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Solution Phase Reactivity of Dibenzo[c,e][1,2]azaborinine: Activation and Insertion into Si-E Single Bonds (E = H, OSi $(CH_3)_3$, F, Cl) by a BN-Aryne

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Abstract: The boron-nitrogen analogue of *ortho*-benzyne, 1,2-azaborinine, is a reactive intermediate that features a formal boron-nitrogen triple bond. We here show by combining experimental and computational techniques that the Lewis acidity of the boron center of dibenzo[c,e][1,2]azaborinine allows interaction with the silicon containing single bonds Si–E through the silicon bonding partner E (E = F, Cl, OR, H). The binding to boron activates the Si–E bonds for subsequent insertion reaction. This shows that the BN-aryne is a ferocious species that even can activate and insert into the very strong Si–F bond.

The replacement of C=C units by the isosteric and isoelectronic B=N units has developed into an important approach for modifying the properties of organic compounds relevant for materials and biomedical applications without compromising favorable structural features.[1] This modification is not limited to stable compounds, but can be transferred to reactive intermediates as well.[2] In this sense, the BN-aryne 1,2-azaborinine (Scheme 1) is the isoelectronic analogue of *ortho*-benzyne (1,2-didehydrobenzene). Arynes were first suggested as reactive intermediates almost 120 years ago,[3] and since developed into useful intermediates in organic synthesis.[4]

Evidence for the existence of BN-arynes emerged only after their initial computational investigation.[5] The dibenzo derivative **1**, the BN analogue of 9,10-phenanthryne[6] (10,9-BN-phenanthryne), was inferred as a reactive intermediate that forms during thermolysis of azide **2** in toluene solution likely by concerted N_2 loss and ring enlargement and undergoes cyclo-oligomerization to **3** and **4** (Scheme 1).[7] The cyclic trimer **4**[8] is a minor product of azide thermolysis,[7a] but the major product of the dehydrochlorination of 6-chloro-5,6-dihydrodibenzo[c,e][1,2]azaborinine **5** under basic conditions (Scheme 1).[8b,9] The direct infrared spectroscopic observation of the parent 1,2-azaborinine was achieved under matrix isolation conditions.[10] This compound is strongly Lewis acidic as bonding to N_2, CO, and Xe as well as [2 + 2] cycloaddition with CO_2 was observed to take place.[10–11] The high reactivity results from the polar BN link that causes significant structural distortion with poor overlap between the in-plane orbitals of N and B.[5,10] As a consequence, the lowest unoccupied molecular orbital (LUMO) is a sp^2-type σ orbital with a large coefficient on boron that is available for interaction even with weak Lewis bases, such as Xe or N_2.[5,10] The electronic structure of this cyclic iminoborane thus differs significantly from that of an acyclic one.[12]

The high reactivity of 1,2-azaborinine discovered in the matrix isolation studies suggests that it may also be able to react with strong covalent bonds in solution. Indeed, thermolysis of **2** in toluene solution in the presence of chlorotrimethylsilane (TMSCl) gave evidence for insertion into the Si–Cl bond.[7a] The single bonds of silicon with fluorine, chlorine, and oxygen (Si–E, E = F, Cl, O) are remarkably strong (142, 106, and 95 kcal mol^{-1}, respectively),[13] but can react with strong electrophiles.[14] While abstraction of fluoride from Si–F has been reported,[15] insertion into Si–F bonds is rare[16] and was studied computationally.[17] On the other hand, insertion reactions were reported for the weaker Si–Cl and Si–O bonds, in particular with transient and stable silylenes.[18]

We here show for the first time that BN-aryne derivatives are accessible photochemically and can be trapped under these conditions even by insertion into the quite inert Si–F bond. The choice to study the reactivity of **1** towards polar Si–E bonds was motivated by the challenge of bond activation as well as by the inertness of the trapping agents towards the strongly Lewis acidic azidoborane **2**.[19]

Treatment of 9-chloro-9-borafluorene with one equivalent of azidotrimethylsilane yields **2** and TMSCl essentially quantitatively based on NMR spectroscopy.[19] As **2** forms a cyclic trimer of limited stability in the solid state[19] and due to the reported tendency of similar trimeric azidoboranes to undergo explosive decomposition,[12a] the reaction solution including one equivalent of TMSCl was used in all the following experiments without further work-up.

