Syntheses of Ring-Fused B−N Heteroaromatic Compounds

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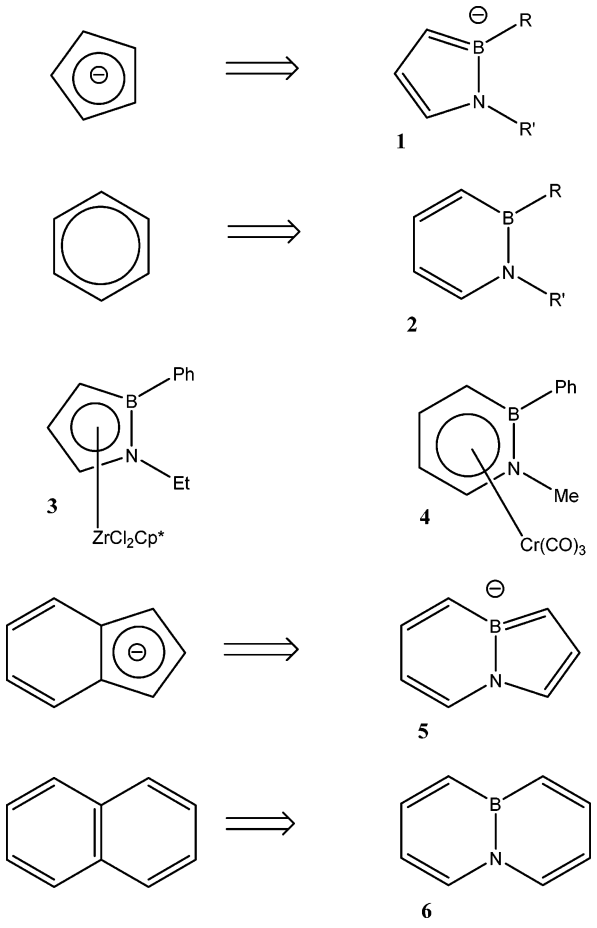
3a,7a-Azaborindene (**14**) has been prepared by two multistep syntheses using the Grubbs ring-closing metathesis from appropriate B-vinyl,N-allyl-aminoboranes. **14** was deprotonated by $KN(SiMe_3)_2$ to give 3a,7a-azaborindenylpotassium (**5**). The reaction of **5** with Cp^*ZrCl_3 afforded the corresponding Zr(IV) complex **18**, which on activation with excess methylaluminoxane, forms a good catalyst for the polymerization of ethylene. The reaction of **5** with methylene chloride and BuLi gave 4a,8a-azaboranaphthalene (**6**), which is isoelectronic and isostructural with naphthalene. DFT calculations on **6** gave a structure that is in good agreement with X-ray diffraction data.

Introduction

Cyclopentadienyl and benzene are the most important aromatic rings and can be regarded as progenitors of all other five- and six-membered aromatic rings. The replacement of one of the C−C π-bonds of cyclopentadienyl and benzene by an isoelectronic B−N π-bond leads to 1,2-azaborolyl (**1**) and 1,2-dihydro-1,2-azaborine (**2**), respectively. 1,2-Azaborolyl has been used as a replacement ligand for Cp in a variety of transition metal complexes.[1−4] Of particular interest is the observation that 1,2-azaborolyl zirconium(IV) complexes, e.g. **3**, have high activity as Ziegler−Natta catalysts for the polymerization of olefins.[5] The aromatic character of 1,2-dihydro-1,2-azaborines has been of interest to chemists for more than 40 years.[6−10] Computational studies suggest that **2** has a considerable delocalization energy.[9] Derivatives of **2** can form arene-like metal complexes, such as **4**.[10]

We have been interested in extending the chemistry of **1** and **2** by developing syntheses of the fused-ring compounds 3a,7a-azaborindenyl (**5**)[11a] and 4a,8a-azaboranaphthalene (**6**).[11b] **5** and **6** are isoelectronic and possibly isostructural with indenyl and naphthalene. Yet since **5** and **6** are constructed only from B−N heterocyclic rings, they should be electronically perturbed from their carbocyclic parents. **6** was first reported in 1968 in a masterful paper by Dewar and Jones.[12] Unfortunately the yield of their synthesis was abysmally low (0.2%), which has limited subsequent investigations of **6**. We have previously reported on the synthesis of **5**.[3b] We report here on details of our work on **5** and on a new efficient synthesis of **6**.



