

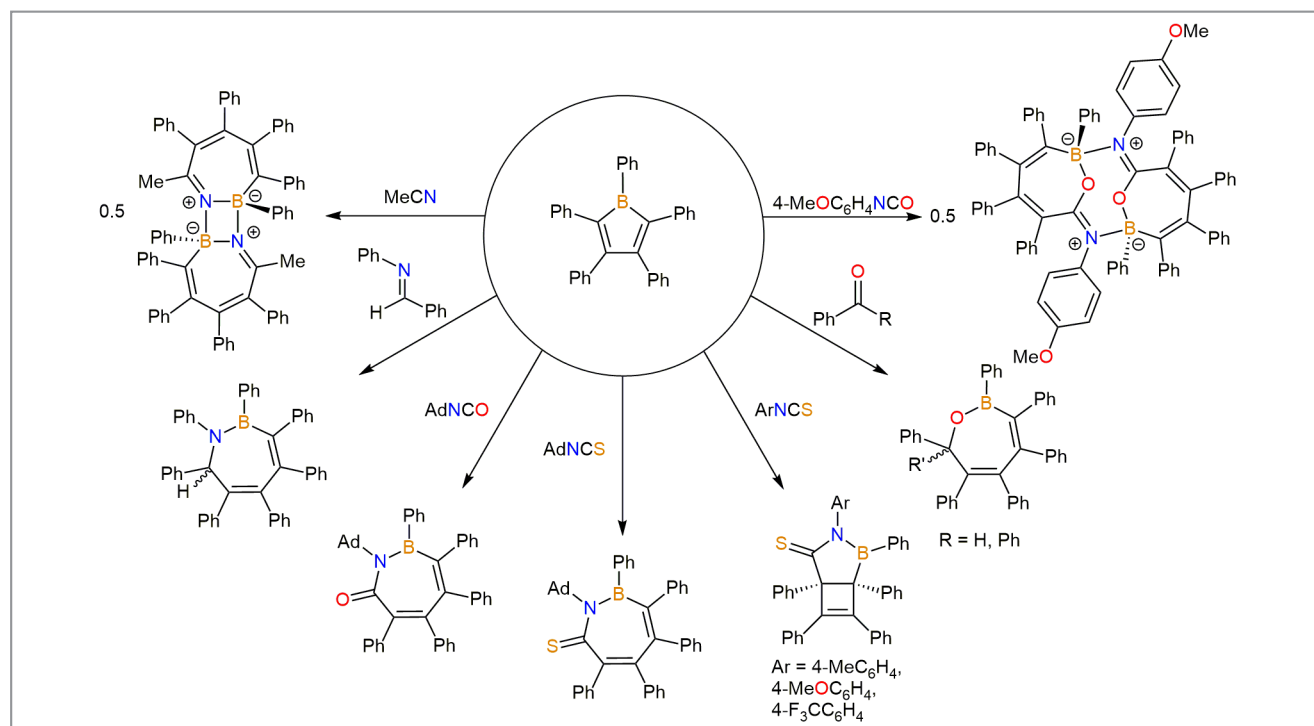
Developing the Chemistry of Boroles to Access Larger Boracycles

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Boron heterocycles are emerging as an attractive class of molecules due to their promise in pharmaceuticals and electronic materials. The first drug containing a boron heterocycle approved by the US FDA was tavaborole in 2014 for the treatment of onychomycosis, a nail fungus.¹ “In regard to applications in electronic materials, when the vacant orbital on boron is in conjugation with an unsaturated system it lowers the energy of the π^* orbital in the molecule, often resulting in properties desirable for organic light emitting diodes (OLEDs) and organic photovoltaic devices (OPVs),” explained Professor Caleb Martin from Baylor University (Waco, Texas, USA). He continued: “Despite the utility of boron heterocycles, there remain challenges in accessing tricoordinate species due to their propensity to form undesirable four-coordinate compounds when nucleophiles are added. Our approach to accessing boron heterocycles is to utilize boroles, unsaturated BC_4 heterocycles, as reagents.² These compounds have diverse reactivity with a Lewis acidic boron center and diene, both of which are accentuated by the anti-aromatic state of the four- π -electron ring system.”