Photolysis (λ = 305–400 nm) of **2** in benzene in the absence of trapping agents resulted in formation of the known trimer[8] **4** in 92% yield. Hence, photolysis of **2** resulted in loss of dinitrogen and ring enlargement to **1** that reacted by cyclotrimerization to **4**. The preferential formation of the cyclic trimer under photolytic conditions differs from the observation of

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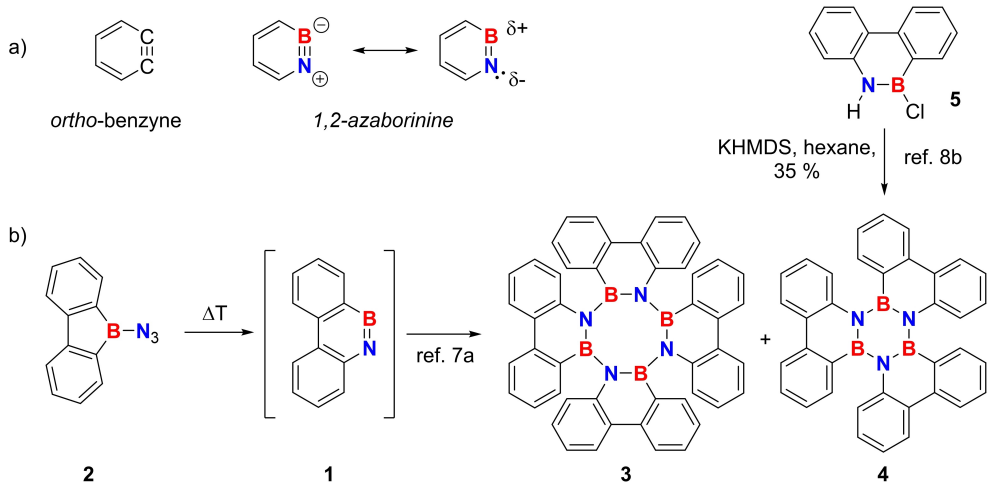
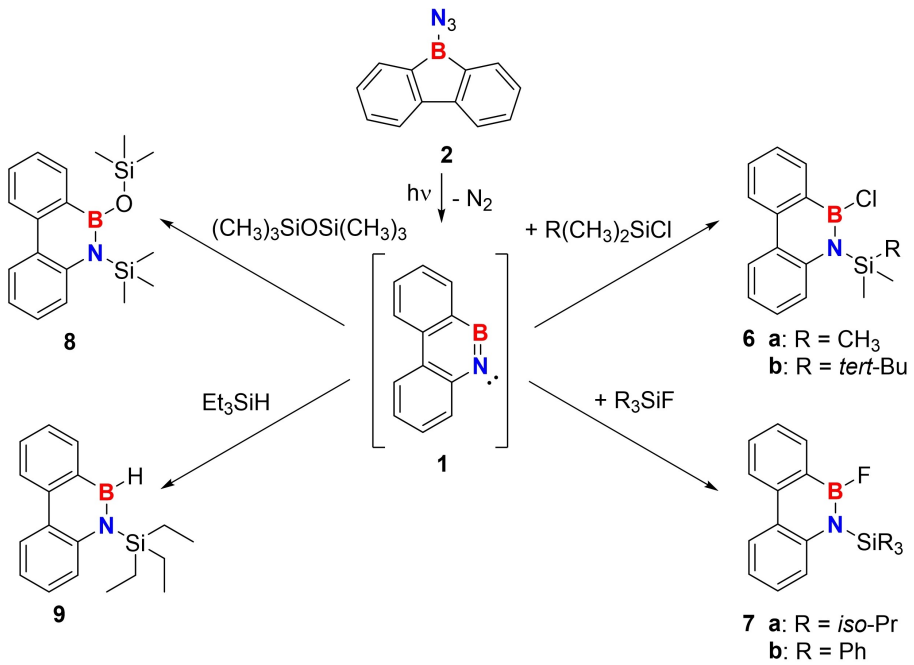