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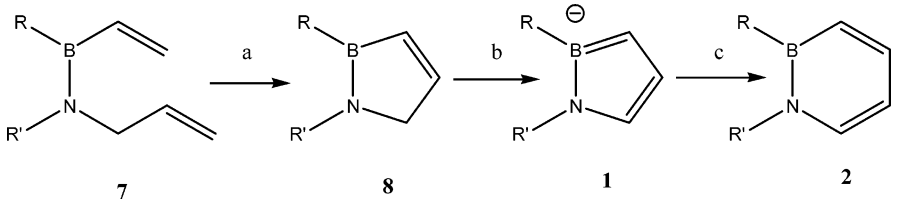
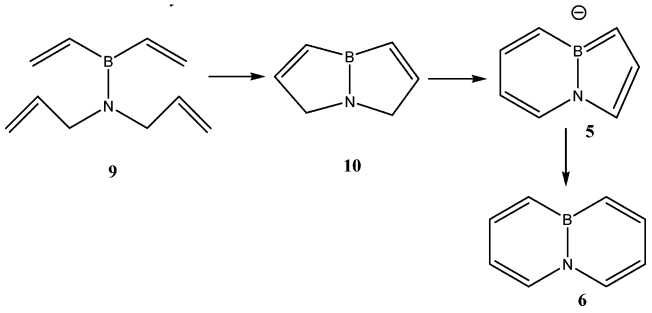
Scheme 1. Syntheses of 1 and 2[a]



[a] Key: a, Grubbs catalyst; b, LDA; c, CH_2Cl_2/base.

Scheme 2. Initial Synthetic Plan



Results and Discussion

Syntheses. 1,2-Dihydro-1,2-azaborines (**2**) have been prepared by a carbenoid ring expansion from the corresponding 1,2-azaborolides (**1**), which in turn can generally be prepared by LDA deprotonation of their conjugate acids (**8**).[10] The Grubbs ring-closing metathesis (RCM) on appropriate B-vinyl,N-allyl aminoboranes **7** usually affords **8**.[3a] See Scheme 1. Hence our initial plan was to convert aminoborane **9** to **10** by RCM and then convert **10** to **5** and **6** by sequential ring expansions (Scheme 2).

The reaction of dibutyldivinylstannane with BCl_3 in pentane at −78 °C afforded divinylboron chloride.[13] Although this sensitive boron halide can be isolated and characterized by NMR spectroscopy, it is more convenient to treat it in situ with 2 equiv of diallylamine to afford **9** directly in 79% yield. Upon treatment of **9** with 5 mol % of Grubbs catalyst at 25 °C in methylene chloride, the monocyclized product **11** was obtained in 62% yield. Even under forcing conditions (higher temperature, excess catalyst) the [5,5]-fused-ring compound **10** was not observed. This observation is precedented by the failure of certain 1-allyl-2-vinyl heterocycles to form [5,5]-fused rings on attempted RCM.[14] We speculate that **10** is somewhat ring strained and its formation may not be thermodynamically favored.