Although boroles have been known since 1969, Professor Martin pointed out that their reactivity had not been investigated until recently. “Our efforts have been focused on developing boroles as reagents for heterocycles via ring-expansion reactions. Unsaturated 1,2-dipolar organic molecules (nitrile, isocyanate, isothiocyanate, imine, ketone, aldehyde) insert into the endocyclic B–C bond to furnish seven-membered rings (Scheme 1)^{3–5},” said Professor Martin.

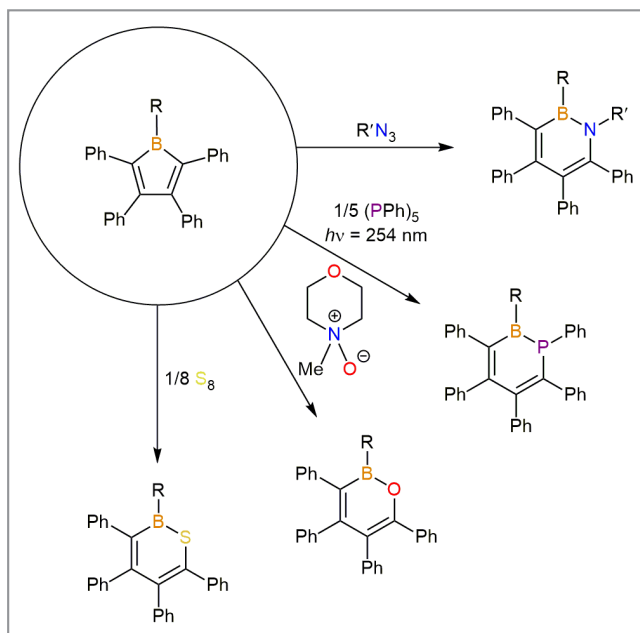
He went on to explain that – with the view of incorporating Group 15 elements – azides serve as a nitrene source and photolyzing $(PPh)_3$ acts as phosphinidene synthon to generate the corresponding 1,2-azaborine and 1,2-phosphaborine ring systems (Scheme 2).^{6,7} “Considering Group 16, the reactions of *N*-methylmorpholine *N*-oxide and elemental sulfur furnish the 1,2-oxaborine and 1,2-thiaborine heterocycles, respectively.^{8,9} In the 1,1-insertion products, incorporation of the lone-pair-bearing heteroatom adjacent to boron represents a two- π -electron substitute for a C=C unit in benzene,” remarked Professor Martin. He continued: “These systems represent hybrid inorganic/organic analogues of benzene which



Scheme 1 Insertion of unsaturated 1,2-dipolar molecules into pentaphenylborole

are planar delocalized systems, are polar, and have significant redshifts in the fluorescence emission for the central ring in comparison to their benzene relative.”

In an effort to enhance the electronic properties of the heteroarenes, the group has been investigating variants of boroles with different groups fused to the central BC_4 ring.



Scheme 2 Synthesis of heteroarenes from boroles

Professor Martin said: “9-Borafluorene is an analogue with a biphenyl backbone and this species also engages in insertion reactions to make six- and seven-membered rings, although it is not as reactive as boroles (Scheme 3).”^{10,11}

“Related to 9-borafluorenes, our group has prepared a borole derivative with a bis(o-carborane) framework in place of the biphenyl backbone (Figure 1),” explained Professor Martin. He concluded: “Efforts are ongoing to further develop compounds containing unsaturated BC_4 rings as reagents for the generation of boracycles that will be of interest to the inorganic, organic, and materials communities.”

