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Investigating the Ring Expansion Reaction of Pentaphenylborole and an Azide

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The reaction between trimethylsilyl azide and pentaphenylborole was recently shown to produce the corresponding 1,2-azaborine. Investigating this transformation theoretically suggests that the reaction proceeds via coordination of the azide to the borole, rearrangement to a bicyclic species, and conversion to a kinetically favoured eight-membered BN_3C_4 heterocycle or expulsion of N_2 to furnish the thermodynamically favoured 1,2-azaborine. The eight-membered species was structurally characterized as a borole adduct and represents an unusual analogue of cyclooctatetraene.

The remarkable isolation of the anti-aromatic pentaphenylborole **A** in 1969 by Eisch marked a significant discovery in heterocyclic chemistry (Scheme 1).[1] This area was revitalized with the determination of the solid-state structure of **A** in 2008.[2] The groups of Piers, Braunschweig and others have recently reported great advances in pursuing the reactivity of boroles and diversifying their synthesis to other species incorporating the borole core.[3-13] Boroles can display redox reactivity within the heterocycle[14-20] and Diels-Alder diene reactivity with the butadiene backbone.[21, 22] In addition, they have been shown to be powerful Lewis acids[23-25] which is underscored in the exposure of Eisch's borole or Piers' borole (perfluoropentaphenylborole, **B**) to an atmosphere of carbon monoxide. This results in a rare example of a reversible main group CO adduct relying purely on σ-donation (**C**).[26,†]

The diverse reactivity of boroles is nicely illustrated by the reaction of Piers' borole with diphenylacetylene which produces two products: a six-membered ring with an exocyclic C-C double bond **D** and the seven-membered borepin heterocycle **E**.[27] The former occurs through coordination of the alkyne to the boron centre, aryl group migration to the β-carbon and finally ring expansion to the six-membered product. The formation of the borepin **E** occurs via a [4 + 2] cycloaddition between the butadiene backbone of the borole and

the alkyne followed by a series of rearrangements. Interestingly, the less Lewis acidic borole **A** only participates in the Diels-Alder pathway.[22]
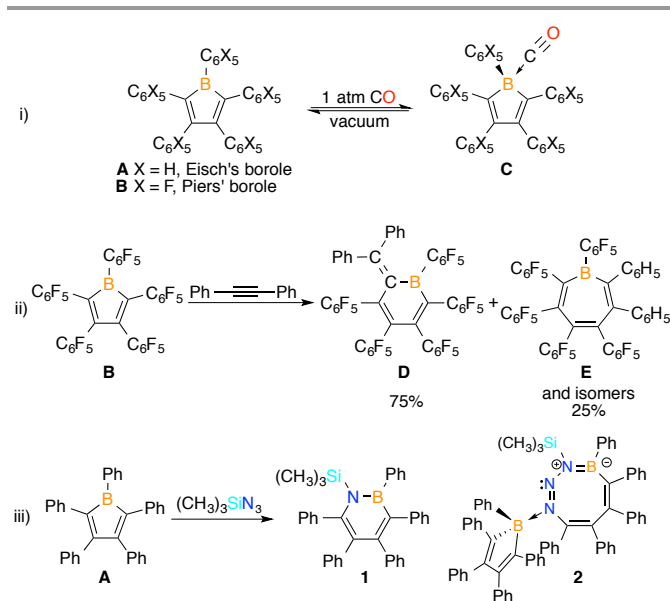
Scheme 1: i) Reaction of boroles with CO, ii) Piers' borole with diphenylacetylene, iii) Braunschweig's report on converting Eisch's borole to the 1,2-azaborine (**1**) and the structure of kinetic product **2** reported in this study.