Deprotonation of **11** with LDA in THF gave a 67% yield of the azaborolide **12**, which could be isolated as a brown solid. Treatment of **12** with LDA and methylene chloride at −78 °C followed by warming lead to the ring-expanded product **13** in 30% yield. The treatment of **13** with 5 mol % of Grubbs catalyst in methylene chloride led to RCM formation of the [6,5]-ring-fused product in 30% yield. Apparently the more favorable geometry about the six-membered 1,2-dihydro-1,2-azaborine ring allowed formation of the ring-closed product. Compound **14** is isoelectronic with indene. Interestingly, the odor of **14** closely resembles that of indene. Although this preparation of the B−N analogue of indene outlined in Scheme 3 was successful, the overall yield of **14** from the dibutyldivinylstannane was rather modest (3%). Thus an alternate route has been developed.

Allyltributylstannane reacted with BCl_3 at −78 °C in pentane to give allylboron dichloride, which was not isolated.[15] In situ addition of 1 equiv of diallylamine followed by 1 equiv of triethylamine afforded **15** in 95% yield. Reaction of **15** with vinylmagnesium bromide gave aminoborane **16** in 84% yield. The treatment of **16** with 5 mol % of Grubbs catalyst in methylene chloride converted it to **17** in 59% yield. Finally the oxidation of **17** with DDQ gave **14** in 30% yield. This sequence, outlined in Scheme 4, allows the preparation of **14** in 14% overall yield from the starting stannane. Thus it represents a significant improvement over the prior preparation.

Azaborindene **14** is readily deprotonated by potassium bis(trimethylsilyl)amide in toluene to afford **5** as a yellow powder in 85% yield. The ^{1}H NMR spectrum of **5** in either DMSO-d_6 or THF-d_8 could be only partially assigned since signals for four of the ring protons occur as a very closely spaced pattern centered at δ 6.70 (DMSO). Fortunately after the addition of 18-crown-6 ether to **5** followed by dissolution in benzene-d_6, a beautiful first-order ^{1}H NMR spectrum was obtained. This spectrum is completely consistent with structure **5**. The reaction of **5** with Cp*$ZrCl_3$ in ether gave a 60% yield of complex **18**, for which an X-ray crystal structure has been obtained.

Finally the reaction of **5** with methylene chloride and BuLi gave a 43% yield of 4a,8a-azaboranaphthalene (**6**) as pale yellow crystals, which have a strong naphthalene-like odor. The mp and ^{1}H and ^{11}B NMR spectra of **6** show that it is identical to the material originally reported by Dewar and Jones.[12,16] Furthermore we have obtained an X-ray crystal structure for **6** that establishes its structure. The overall yield of the above preparation from commercially available allyltributylstannane is 5.6%. This is nearly a 30-fold improvement over the Dewar−Jones preparation. Thus 4a,8a-azaboranaphthalene is now more readily available for study.

Polymerization Studies. Indenyl zirconium(IV) derivatives have been widely used as highly active and stereoselective catalysts for olefin polymerization.[17] Thus it was of major interest to prepare and study the polymerization activities of

(11) Chemical Abstracts names: (a) 1H-[1,2]azaborolo[1,2-*a*][1,2]-azaborinyl. (b) [1,2]Azaborino[1,2-*a*][1,2]azaborine.