Scheme 1. a) Isoelectronic relationship between *ortho*-benzyne and 1,2-azaborinine; b) self-trapping of dibenzo[c,e][1,2]azaborinine **1** during thermolysis of 9-azido-9-borafluorene (**2**) and formation of the trimer **4** of **1** by dehydrochlorination of **5**.

thermolysis of **2** that resulted in formation of the cyclic tetramer **3**. Cyclooligomerization of **1** involves its dimer according to a previous computational study that either dimerizes to tetramer **3** or reacts with **1** to **4**.[7b] The preferred reaction product, tetramer **3** or trimer **4**, thus most likely depends of the rate of monomer formation.

Solution phase trapping experiments during photolysis ($\lambda =$ 305–400 nm) of **2** were conducted in benzene solutions at room temperature with large excesses of trapping reagents to reduce the tendency towards self-trapping. During all photolysis experiments product mixtures resulted with trimer **4** dominating.

The photolysis of **2** in the presence of a large excess of TMSCl was monitored by NMR spectroscopy. During photolysis signals at $\delta^{11}B = 39.9$ ppm and $\delta^{29}Si = 14.6$ ppm grew concomitantly. The computed (B3LYP/def2-TZVP//B3LYP-D3/6-311+G**) shifts for the hitherto unknown Si–Cl insertion product **6a** (Scheme 2) are 40.9 ppm for boron and 15.8 ppm for silicon, in support of the assignment to **6a**. The sum formula of **6a** could be proven after work-up by high-resolution EI mass spectrometry. Compound **6a** was slowly decomposing under vacuum to **4**, precluding its purification. After photolysis, crystals of **4** could be isolated as shown by comparison with the known lattice parameters of **4**.[8c,20] Note that evidence for trapping with



Scheme 2. Trapping reactions of dibenzo[c,e][1,2]azaborine **1** obtained by photolysis ($\lambda = 305$–400 nm) of azide **2** in benzene solution at room temperature.

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TMSCl was also obtained during thermolysis of **2** in toluene solution.[7a]

As 1-(*tert*-butyldimethylsilyl)-2-chloro-1,2-dihydro-1,2-azaborinine is stable[1b,c,21] while *B*-chloro derivatives of 1,2-azaborinines with the smaller trimethylsilyl groups have never been reported, we studied the photolysis of **2** in the presence of *tert*-butyl-dimethylsilylchloride. The major product **6b** has ^{11}B and ^{29}Si signals at 40.0 ppm and 20.3 ppm, in good agreement with the values computed (δ^{11}B = 42.0 ppm, δ^{29}Si = 24.8 ppm) for the product **6b** of insertion into the Si–Cl bond (Scheme 2). High-resolution EI-MS again confirms the identity of **6b**. The compound sublimes (10^{-6} mbar, 40 °C) along with unidentified compounds. Two-dimensional NMR spectroscopy allowed characterization of **6b** among the mixture obtained by sublimation.

The trapping with triisopropylfluorosilane[22] results in formation of fluoroborane **7a** based on HR-MS and NMR spectroscopy, in addition to trimer **4**. Sublimation (10^{-6} mbar, 30 °C) resulted in an almost pure compound **7a** without thermal decomposition. Only some unidentified silicon compound co-sublimed. The yield of **7a** was determined by ^{19}F NMR to be 13% (averaged over seven experiments, see Supporting Information for technical details). Combining the seven runs, trimer **4** was isolated in a yield of 73% by washing intensively with pentane. Note that the *B*-fluoro 1,2-azaborinines have not been reported before. The reaction with triphenylfluorosilane gave **7b** (Scheme 1) that could not be obtained in pure form (see Supporting Information).

