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Successive Carbene Insertion into 9-Phenyl-9-Borafluorene

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COMMUNICATION

Successive carbene insertion into 9-phenyl-9-borafluorene

Tyler A. Bartholome, Kristen R. Bluer and Caleb D. Martin*

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The reactions of 9-phenyl-9-borafluorene with trimethylsilyldiazomethane in a 1:1 and 1:2 stoichiometry furnished the corresponding BC_5 and BC_6 heterocycles *via* the formal insertion of one and two carbene units.

Unsaturated BC_4 heterocycles have recently been recognized as promising reagents for the synthesis of six- to eight-membered boracyclic systems *via* the formal insertion of one, two, or three atoms into the endocyclic B-C bond.[1-3] Developing efficient methodologies to access heterocycles featuring tri-coordinate boron centers is of paramount interest as they have applications in electronic materials and pharmaceuticals.[4-13] In this vein, two types of unsaturated BC_4 systems have been of focus, boroles (**1**)[14] and their biphenyl-fused variants, 9-borafluorenes (**2**).[15, 16] Boroles are more reactive than 9-borafluorenes as they have greater anti-aromatic character and Lewis acidity.[17-22] The intermolecular insertion chemistry of boroles has been investigated with a number of unsaturated molecules[23-44] whereas the corresponding chemistry with 9-borafluorenes is less developed.[19, 45-53]

The first intermolecular insertion reaction of a 9-borafluorene was reported in 2016 by Fukushima and coworkers with the insertion of alkynes into the endocyclic B-C bond of 9-chloro-9-borafluorene (**2Cl**) to furnish unsaturated BC_6 heterocycles (**A** and **B**; Fig 1a).[52] Our group, and He, discovered that 9-borafluorenes react with organic azides to generate 9,10-B,N-phenanthrenes (**C** and **D**, Fig 1b) *via* the insertion of either the α- or γ-nitrogen atom.[19, 51] Investigations with 1,2-dipolar substrates resulted in adducts (imine, nitrile, isocyanide) or seven membered rings (aldehyde, ketone, ketene, isocyanate, carbodiimide, phosphaalkyne) in which the negatively polarized atom is bound to boron and the positively polarized atom to carbon (Fig 1c).[46-48]

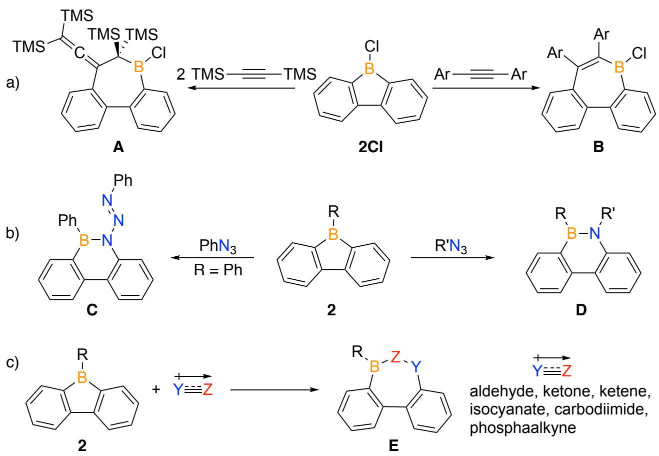

Figure 1: Reported intermolecular insertion reactions of alkynes (a), azides (b), and unsaturated 1,2-dipolar molecules (c) with 9-borafluorenes. TMS = trimethylsilyl.

The Ashe, Brown, and Matteson groups have demonstrated that the combination of halomethane/base can serve as a carbene source that inserts into B-C bonds.[54-62] The insertion of CR_2 units into boron-carbon bonds has also been reported using diazo reagents with notable recent work by the Stephan and Melen groups.[63-69] Braunschweig and coworkers investigated the reactions of boroles (**1**) with diazo reagents observing two outcomes (Fig 2).[24] The reaction with a bulky diazo species featuring two *para*-tolyl groups on the α-carbon generated a

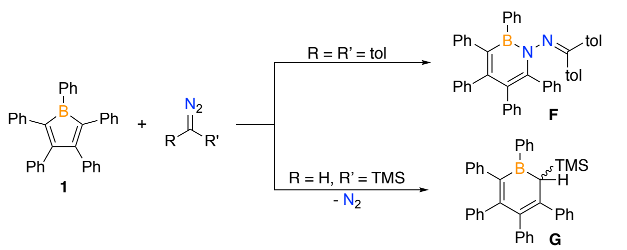

Figure 2: Reactions of pentaphenylborole (**1**) with diazo reagents (tol = *para*-tolyl).

Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX 76798, USA. E-mail: caleb_d_martin@baylor.edu
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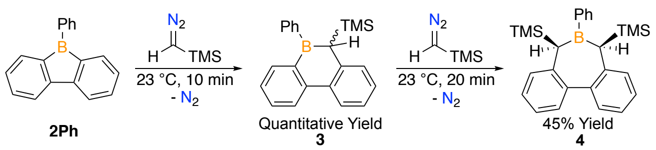
1,2-azaborine (**F**) *via* insertion of the terminal nitrogen into the B-C bond whereas the reaction with trimethylsilyldiazomethane resulted in insertion of a $CH(SiMe_3)$ unit into the endocyclic boron-carbon bond of **1** to provide a six-membered ring (**G**) with concomitant release of N_2 gas. Given the insertion chemistry of azides into boroles, we sought to examine the reactivity of trimethylsilyldiazomethane with 9-phenyl-9-borafluorene (**2Ph**).

The 1:1 stoichiometric reaction of **2Ph** with trimethylsilyldiazomethane at room temperature resulted in gas evolution accompanied by a color change from yellow to colorless (Scheme 1). No significant change was observed by *in situ* ^{11}B NMR spectroscopy; however, *in situ* ^{1}H NMR spectroscopy indicated complete consumption of trimethylsilyldiazomethane within 10 minutes by the disappearance of the trimethylsilyl peak at -0.04 ppm accompanied by the emergence of a singlet at -0.30 ppm. A diagnostic singlet in the aliphatic region at 3.88 ppm was assigned to the proton derived from the diazo α-carbon. Removing the volatiles *in vacuo* gave a pale yellow solid in quantitative yield. An X-ray diffraction study on crystals grown revealed the product as the BC_5 heterocycle (**3**, Fig 3) from the formal insertion of a carbene unit into one of the B-C bonds. The product crystallizes in the P-1 space group, indicating a 50:50 racemate of **3** in the unit cell. The geometry about the boron center is trigonal planar [angular sum = 359.9(2)°] and the biphenyl backbone has a slight twist [interplanar angle = 9.9(2)°].



Scheme 1. Reaction of trimethylsilyldiazomethane with **2Ph**.

To determine if another equivalent of trimethylsilyldiazomethane would react with **2Ph**, the 1:1 reaction of trimethylsilyldiazomethane with **3** was conducted at room temperature. Gas evolution was observed upon addition and *in situ* ^{11}B NMR spectroscopy indicated conversion after 20 minutes to a new resonance at 75.4 ppm, shifted downfield from **3** (c.f. 65.8 ppm). After work up, colorless crystals were isolated in a 45% yield. Alternatively, the same product could be obtained by reacting **2Ph** with trimethylsilyldiazomethane directly in a 1:2 stoichiometric ratio. Redissolving the solids in C_6D_6 and acquiring an ^{1}H NMR spectrum revealed two singlets at -0.07 ppm and -0.59 ppm integrating in a 9:9 ratio, shifted upfield from trimethylsilyldiazomethane (-0.04 ppm). Singlets at 3.24 ppm and 2.70 ppm, each integrating to one, indicate the presence of two aliphatic protons. A single crystal X-ray diffraction study unambiguously identified the compound as the BC_6 heterocycle **4** from a second carbene insertion into the other $B\text{-}C_{biphenyl}$ bond of **2Ph**. The X-ray crystal structure revealed that the product is a single *meso* isomer in which the trimethylsilyl groups are oriented *cis* with respect to each other.[70] The BC_6 ring adopts a boat-like conformation which does not include a plane of symmetry about the boron heteroatom (Fig S-16), rationalizing the presence of non-equivalent ^{1}H NMR signals for the two trimethylsilyl groups and the aliphatic protons assigned to those on the chiral carbon centers adjacent to boron.[71] The geometry at boron is trigonal planar [angular sum = 360.0(2)°], and the twist in the biphenyl group is significantly more pronounced with an interplanar angle of 48.7(2)° [c.f. **3** = 9.9(2)°].