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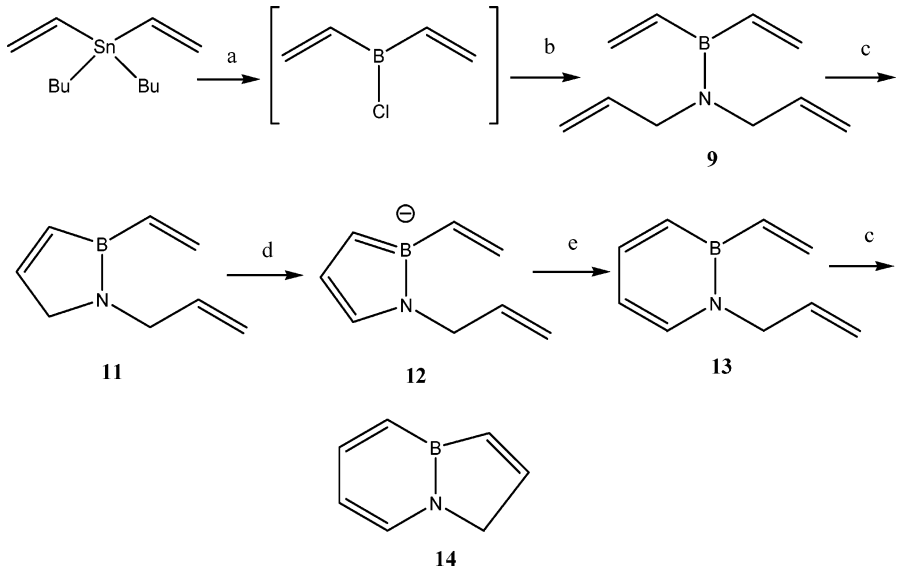
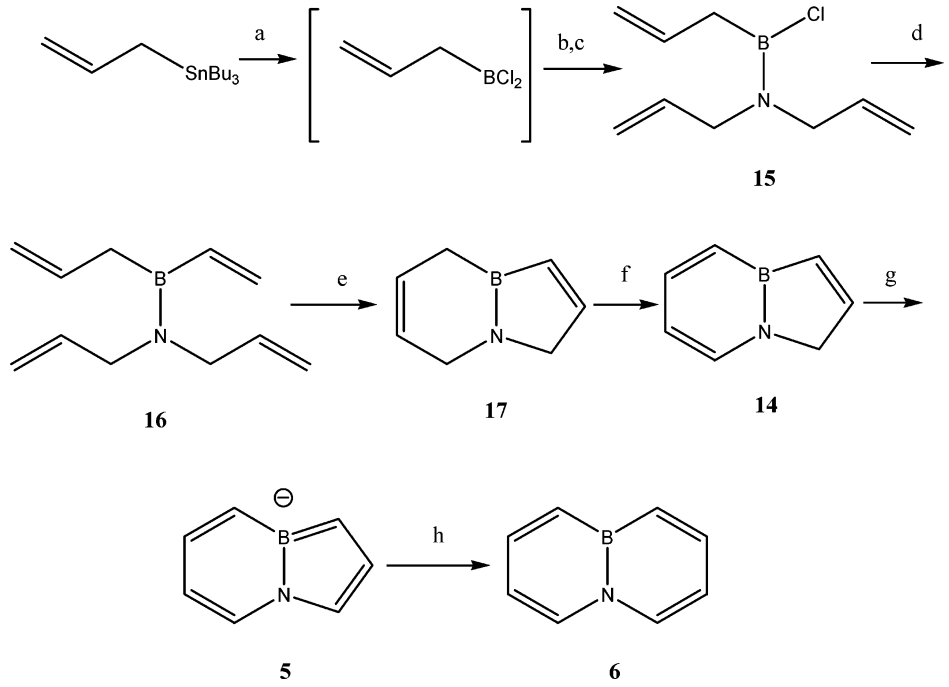
Scheme 3. Preparation of Azaborindene[a]



[a] Key: a, BCl_3; b, $HN(allyl)_2$; c, Grubbs catalyst; d, LDA; e, CH_2Cl_2/base.

Scheme 4. Alternate Synthesis of 14 and Its Conversion to 5 and 6[a]



[a] Key: a, BCl_3; b, $HN(allyl)_2$; c, NEt_3; d, C_2H_3MgBr; e, Grubbs catalyst; f, DDQ; g, $KN(SiMe_3)_2$; h, CH_2Cl_2/BuLi.

azaborindenyl zirconium(IV) complexes. As previously reported, the reaction of **5** with Cp^*ZrCl_3 afforded a 60% yield of **18**. Similarly the reaction of **17** with LDA followed by Cp^*ZrCl_3 gave a 55% yield of complex **19**. The crystal structures of **18** and **19** show that the complexes have very similar structures, which closely resemble that of $Cp^*(Ind)ZrCl_2$[18] (**20**).

