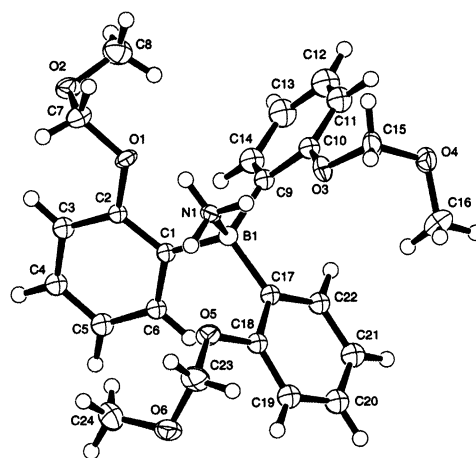
reagent derived from *o*-bromoanisole. In a similar manner, the complexes derived from methoxymethyl-phenol (**3b**) and veratrole (**3c**) were synthesized. The known ammonia adduct of tris(2,6-dimethoxyphenyl)borane (**3d**) was prepared using a previously reported procedure.<sup>6</sup>

The complexes **3a–d** are high-melting, crystalline solids that are stable toward silica gel chromatography. With the exception of **3d**, they display intense M<sup>++</sup> and [M<sup>++</sup> – 17] peaks in an 80 eV EI mass spectrum.

Compounds **3a–c** were further studied by X-ray crystallography (Figure 1). Each adopts an approximately C<sub>3</sub> symmetric, propeller-shaped conformation, wherein the alkoxy substituents on the aryl blades are oriented toward the ammonia moiety. Less than 2.2 Å separates the ammonia hydrogens from the phenolic oxygen atoms, and the N–H–O bond angle is about 127°. Furthermore, these hydrogens show a marked downfield shift in the <sup>1</sup>H NMR spectra. The criteria for hydrogen bonding, therefore, appear to be fulfilled.

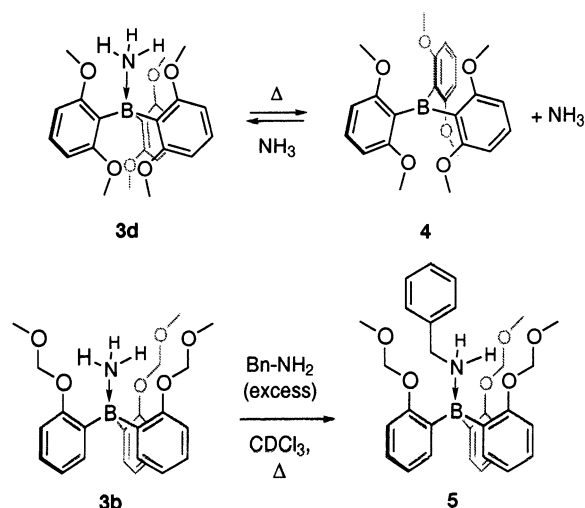
Prolonged heating of complexes **3a–c** in a coordinating solvent such as THF did not result in loss of ammonia. By contrast, complex **3d** proved to be markedly less stable

(6) Wada, M.; Kanzaki, M.; Ogura, H.; Hayase, S.; Erabi, T. *J. Organomet. Chem.* **1995**, 465, 127. The possibility of hydrogen bonds is not mentioned in this paper.

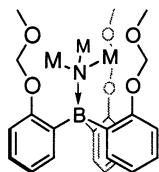
Figure 1. X-ray crystal structure of **3b**.

(Scheme 2). Due to steric crowding of the ortho methoxy substituents upon pyramidalization of the boron center, **1d** gradually released ammonia upon recrystallization from hot hexanes. This process was found to be reversible. Hence, the affinity of the complexes **3** for ammonia can be fine-tuned by appropriate choice and placement of substituents. Heating of **3b** with excess benzylamine in an open vessel led to gradual displacement of ammonia by the primary amine. Complexes of this type could not be obtained directly by treatment of the corresponding arylmagnesium compound with BF<sub>3</sub>·OEt<sub>2</sub>, followed by quenching with a primary amine and aqueous workup.

Scheme 2

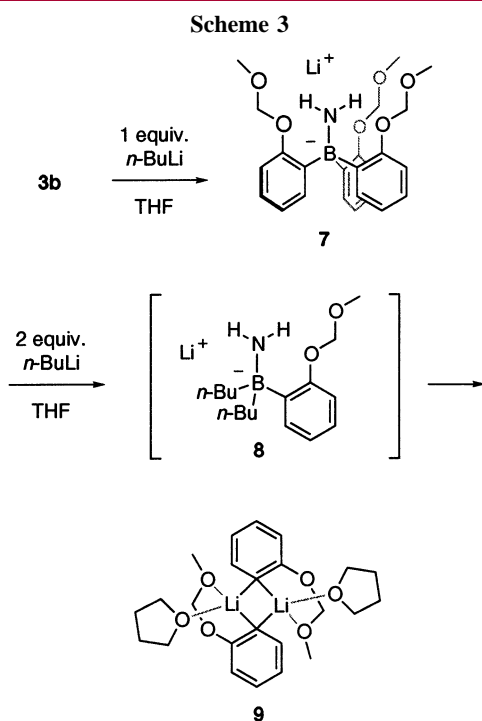


The chemical reactivity of complex **3b** was further studied. In an attempt to prepare “soluble metal nitrides” (**6**), the consecutive replacement of the ammonia hydrogens for metal atoms was investigated. We speculated that the MOM groups in compound **6** would stabilize such an array by contributing to the coordination sphere of the metal atoms.



