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A Synthesis of Aromatic Five- and Six-Membered B–N Heterocycles via Ring Closing Metathesis

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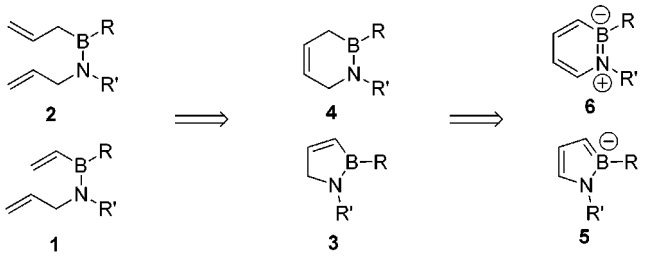
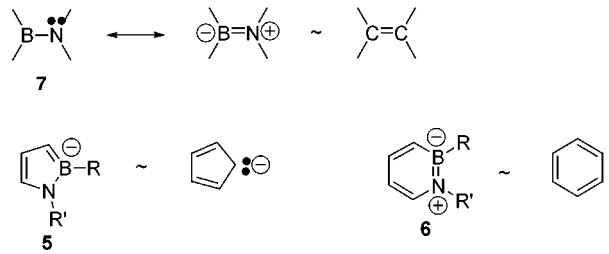
ABSTRACT



The ring closing metathesis on appropriate vinyl or allyl aminoboranes (1 or 2) gives azaboracycloalkenes (3 or 4) which can be converted to azaborolides (5) or azaborines (6).

Aminoboranes **7** have substantial B−N π-bond character which makes them isoelectronic with olefins.[1−6] The B−N heterocycles, 1,2-azaborolide (**5**) and 1,2-azaborine (**6**), are isoelectronic with cyclopentadienide and benzene, respectively (Scheme 1). In 1980 Schmid reported the synthesis of *N*-*tert*-butyl- and *N*-trimethylsilyl-1,2-azaborolide **5a** and **5b**, which have been used as replacement ligands for Cp in a number of transition metal complexes.[7,8] The recent report in the patent literature that Zr complex **8a** is a good precatalyst for the polymerization of olefins has increased the interest in **5**.[9] 1,2-Azaborines were reported in the early 1960s by Dewar[10] and by White.[11] However, the claims of

Scheme 1



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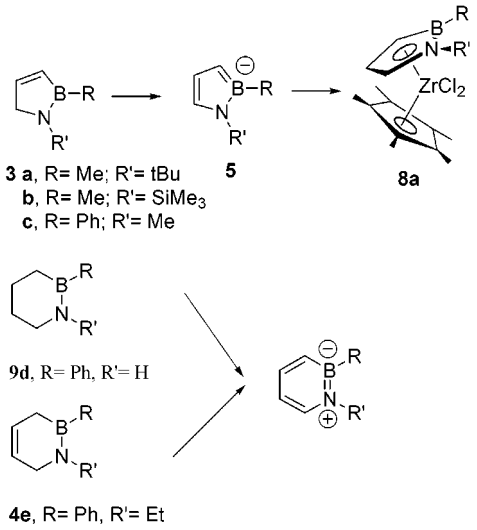
aromaticity of **6** were supported only by slender experimental data. Although a number of ring-fused derivatives of **6** have been reported, investigation of monocyclic 1,2-azaborines has been minimal.[12] However, several recent computational studies on **6** suggest it has considerable stability.[13,14]

A good general synthesis of **5** and **6** would greatly facilitate the study of these interesting heterocycles. The Schmid synthesis of **5a**,**b** involved LTMP deprotonation of **3a** or **3b**, while the White synthesis of **6d** involved Pd-catalyzed dehydrogenation of **9d**. On this basis it seemed likely that azaboracycloalkenes **3** and **4** should be good precursors to **5** and **6**, respectively. In principle, **3** and **4** should be available using the ring closing metathesis (RCM) on appropriate vinyl or allyl aminoboranes (Scheme 2).[15,16]

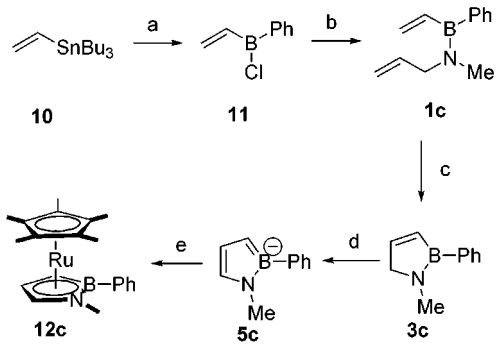
Scheme 2



RCM using the Grubbs catalyst ($(Cy_3P)_2(PhCH)RuCl_2$) is tolerant of a variety of oxygen, sulfur, and nitrogen functional groups and has been used to prepare alkenylboronates,[17] but to the best of our knowledge, it has not previously been applied to organoboron heterocycles. We wish to report that **5c** and **6e** can be obtained in high yield by easy reaction sequences involving RCM.