On activation by 1000 molar excess of methylaluminoxane (MAO) in a hydrocarbon solvent, **18** and **19** form active catalysts for the polymerization of ethylene and 1-octene.[19] The polymerization results are summarized in Table 1, which also shows data for complex **3**. All three complexes gave polyethylene with the incorporation of approximately 1% 1-octene. It has been estimated that complex **3** is approximately 10 times more active than Cp_2ZrCl_2 for ethylene polymerization.[3a] Thus it seems safe to conclude that **18** and **19** must form more active catalysts than does Cp_2ZrCl_2.

Table 1. Comparison of the Efficiency of Ethylene/1-Octene Polymerization of 3, 18, and 19

complex	efficiency (g polymer/mol Zr atom)	ref
3	234×10^4	3c
18	120×10^4	this work
19	66×10^4	this work

MAO-activated indenyl zirconium(IV) complexes are usually found to be more active catalysts than are the corresponding Cp zirconium(IV) complexes. For example Alt and co-workers reported that $Cp^*(Ind)ZrCl_2$ was 3 times more active than Cp^*-

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(19) For details of polymerization conditions see refs 3c and 5b and Ashe, A. J., III; Fang, X.; Hokky, A.; Kampf, J. W. *Organomettalics* **2004**, *23*, 2197.

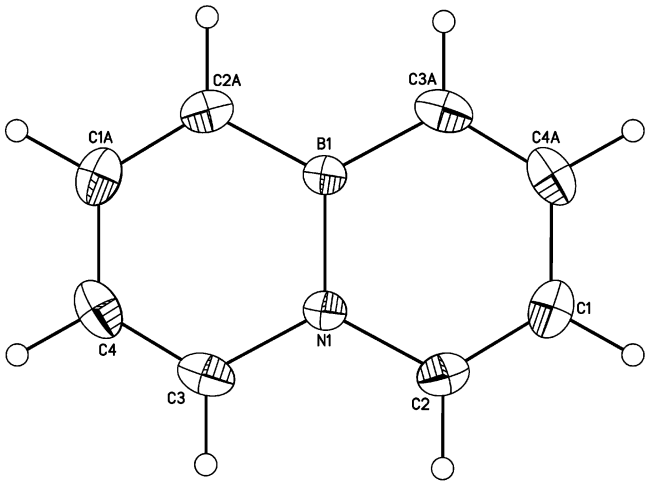


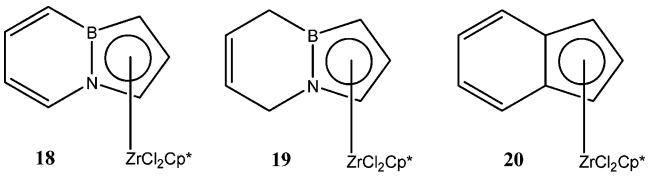
Figure 1. Solid-state structure of **6** (ORTEP). B(1) and N(1) are not crystallographically distinguished. Thermal ellipsoids are at the 50% probability level.

Table 2. Comparison of Experimental and Calculated Bond Distances (Å) for 6

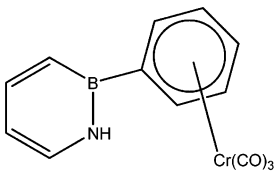
bond	experimental (X-ray)	calculated (DFT)
B(1)−N(1)	1.461(1)	1.479
C(1)−C(4)	1.431(1)	1.430
N(1)−C(2)	1.445(1)[a]	1.383
B(1)−C(3)	1.455(1)[a]	1.522
C(1)−C(2)	1.360(1)[b]	1.370
C(3)−C(4)	1.357(1)[b]	1.362

[a] Distances N(1)−C(2) and B(1)−C(3) are averaged by disorder. [b] Distances C(1)−C(2) and C(3)−C(4) are averaged by disorder.