Braunschweig et al. recently reported the reaction of trimethylsilyl (TMS) as well as organic azides with boroles that produced the corresponding 1,2-azaborines (**1**) in high yield.[28] This is a very efficient route to 1,2-azaborines which have garnered a lot of attention to potentially serve as pharmaceuticals as well as in electronic materials.[29] In these studies, they observed a solution
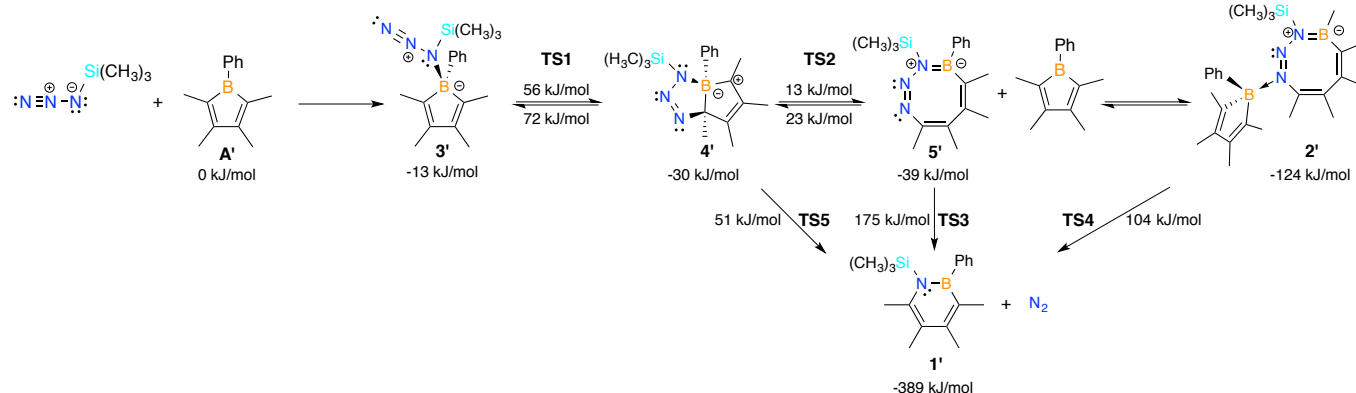
Scheme 2: Calculated pathway leading to compounds **5'** and **1'**. The energy under the compounds represents the relative energy (ΔG) of that compound with respect to **A'**. The energies over the arrows represent ΔG‡ for the transformation in the indicated direction. Note: the ' symbol signifies methyl groups have been used to differentiate the model system from the all phenyl system in experiments.

colour change from the blue borole solution to red and eventually to colourless. During the course of this reaction, N_2 gas evolved as the by-product. At the same time as this study appeared in the literature we observed the same results in comparable yield. Fascinated by this transformation, we investigated this chemistry further both computationally and experimentally allowing us to shed light on the mechanism as azides can show a variety of reaction pathways.[30] These include Diels-Alder cycloaddition and coordination chemistry, both of which were observed in the aforementioned alkyne chemistry. In addition, azides can act as sources of nitrene fragments. Through these studies, we suggest that the reaction proceeds via coordination of the azide to form an adduct with the borole which then forms a fused bicyclic species. This species can then convert to an eight-membered analogue of cyclooctatetraene via a reversible low barrier pathway. Ultimately the bicyclic species expels N_2 to form the thermodynamic product, the 1,2-azaborine.

Conducting the same 1:1 reaction as the earlier report of TMS-azide and borole in toluene, we observed the same colour change to red after stirring the mixture for 1 min. Removing the solvent *in vacuo* produced a red powder that displayed multiple TMS resonances by ^{1}H NMR spectroscopy. Storing a saturated Et_2O solution of the redissolved solids at -35°C resulted in the formation of red crystals. An X-ray diffraction study revealed a 1:2 azide to borole containing product (**2**; Fig. 1, Scheme 1). The three nitrogen atoms from the azide moiety were incorporated into one of the borole rings generating an eight-membered BN_3C_4 ring. The γ-nitrogen atom formerly from the azide was found to be coordinated to a second equivalent of borole. Interestingly, this new eight-membered heterocycle represents an analogue of cyclooctatetraene.[31] This species is only the second report of any sort of a B,N-analogue of cyclooctatetraene. The other example was recently reported by Bettinger, a B_4N_4 heterocycle featuring alternating boron and nitrogen atoms.[32, 33] However, complex **2** is the first report of a hybrid inorganic/organic species. Much like its carbonaceous relative and the inorganic B_4N_4 system,[31, 32] **2** avoids an anti-aromatic configuration by adopting a non-planar geometry with alternating single and double bonds in a pseudo-boat conformation.

Compound **2** could be isolated as crystals in 8% yield when altering the stoichiometry to a 1:2 ratio of TMS-azide to borole and working up the reaction after 1 minute allowing us to characterize **2**. Redissolving the crystals in CD_2Cl_2 and acquiring a ^{1}H NMR spectrum revealed signals for a species containing two pentaphenylborole units to one TMS group (aryl multiplets δ = 7.74-