The Schmid azaborolide syntheses were limited to *N-tert*-butyl and *N*-trimethylsilyl derivatives.[7] To examine other substitution patterns, we chose initially to investigate the synthesis of the *B*-phenyl *N*-methyl derivative **5c** (Scheme 3). Treatment of tributylvinyl tin[18] (**10**) with phenylboron dichloride gave phenyl vinyl boron chloride (**11**) in 78% yield. Reaction of **11** with allylmethylamine in pentane containing triethylamine afforded a 95% yield of aminoborane **1c**. The substantial π-bond character of the B−N bond makes rotation about the bond slow on the NMR time scale.[19] The ^{1}H and ^{13}C NMR spectra of **1c** are consistent with it existing as a 1:1 mixture of B−N rotomers. However, the two rotomers are readily interconverted since the mixture undergoes RCM in high yield. Thus, upon treatment of **1c** with 5 mol % of Grubbs catalyst in CH_2Cl_2 at 25 °C for 10 h, cyclization occurred smoothly to give **3c** in 82% yield. Reaction of **3c** with LDA in ether gave 81% conversion to azaborolide **5c**. The ^{1}H, ^{11}B, and ^{13}C NMR chemical shift values for the ring atoms of **5c** closely follow those reported for the corresponding positions of **5a** and **5b**.[7,8] Reaction **5c** with $[Cp^*RuCl]_4$ afforded expected sandwich complex **12c**.[7c]

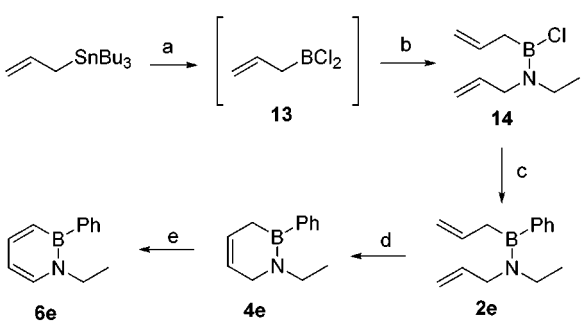
Scheme 3[a]



[a] Key: (a) $PhBCl_2$, pentane; (b) $(C_3H_5)MeNH$, Et_3N; (c) $(Cy_3P)_2(PhCH)RuCl_2$, CH_2Cl_2; (d) LDA; (e) $[Cp^*RuCl_4]$.

Azaborine **6e** was prepared by an analogous route illustrated in Scheme 4. Allyltributyltin[20a] reacted with BCl_3 in pentane at −78 °C to afford allylboron dichloride (**13**) which was not isolated.[20b] In situ addition of ethylallylamine

Scheme 4[a]



[a] Key: (a) BCl_3, pentane; (b) $(C_3H_5)EtNH$, Et_3N; (c) PhLi; (d) $(Cy_3P)_2(PhCH)RuCl_2$; (e) DDQ, pentane.

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at −78 °C followed by triethylamine gave adduct **14** which was isolated by distillation in 68% yield. The reaction of **14** with phenyllithium afforded an 81% yield of aminoborane **2e**. Both **14** and **2e** display complex NMR spectra which indicate the presence of B−N rotomers. The treatment of **2e** with 5 mol % of Grubbs catalyst in CH_2Cl_2 at room temperature for 10 h gave an 86% yield of the ring-closed product **4e**. To our delight, the reaction of **4e** with DDQ in pentane at 35 °C for 24 h afforded azaborine **6e** as a pale yellow oil which was contaminated with a small amount of biphenyl. On column chromotography, pure **6e** was obtained in 58% yield. The ^{1}H, ^{11}B, and ^{13}C NMR spectra of **6e** are consistent with our expectation that it is weakly aromatic. In fact, Clark and Kranz have calculated the ^{11}B and ^{13}C NMR chemical shift values for the parent 1,2-azaborine **6f**[14] from their ab initio MO calculations using the IGLO method.[21] Comparison of their calculated chemical shift values for **6f** with our experimental values for **6e** show a modest level of agreement (see Figure 1). The fact that this prediction preceded experiment enhances our confidence in their MO treatment.

In summary, we have shown that the Grubbs RCM procedure allows efficient synthesis of 1,2-azaborolide **5c** and 1,2-azaborine **6e**. Since the B- and N-substituents can likely be changed, the syntheses give promise of being general. We are presently attempting to extend the RCM procedure for the syntheses of other heteroaromatic compounds.

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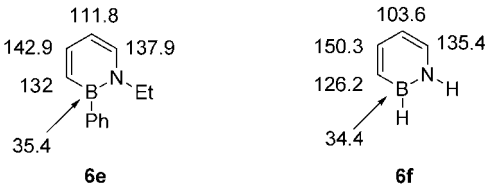

Figure 1. Experimental ^{11}B and ^{13}C chemical shifts for **6e** and the calculated chemical shifts for **6f**.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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