$(Cp)ZrCl_2$.[18] Thus it was surprising to find that azaborolyl complex **3** was 2 times more reactive than azaborindenyl complex **18**. However the difference in substitution between the complexes makes this comparison tenuous. The structural similarity of **18** and **19** makes them a better pair for comparison. The 2-fold greater activity of **18** vs **19** indicates that the BN complexes show the normal effect. The significant polymerization activity of **18** and **19** makes the syntheses of their bridged derivatives attractive targets for future investigations.



18 **19** **20**



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X-ray and DFT Structures for 6. It was of interest to obtain structural data for 4a,8a-azaboranaphthalene. Crystals of **6** suitable for an X-ray diffraction study were obtained by recrystallization from pentane. The molecular structure of **6** is illustrated in Figure 1, and bond distances are listed in Table 2. It was found that **6** is isostructural with naphthalene. There is an inversion center located at the midpoint of the B−N bond, which means that the boron and nitrogen atoms are not crystallographically distinguished. This partial disorder severely limits the structural information available for **6**. To a first approximation the B−N bond length and the C(1)−C(4) bond length are unaffected by this disorder. However the C(2)−N and the B−C(3) distances must average, as do the C(1)−C(2) and C(3)−C(4) distances.

The B−N bond distance (1.461(1) Å) of **6** is 0.03 Å longer than that of **21** (1.430(5) Å). Similarly the C(1)−C(4) distance (1.431(1) Å) of **6** is 0.02 Å longer than the corresponding C−C distances of **21**.[20] The longer bonds in the fused-ring **6** vs the monocyclic **21** find analogy in the difference between naphthalene and benzene. The C−C bond at the ring-fusion of naphthalene is also 0.03 Å longer than C−C bond of benzene, and the C(2)−C(3) bond of naphthalene is 0.02 Å longer than that of benzene.[21−23]

There are several prior theoretical studies of **6**, although there are no reported computational structural data.[24] To obtain more information about the structure of **6**, we have performed density functional theory (DFT) calculations at the B3LYP/6-31G* level. The calculated distances are tabulated in Table 2. The calculated B−N distance is 0.018 Å longer than the crystallographic distance, while the calculated and crystallographic distances for C(1)−C(4) are identical. The calculated mean values for the heteroatom−C distances (1.453 Å) and the mean of C(1)−C(2) and C(3)−C(4) distances (1.366 Å) are within 0.01 Å of the crystallographic distances. Thus the calculated and experimental structures for **6** are in reasonable agreement.

Summary. In summary the synthesis of the B−N fused analogue of indenyl **5** allows exploration of its coordination chemistry. Zr(IV) complex **18** behaves as a perturbed indenyl complex. On activation by excess MAO, **18** shows significant activity as a polymerization catalyst. The carbenoid ring expansion of **5** allows a facile preparation of the B−N fused naphthalene analogue **6**. The way is now open for further exploration of the chemistry of these fused-ring aromatics.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried using standard procedures. High-resolution mass spectra were recorded on a VG-250S spectrometer with an electron inact at 70 eV. The NMR spectra were obtained using either a Varian INOVA 400 or 500, a Brucker WH 300, or an AM 300 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4Si. The ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Elemental analyses were obtained by the Analytical Services of the Department of Chemistry at the University of Michigan using a Perkin-Elmer 240 CHN analyzer.