Photolysis of **2** in the presence of hexamethyldisiloxane results in formation of **8** (Scheme 2) as the major product based on the HR-EI-MS and the good agreement between the measured and computed ^{11}B and ^{29}Si NMR shifts (δ^{11}B = 31.4 ppm, calc. 30.3 ppm). A more detailed characterization was not possible due to TMS_2O elimination during removal of the solvent.

Trapping of the photolysis product with triethylsilane results in **9** (Scheme 2) that could be isolated by sublimation (10^{-6} mbar, 100 °C) in an almost pure state. The ^{11}B NMR spectrum only shows two additional peaks (45.0 ppm and 26.7 ppm) with much weaker intensity than that of **9** (δ^{11}B = 39.4 ppm, calc. 36.3 ppm). The ^{29}Si shift of 17.4 ppm is in good agreement with the computed value (17.8 ppm). The ^{1}H and ^{13}C NMR spectra of **9** confirmed the ring enlargement to the BN-phenanthrene motif, assuming that one ^{13}C signal cannot be detected due to the quadrupole moment of the directly bound boron center. Finally, HR-MS confirmed the formula assigned to **9**.

To shed light on the mechanism of the trapping reactions of **1** we have performed computational chemistry investigations at the DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3/6-311+G** level of theory (see Supporting Information for details).[23] The polarized continuum model (PCM) was used to elucidate the effect of solvation using benzene as a solvent. The reactions of **1** are highly exothermic ($\Delta_r H°$(298.15 K) between −57 and −72 kcal mol^{-1}) and exoergic with $\Delta_r G°$(298.15 K) between −43 and −59 kcal mol^{-1} due to formation of two covalent bonds (B–E and N–Si) at the expense of one covalent Si–E single bond (Table S1). We find that **1** forms complexes (see Figure 1a) with

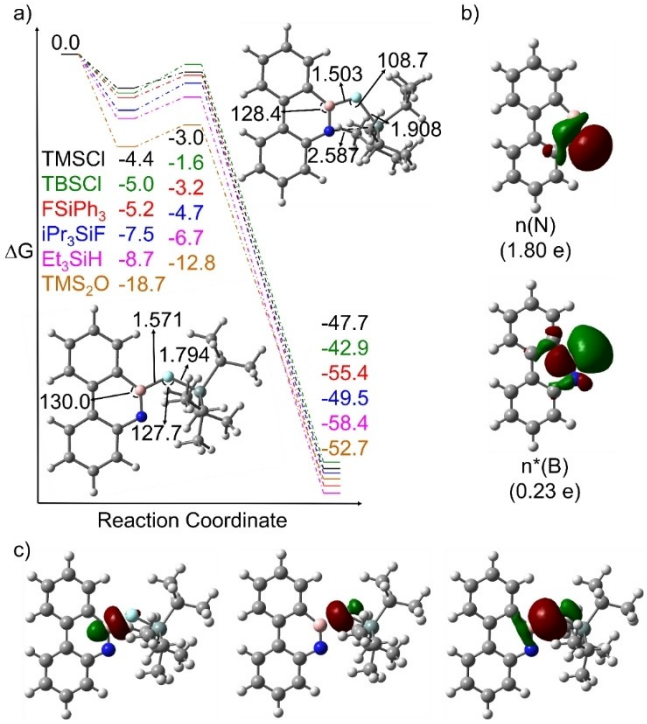

Figure 1. a) Gibbs energy profile at 298.15 K (in kcal mol^{-1}) for the insertion of **1** into the Si–E bond as computed at the DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3/6-311+G** level of theory involving benzene solvent corrections. For reaction **1** + *i*Pr$_3$SiF the structures of the van der Waals complex and the transition state are given (important distances and angles are given in Å and degree, respectively). b) In-plane NBO involving the BN unit and their occupation numbers of **1**. c) Acceptor (left), donor (center) NBO and corresponding NLMO (right) associated with the F→B interaction in the **1**·*i*Pr$_3$SiF complex.

the trapping reagents that are bound on the ΔG(298.15 K) scale by 4–9 kcal mol^{-1} (the silyl halides and hydride) and even by 19 kcal mol^{-1} in the case of hexamethyldisiloxane despite the entropy penalty due to association of two molecules (see Table S1).

