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Two-Way Street Transformation of Boronium and Borane Complexes Facilitated by Amino-Linked N-Heterocyclic Carbene

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Summary: We have obtained boronium complexes upon reaction of an amino-NHC lithium bromide adduct with borane. Unexpectedly, the treatment of the boronium complexes with silver triflate led to the isolation of a bis-borane compound containing two chemically different boron centers. The bis-borane and boronium complexes can interconvert via a four-membered intermediate metallacycle consisting of a three-center, two-electron B−H−B bonding motif assisted by the pendant amine arm.

The employment of N-heterocyclic carbenes (NHCs) as strong neutral σ-donating, but weak π-accepting scaffolds has generated interesting reactivities and major advancements in homogeneous catalysis.[1] However, the use of NHCs in supporting group 13 elements such as boron is limited to very few cases.[2−4] Obviously, such structural and reactivity studies in these complexes may have created a new vista into future catalysis, material, and medicinal applications. For example, the elegant concept of frustrated Lewis pairs has spurred great interest in the use of bulky NHC-B$(C_6F_5)_3$ for hydrogen activation.[3] Recent seminal works by Fensterbank, Lacôte, Malacria, and Curran have demonstrated nontoxic NHC boranes that are stable radical hydrogen atom donors.[4] Subsequently, these NHC-boranes are found to be efficient co-initiators for radical acrylate photopolymerization.[5]

Previously, we have reported amine-linked NHC-aluminum complexes and the noninnocent nature of Al−NHC bonding.[6] Examples of the use of functional NHC ligands for boron, in particular secondary amino-NHC, appear to be nonexistent, despite the widespread use of these functionalized ligands in transition metals.[7] Delving into boron chemistry, we were curious as to whether the pendant amino arm of functional-NHC would facilitate and lead to a distinct reactivity different from that of symmetrical NHC. More importantly, functional linked NHC ligands have never been introduced in stabilizing boron cations $(LBR_2)^+$. Stimulated by this possibility, we attempted to synthesize the borane complexes supported by this ligand framework.

The amino-pendant-linked NHC **1-LiBr** adducts were readily introduced to BH_3 in THF to produce **2** (Scheme 1). In contrast to most borane complexes, compound **2** is found to be sparingly soluble in most organic solvents (toluene, ether, and THF) with the exception of methylene chloride, suggesting the formation of an ion-pair species in solution. The ^{1}H NMR spectroscopic features of **2** are notably different from the LiBr-NHC adduct, displaying a new singlet integrating to 9 H at 1.07 ppm for the amino *tert*-butyl group protons and three distinct singlets originating from the mesityl group at 1.89, 2.03, and 2.07 ppm with an equal integration for a total of nine protons. In the course of acquiring

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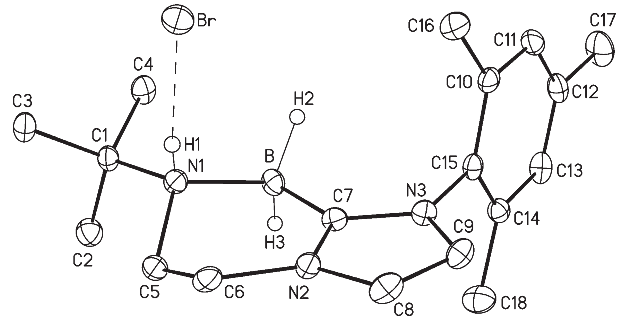
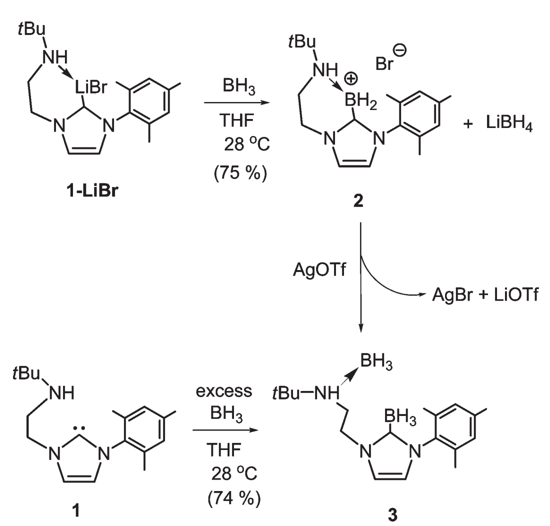


Figure 1. Molecular diagram of **2** with thermal ellipsoids drawn at the 30% probability level. Atoms H1, H2, and H3 were located from the difference map and refined with a riding model. All other hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B−C(7) 1.595(6), B−N(1) 1.608(5), C(7)−B−N(1) 105.8(3), C(5)−N(1)−B 109.5(3), C(1)−N(1)−B 116.9(3).