(Diallylamino)divinylborane (9). A solution of dibutyldivinylstannane (56 g, 0.194 mol) in 30 mL of pentane was added dropwise to a solution of BCl_3 (20.7 g, 0.176 mol) at −78 °C. The mixture was stirred at −78 °C for 1 h and at 25 °C for 30 min. After cooling to −78 °C the mixture was further stirred until it solidified. Diallylamine (17.1 g, 0.176 mol) was added via a syringe followed by triethylamine (17.8 g, 0.176 mol). The mixture was stirred for 10 h. After filtration and removal of the volatiles the product was

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obtained by vacuum distillation (21.9 g, 79%), bp 38 °C at 0.05 Torr (oil bath temperature was kept under 80 °C). ^{1}H NMR (C_6D_6, 400 MHz): δ 6.39 (dd, 2H, J = 19.0, 14.3 Hz, CHB), 5.91 (m, 4H, alkene), 5.60 (m, 2H, alkene), 5.00 (m, 4H, alkene), 3.60 (d, 4H, J = 5.2 Hz, CH_2). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 138.6 (br), 136.7, 132.8, 115.9, 52.1. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 37.8. HRMS (EI, *m*/*z*): calcd for $C_{10}H_{15}{}^{11}BN$ ([M − H]$^+$), 160.1298; found, 160.1305. Anal. Calcd for $C_{10}H_{16}BN$: C, 74.57; H, 10.01; N, 8.70. Found: C, 75.21; H, 10.18; N, 8.74.

1-Allyl-2,5-dihydro-2-vinyl-1,2-1*H*-azaborole (11). A solution of **9** (7.3 g, 45.3 mmol) in 90 mL of CH_2Cl_2 was added dropwise to a flask containing bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (5 mol %) at −78 °C. The mixture was stirred at −78 °C for 1 h and at 25 °C for 9 h. After slow removal of the solvent at 0 °C, the product was obtained by vacuum distillation as a clear colorless liquid (62%), bp 25 °C at 0.05 Torr. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.83 (d, 1H, J = 10 Hz, C(3)H, 6.52 (d, 1H, J = 10 Hz, C(4)H, 6.43 (dd, 1H, J = 16, 14.4 Hz, vinyl BCH), 6.18 (dd, 1H, J = 16, 4 Hz, cis-vinylH), 6.05 (d(br), 1H, J = 14.4 Hz, trans-vinylH), 5.59 (m, 1H, allyl), 4.90 (m, 2H, allyl), 3.65 (d, 2H, J = 4 Hz, ring-CH_2), 3.44 (m, 2H, allyl-CH_2). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 148.3, 137.3, 134.5, 134.2 (br), 133.6 (br), 114.9, 60.3. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 37.4. HRMS (EI, *m*/*z*): calcd for $C_8H_{13}{}^{11}BN$ (M^+), 134.1141; found, 134.1147.

Lithium 1-Allyl-2-vinyl-1,2-azaborolide (12). A solution of **11** (4.3 g, 32 mmol) in 15 mL of ether was added dropwise to a solution of LDA (1 equiv) in 12 mL of ether at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 10 h. The volatile components were removed under reduced pressure, and the residue was washed with 2 × 20 mL of pentane. The residue was dried under vacuum to give the product as a brown solid (67%). ^{1}H NMR (THF-d_8, 400 MHz): δ 6.39 (dd, 1H, J = 19.4, 13.5 Hz, vinyl BCH═), 5.92 (m, 1H, allyl), 5.79 (m, 2H, H(4) and H(5)), 5.29 (dd, 1H, J = 19.4, 5.1 Hz, trans-vinylH), 5.11 (dd, 1H, J = 13.5, 5.1 Hz, cis-vinylH), 4.92 (dq, 1H, J = 17.2, 2 Hz, trans-allylH), 4.84 (dq, 1H, J = 10.3, 2 Hz, cis-allylH), 4.34 (dd, 1H, J = 5.1, 2 Hz, H(3)), 4.23 (dt, 2H, J = 5.5, 2 Hz, NCH_2). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 141.1, 140.6 (br), 117.9, 113.0, 112.2, 112.1, 86.2 (br), 51.4. ^{11}B NMR (THF-d_8; 115.5 MHz): δ 27.6.