5.94 ppm and singlet at δ = -0.22 ppm, respectively, integrating in a 50:9 ratio) consistent with the X-ray diffraction data. After storing the NMR tube for 4 days, the solution colour changed from red to the blue, the colour of free borole **A**. Obtaining ^{1}H and ^{11}B NMR spectra of the same sample in CD_2Cl_2 showed diagnostic signals consistent with the quantitative conversion to the 1,2-azaborine product **1** (^{1}H NMR: δ_{TMS} = -0.16 ppm and ^{11}B{^{1}H} NMR δ = 40 ppm) and the free borole **A** (^{11}B{^{1}H} NMR δ = 65 ppm).[2, 28] This confirming that eight-membered complex **2**, is indeed converted to the thermodynamic product **1** over time and that adduct formation is reversible.
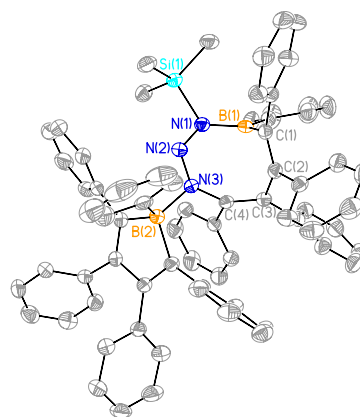

Fig 1: Solid-state structure of **2**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Endocyclic bond lengths (Å): B(1)-N(1) 1.477(3), N(1)-N(2) 1.340(3), N(2)-N(3) 1.284(3), N(3)-C(4) 1.467(3), C(4)-C(3) 1.356(3), C(3)-C(2) 1.503(3), C(2)-C(1) 1.353(3), C(1)-B(1) 1.574(4).

Theoretical studies were undertaken to establish the veracity of the proposed mechanism (Scheme 2) using B3LYP-D3BJ/6-31+G(d) geometries and SCS-MP2/6-31+G(d)//B3LYP-D3BJ/6-31+G(d) energies. In the computational studies a model system was employed that retained the full trimethylsilyl group on the azide but with a simplified B-phenyl/C-methyl substituted borole systems for computational efficiency (notation of ' is used to represent the model system). All transition states were confirmed to connect the

associated minima from extensive IRC calculations. The formation of the initial adduct of TMS-azide with the borole (**3'**) was determined to be almost thermodynamically neutral (ΔG = -13 kJ/mol) with respect to the separated reagents, consistent with the lack of observation of this complex in solution. This adduct is connected to a bicyclic intermediate **4'** via a transition state (**TS1**), with a barrier of 56 kJ/mol. The bicyclic intermediate **4'** is a key intermediate, due to its presence in the reaction path to both products **1'** and **2'**.

Conversion of **4'** to cyclooctatetraene derivative **5'** occurs via a low transition barrier of 13 kJ/mol (**TS2**). The formation of the cyclooctatetraene from **4'** is thermodynamically favourable with a ΔG of -9 kJ/mol. However, direct elimination of N_2 from **5'** to generate **1'** proceeds via a transition state with a barrier of approximately 175 kJ/mol (**TS3**), which is much too high for the experimentally observed rate and temperature of the reaction. If instead we consider **2'**, which is the thermodynamically favoured and borole adduct of **5'** (ΔG = 85 kJ/mol from **5'**), the barrier for N_2 elimination to form **1'** is also too high (104 kJ/mol, **TS4**) for the observed reaction. However, the calculated barrier from **4'** to **1'** is readily surmountable at room temperature (51 kJ/mol). This reaction involving elimination of N_2 to form **1'** is highly favourable (ΔG = -359 kJ/mol from **4'**), making the final transformation irreversible. The ability to isolate **2** if the reaction is stopped quickly can be rationalised by **2** lying in an energy well provided by favourable adduct formation with the second equivalent of borole. The formation of **2** at the start of reaction is due to the lower barrier at **TS2** as compared to **TS5**. The complete conversion to **1** in the initial reaction and the observation that **2** converts to **1** if isolated and subsequently redissolved can be explained by modest barriers for the reverse reaction over **TS2** (23 kJ/mol) leading back to **3'**. No transition state could be found for the formation of adduct **2'** from **5'**, but the barrier is not likely to be large, especially given the ease with which the reverse reaction is observed to occur.

This report demonstrates that an azide reacts with a borole initially through coordination of the nitrogen atom to the borole rather than via a Diels-Alder or a nitrene route. The coordination is followed by a bicyclic ring formation that can proceed via two pathways, a reversible pathway to an eight-membered heterocycle, which could be experimentally isolated, or an irreversible pathway to yield the 1,2-azaborine product. The kinetic product represents the first isolated hybrid inorganic/organic analogue of cyclooctatetraene. The described synthesis of 1,2-azaborines from boroles is restricted to peraryl derivatives. However, highly substituted 1,2-azaborines are challenging to prepare and this synthesis could provide a facile route to such species. In summary, we herein further demonstrate the diverse, as well as peculiar, reactivity of boroles and anticipate that this study will provide insight on new avenues in borole chemistry.

Notes and references

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† With Eisch's borole, at low temperatures the adduct is stable, but at room temperature it ring expands to a six-membered ring.

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