The limit of the reactivity of **2Ph** was examined by conducting the reaction with excess trimethylsilyldiazomethane at 80 °C upon which, only the BC_6 product **4** was observed by ^{1}H and ^{11}B NMR spectroscopy. Examining the corresponding reaction of excess trimethylsilyldiazomethane with the borole variant, **1**, only gave the BC_5 product (**G**) from reaction with one

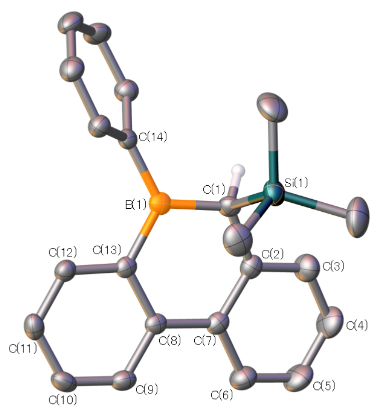


Figure 3. Solid-state structure of **3**. Hydrogen atoms are omitted for clarity (except at the chiral center), and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B(1)-C(1) 1.541(3), C(1)-Si(1) 1.948(2), C(1)-C(2) 1.500(3), C(2)-C(7) 1.406(3), C(7)-C(8) 1.484(3), C(8)-C(13) 1.422(3), C(13)-B(1) 1.551(3), B(1)-C(14) 1.570(3), C(13)-B(1)-C(14) 122.26(18), C(13)-B(1)-C(1) 116.48(16), C(14)-B(1)-C(1) 121.17(16).

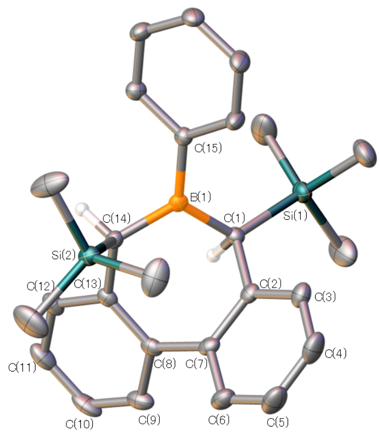


Figure 4. Solid-state structure of **4**. Hydrogen atoms are omitted for clarity (except at chiral centers), and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B(1)-C(1) 1.587(3), C(1)-C(2) 1.523(2), C(2)-C(7) 1.409(3), C(7)-C(8) 1.486(3), C(13)-C(14) 1.509(2), C(14)-Si(2) 1.9302(17), C(14)-B(1) 1.567(3), B(1)-C(15) 1.568(3), C(14)-B(1)-C(15) 119.08(15), C(14)-B(1)-C(1) 117.36(15), C(15)-B(1)-C(1) 123.54(15).

equivalent. Upon heating to 80 °C for 24 hours, an indiscernible mixture was observed by *in situ* ^{11}B and ^{1}H NMR spectroscopy.

In summary, the reactions of trimethylsilyldiazomethane with 9-phenyl-9-borafluorene result in the sequential insertion of two carbene units, one into each of the endocyclic B-C bonds of the central BC_4 ring. This represents the first example in which insertion into both B-C bonds is observed for a 9-borafluorene. Interestingly, the chemistry of pentaphenylborole differs as only a single insertion occurs cleanly. The results further demonstrate the potential of 9-borafluorenes to serve as reagents for the preparation of polycyclic boron species.

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Conflicts of interest

There are no conflicts to declare.

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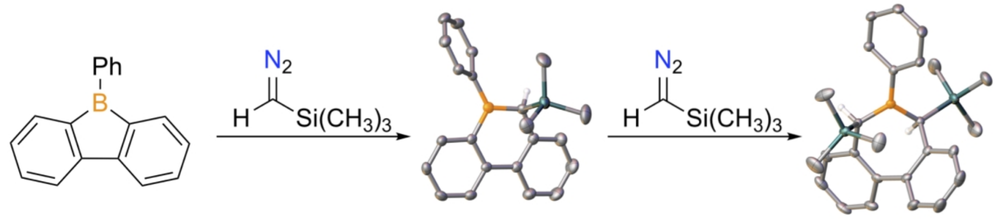
70. From the experiments it is not clear if the observed *meso* isomer is the kinetic or thermodynamic product.
71. A variable temperature ^{1}H NMR spectroscopy experiment from -60 °C to 90 °C in toluene-d^8 did not reveal any signs of coalescence of the signals.



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