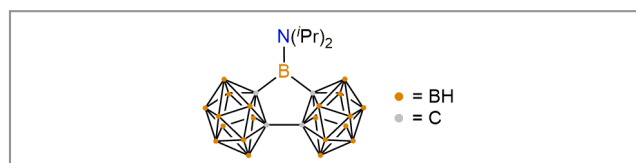
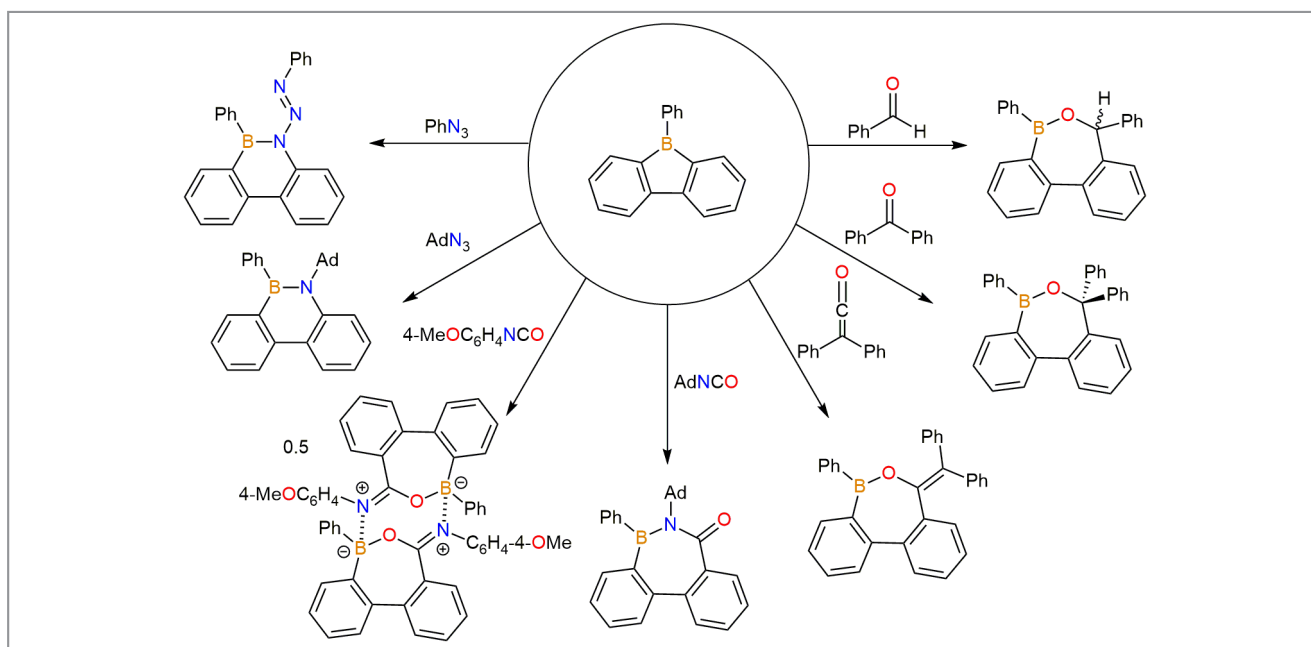


Figure 1 Analogue of 9-borafluorene with a bis(o-carborane) backbone

Finally, Professor Martin paid tribute to his team, saying: “The members of my group, both past and present, are thanked for their invaluable contributions since the inception of this project in 2014.”

Martin Fenske

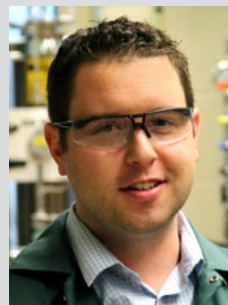


Scheme 3 Intermolecular insertion reactions of 9-phenyl-9-borafluorene

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About the author



Prof. C. Martin

Caleb Martin grew up in New Brunswick, Canada and attended Mount Allison University (Canada) for his BSc, conducting research with Glen Briand and Steve Westcott. In 2007 he moved to Western University (Canada) for his PhD, which focused on chalcogen and phosphorus chemistry with Paul Ragogna. He then moved to the USA to work for Guy Bertrand on carbene chemistry at University of California Riverside and University of California San Diego. In 2013, he accepted a position at Baylor University (Texas, USA). His research program is aimed at exploring the reactivity and properties of unusual boron compounds.