Scheme 1



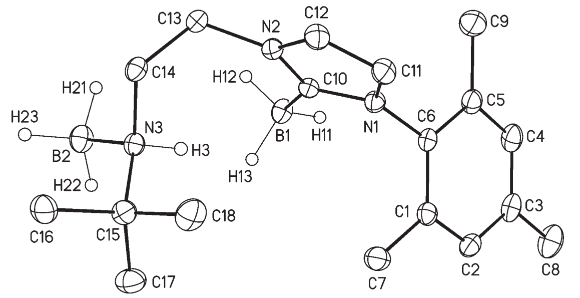


Figure 2. Molecular diagram of **3** with thermal ellipsoids drawn at the 30% probability level. Atoms H11, H12, H13, H21, H22, H23, and H3 were located from the difference map and refined with a riding model. All other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)−C(10) 1.592(2), B(2)−N(3) 1.623(2), N(1)−C(10) 1.3542(19), N(2)−C(10) 1.3515(19), N(2)−C(10)−N(1) 104.76(13), N(2)−C(10)−B(1) 128.26(14), N(1)−C(10)−B(1) 126.97(14).

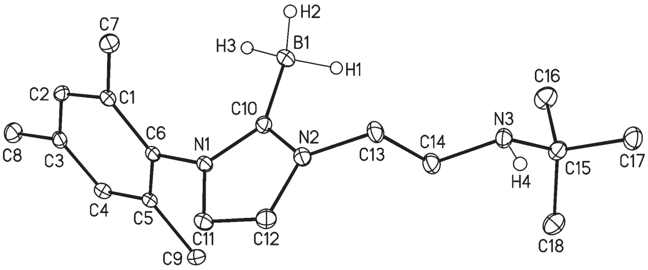


Figure 3. Molecular diagram of **4** with thermal ellipsoids drawn at the 30% probability level. Atoms H1, H2, H3, and H4 were located from the difference map and refined with a riding model. All other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)−C(10) 1.595(2), N(1)−C(10) 1.3553(18), N(1)−C(11) 1.3852(19), N(2)−C(10)−N(1) 104.91(13).

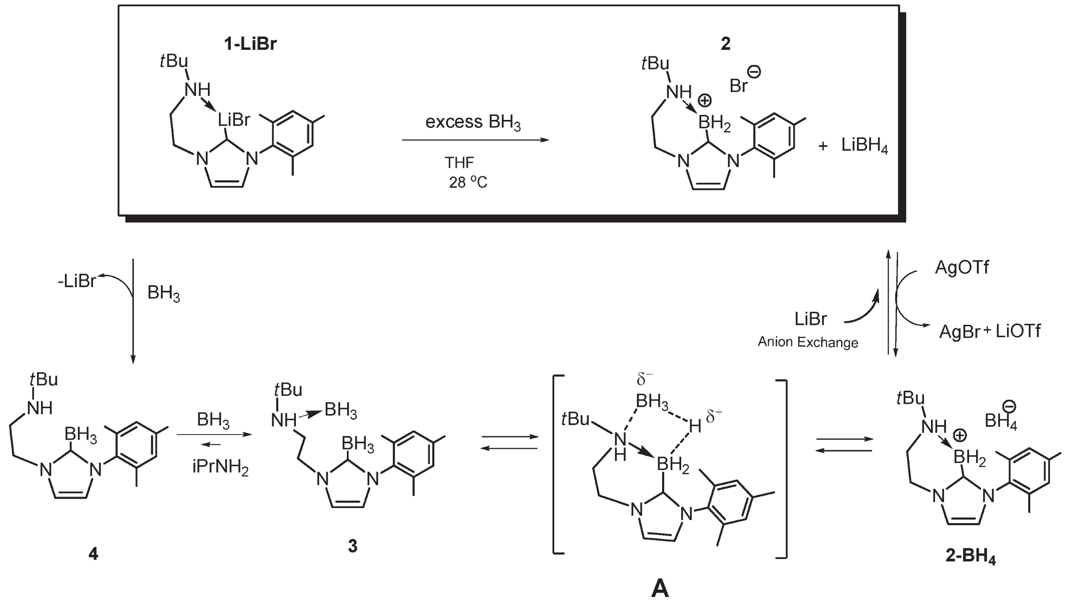
the ^{13}C NMR spectrum of compound **2**, the quadrupole nature of boron has prevented us from obtaining useful information regarding the carbenic signal. Single crystals of **2** suitable for X-ray analysis were grown by layering a CH_2Cl_2 solution of the boron compound with ether at ambient temperature, the structural model of which is presented in Figure 1.