The insertion reactions are one-step processes from the complex (see Figure 1a). The barriers, $\Delta G^{\ddagger}$(298.15 K), for insertion into the Si–E bonds based on the free energies of the complexes range from 1.4 to 3.4 kcal mol^{-1} for E = Cl, F, H, and 5.9 kcal mol^{-1} for E = OTMS. In the complexes of **1** with the trapping reagents the Si–E bonds are significantly stretched (5.1–7.8%), while the B–E distances are quite short as they are only 11.2–18.1% longer than in the final products (see Table S2). The structural changes of the Si–E bonds suggest that the complexation of **1** results in an activation of these bonds for the subsequent nucleophilic attack of the nitrogen at the silicon center.

Further insight into this activation process is provided by natural bond orbital (NBO) analysis. The remarkable structural feature of **1** is the distorted azaborinine ring with a small angle at nitrogen and a wide angle at boron that is due to the electronegativity difference between these two elements.[5,7a] While the nitrogen atom has in-plane lone pair orbital with an occupancy of 1.80 electrons, the boron center has an in-plane

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empty orbital with strong p character and an occupancy of 0.23 electrons (see Figure 1b), similar to parent 1,2-azaborinine.[10] The magnitude of the E–B interaction in the complexes, assessed via second-order perturbation theory analyses in the NBO basis, shows strong stabilization due to n(E)→n*(B) delocalization for E = F, Cl, O (Figure 1c, Table S3 for E(2) values). The corresponding natural localized molecular orbitals (NLMO) have a major contribution from the F, Cl, O lone-pair orbitals and "delocalization tails" (11–15 %) from a slightly hybridized vacant orbital at boron (Tables S3 and S4). In case of complex formation with Et_3SiH, the NLMO shows a three-center two-electron interaction involving B, H, and Si atoms (Table S3).

It is remarkable that the behavior of the silyl halides is altered from being silicon electrophiles to acting as Lewis bases towards to the boron center of **1**. Only after complex formation the nitrogen and silicon atoms engage in their expected reactivity. Formation of the complexes involving **1** and the trapping reagents thus activates the substrates for bond breaking, and the boron and nitrogen centers act in a synergistic fashion in these reactions. Our computational investigation confirms the high reactivity of **1** and its very facile reaction with the Si–E bonds of the trapping reagents.

In summary, our study shows that the photodecomposition of azide **2** in solution phase at room temperature results in self-trapping of the BN-aryne photoproduct **1** to give the cyclic trimer **4**. The products identified after photolysis of **2** at room temperature in the presence of large excesses of trapping reagents featuring Si–E bonds (E = H, F, Cl, OTMS) confirms successful trapping of the BN-phenanthryne **1** during azide photolysis. The study further shows that BN-phenanthryne is a ferociously reactive intermediate that inserts into very strong covalent Si–E bonds. The computational investigation reveals that the insertion involves rather strongly bound van-der-Waals complexes between the boron center of **1** and the trapping reagents that collapse to the products in the subsequent reaction step. The boron center thus acts towards activation of the Si–E bond for insertion reaction.

Experimental Section

Safety Considerations: Azide **2** may be explosive or form explosive HN_3 upon undesired hydrolysis. Although no explosions were experienced, appropriate measures should be taken when experimenting with **2**.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: arynes · boron · fluorine · insertion · reactive intermediates

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