6: M = Li, Na, MgX etc.

To this end, 3 equiv of *n*-BuLi were added consecutively to a solution of complex **3b** in THF-*d*<sub>8</sub>, and the reaction was followed by NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, and <sup>15</sup>N NMR). Complex **3b** was cleanly deprotonated after addition of the first equivalent to afford intermediate **7**, which is perhaps best formulated as the “ate” complex shown in Scheme 3.<sup>7</sup>



Compound **7** shows only a single set of signals in the <sup>1</sup>H NMR corresponding to the aryl substituents, indicating fast rotation of the amide moiety on the NMR time scale. Quenching a solution of **7** with excess CD<sub>3</sub>OD resulted in *complete* replacement of the ammonia hydrogens to afford a fully deuterated version of **3b**, suggesting rapid base-catalyzed exchange.

Adding an additional 2 equiv of *n*-BuLi led to formation of a new species in almost quantitative yield (by NMR). Unfortunately, this compound did not turn out to be the desired lithium nitride **6**. Careful crystallization from THF/hexanes and X-ray structure analysis identified the product as a dimer and THF adduct of ortho MOM-phenyllithium (**9**) (Scheme 3).<sup>5b</sup> Redissolving the crystalline material in THF-*d*<sub>8</sub> gave spectra identical to the ones observed before.

(7) In a sense, compounds of type **7** are analogous to lithium aminoborohydrides, LiH<sub>3</sub>B–NR<sub>2</sub>, recently established as powerful hydride reducing agents. See: Thomas, S.; Huynh, T.; Enriquez-Rios, V.; Singaram, B. *Org. Lett.* **2001**, *3*, 3915 and references therein.

The detailed mechanism of this interesting boron–lithium exchange reaction (**3b**→**9**) is currently being studied. Presumably, the reaction is initiated by expulsion of ortho MOM-phenyllithium from complex **7** and involves *n*-butylborate complexes of type **8** as intermediates. Thermodynamically, it is driven by the stability of the aryllithium species **9**. Notably, in the presence of 3 equiv of LiHMDS, only compound **7** is formed (by NMR), which does not further decompose under these conditions.

The solid-state structure of **9** provides insight into the structure of ortho-lithiated compounds obtained by directed metalation (Figure 2). The 3c2e bonding situation previously

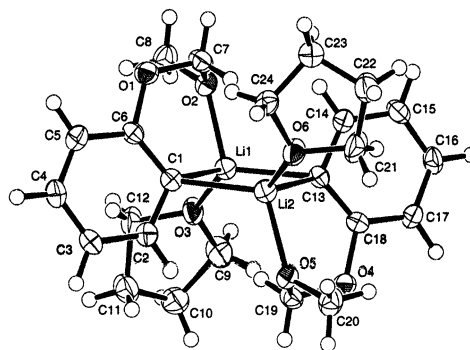


Figure 2. X-ray crystal structure of **9**.

found in dimeric [PhLi(tmeda)]<sub>2</sub><sup>8</sup> and Lewis base-free phenyllithium<sup>9</sup> is also present in **9**. Two lithium and two carbon atoms of the aryl moiety form a Li<sub>2</sub>C<sub>2</sub> four-membered ring. The two remaining coordination sites of each lithium atom are occupied by the ortho methoxymethyl group and a THF molecule. In contrast to what is sometimes depicted in the literature, the phenolic oxygens do not contribute to the coordination sphere.

In summary, a new class of triaryl boranes that strongly bind ammonia has been described and the reactivity of these compounds was tested. The X-ray crystal structure of MOM-phenyllithium has also been presented. Future investigation will focus on the measurement of binding constants *K* and *pK<sub>a</sub>* values of compounds **3a–d**. The potential of complexes of type **7** as a source of organolithium reagents (and a Lewis acid) remains to be determined.

**Acknowledgment.** We thank Prof. Howard W. Whitlock (University of Wisconsin–Madison) for stimulating discussions and Dr. Frederick J. Hollander and Dr. Allen G. Oliver for the crystal structure determination of compounds **3b** and **9**.

**Supporting Information Available:** Spectroscopic and analytical data for compounds **3a–c**, **7**, and **9** and X-ray structural data of compounds **3b** and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *J. Am. Chem. Soc.* **1998**, *120*, 1430.