The structure of **2** consists of a tetrahedrally distorted cationic boron center featuring a bidentate coordination mode of the amino-NHC ligand with a bromide counterion. The formation of a half-chair, six-membered-ring metallacycle upon chelation distorts the ideal coordination geometry of boron with a bite angle of C(7)−B−N(1) = 105.8(3)°. The boron−carbene bond length is 1.595(6) Å, in line with previously reported values of BH_3-NHC complexes (~1.59 Å),[2b] but shorter than its BEt_3 and BBr_3 counterparts (~1.65 Å).[2a] The B−N(1) bond length (1.608 (5) Å) is considered to be normal for the typical boron-amine dative interaction. Notably, there is a close intermolecular contact associated with the bromide and the amine through a N−H···Br interaction (N(1)−H(1)···Br(10), 2.563 Å, 3.363 Å, 174°)

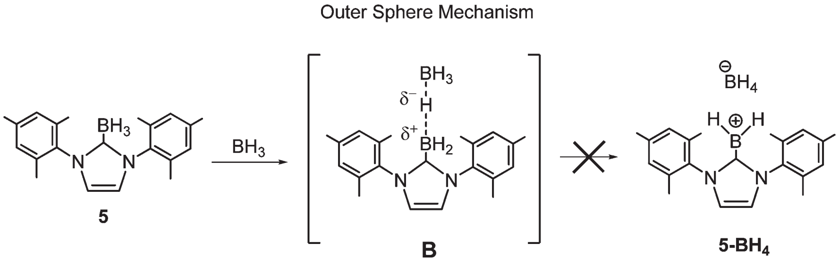
Attempts were made to replace bromide with a noncoordinating anion. The reaction with AgOTf resulted in an unexpected compound, **3** (Scheme 1). ^{11}B NMR spectroscopic analysis of the reaction mixture revealed two separate peaks at −37.1 and −18.8 ppm, illustrating two chemically distinct boron atoms in compound **3**. Single-crystal X-ray diffraction analysis further confirms the NMR finding, displaying two boranes coordinated separately to the amine and carbene sites (Figure 2). Interestingly, compound **3** can also be accessed via the reaction of free amino-NHC with excess BH_3. The structural parameters of **3** are unremarkable and no different from boronium **2**, as the boron−carbene bond distance is about 1.595(6) Å.

The reaction pathway toward the unanticipated formation of boronium **2** and bis-borane **3** is very intriguing, and we have proposed a plausible mechanism for this transformation, as shown in Scheme 2. At first, **1-LiBr** may react with 1 equiv of BH_3 to generate the monoboron species **4**, prior to the formation of bis-borane **3**. In that respect, we were able to isolate compound **4** by treating compound **3** with an excess of iPr$_2$NH to remove 1 equiv of borane. The structural analysis of **4** (Figure 3), combined with solution-state NMR studies, illustrates the free dangling amine arm pointing away from the boron center (4.68 Å). As a consequence, the nonchelating amine pendant arm in complex **4** is free to coordinate another borane to afford bis-borane species **3**. We postulate that the intermediate **A**, consisting of a four-membered-ring metallacycle with a three-center, two-electron (3c, 2e) B−H−B bonding motif, is inferred along the transformation of bis-borane **3** to boronium **2-BH$_4$**. Such a claim with regard to a B−H−B motif is not unprecedented, and solid structures are

Scheme 2. Proposed Reaction Pathway for Boronium 2



Scheme 3



well-established in the literature.[8] In the final cycle of the reaction pathway, the boron cation **2-BH$_4$** undergoes anion exchange in the presence of LiBr to furnish the unexpected product **2**.

There are a few issues regarding intermediate **A** that are noteworthy of comment. First, a closer examination of structure **3** shows a weak intermolecular interaction between the two boron atoms with a distance of 3.99 Å. The value is considered to be significantly longer than the 1,8-bisdiborylnaphthalenes (3.00−3.500 Å),[9] a consequence of the unfavorable steric crowding incurred by the close proximity between the *tert*-butyl and mesityl side arm. Nevertheless, a short intermolecular interaction of B1···N3 (3.54 Å) may have rendered B2 at the amino site to be more electron deficient and therefore more suitable for possible hydride abstraction, resulting in intermediate **A**. Second, such a transformation to boronium **2** is possibly operative via an outer-sphere mechanism, in which free BH$_3$ in solution can abstract the hydridic proton from borane at the carbene site. To verify such a possibility, we have conducted a control experiment by preparing symmetric NHC borane **5**. Treating **5** with excess BH$_3$ in the presence of LiBr salt gave no product resembling **5-BH$_4$** or the boronium species (Scheme 3). Therefore, the prospect that the transformation involved an outer-sphere manifold was ruled out. Therefore, the amine side arm did play a crucial role in assisting formation of boron cation species via complex **3**.

In summary, reacting the amino-linked NHC with borane in the presence of lithium bromide led to the unexpected and unique boronium complex **2**. Interestingly, treating the boronium species **2** with AgOTf resulted in complex **3**, with the two chemically dissimilar boron centers. The reversible chemical transformation between **2** and **3** is postulated to involve a four-membered-ring metallacycle encompassing a three-center, two-electron B−H−B motif through the assistance of the pendant amine arm on NHC. We hope to extend the NHC-borane reactivity in order to open up a new door for activating small molecules.

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Supporting Information Available: The preparation, characterization, and CIF files of crystallographic data of **2**, **3**, and **4** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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