1-Allyl-1,2-dihydro-2-vinyl-1,2-azaborine (13). A suspension of **12** (2.53 g, 18.1 mmol) in 15 mL of CH_2Cl_2 was treated dropwise with a solution of LDA (1.93 g, 18.1 mmol) in 12 mL of ether at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 10 h. The volatile components were removed under reduced pressure. The residue was extracted with 20 mL of pentane. After filtration and removal of the solvent at 0 °C, the brown oily residue was vacuum distilled to give the product as a clear colorless liquid (0.79 g, 30%), bp 28 °C at 0.05 Torr. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.51 (dd, 1H, J = 11, 6.6 Hz, H(4)), 7.11 (d, 1H, J = 6.6 Hz, H(6)), 6.57 (d, 1H, J = 6.6 Hz, H(3)), 6.52 (dd, 1H, J = 19.5, 13.5 Hz, vinyl-BCH), 6.17 (dd, 1H, J = 19.5, 4.1 Hz, trans-vinylH), 6.07 (t, 1H, J = 6.6 Hz, H(5)), 5.92 (dd(br), 1H, J = 13.5, 2.8 Hz, cis-vinylH), 5.49 (m, 1H, allyl), 4.78 (m, 1H, allyl), 4.67 (m, 1H, allyl), 3.83 (d, 2H, J = 2.8 Hz, allyl-CH_2). ^{13}C NMR (C_6D_6, 90.6 MHz): δ 142.9, 138.5, 138 (br), 136.0, 130.9, 129 (br), 115.7, 111.3, 55.7. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 33.1. HRMS (EI, *m*/*z*): calcd for $C_9H_{12}{}^{11}BN$ (M^+), 145.1063; found, 145.1064. Anal. Calcd for $C_9H_{12}BN$: C, 74.55; H, 8.34; N, 9.66. Found: C, 74.40; H, 8.52; N, 9.48.

3a,7a-Azabora-1-indene (14). A solution of **13** (3.24 g) in 20 mL of CH_2Cl_2 was added dropwise to a solution of bis(cyclohexylphosphine)benzylideneruthenium(IV) dichloride (5 mol %) in 20 mL of CH_2Cl_2 at 25 °C. Bubbles formed intensively. The mixture was stirred at 25 °C for 10 h. The reaction was followed by GC-MS. The volatile components were removed under reduced pressure at 0 °C. The product was obtained by vacuum distillation as a clear, colorless liquid, bp 25−26 °C at 0.05 Torr. HRMS: *m*/*z* calcd for $C_7H_{10}{}^{11}BN$ 117.0750, found 117.0752. ^{1}H NMR (C_6D_6, 400 MHz): δ 3.52 (br s, 2H, CH_2N), 6.11 (t, J = 6.3 Hz, 1H, C(5)H), 6.52 (m, 2H, C(1)HC(2)H), 6.94 (d, J = 6.3 Hz, 1H, C(4)H), 7.06 (d, J = 11.1 Hz, 1H, BCH), 7.61 (dd, J = 11.1, 6.3 Hz, 1H, C(6)H). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 34.2. ^{13}C NMR (C_6D_6, 100.5 MHz): δ 58.8, 109.5, 124 (br), 133.6 (br), 135.3, 143.2, 144.2. Anal. Calcd for $C_7H_{10}BN$: C, 71.87; H, 6.91; N, 11.98. Found: C, 71.77; H, 7.04; N, 11.85.

Table 3. Crystal and Data Collection Parameters for 6

empirical formula	C_8H_8BN
fw	128.96
temp K	123(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2(1)/c$
a, Å	7.961(2)
b, Å	5.989(2)
c, Å	8.112(2)
β, deg	114.284(7)
V, Å^3, Z	352.6(2), 2
calcd density, Mg/m^3	1.215
abs coeff, mm^{-1}	0.070
F(000)	136
cryst size, mm	0.50 × 0.40 × 0.22
limiting indices	$-12 \le h \le 11$; $-9 \le k \le 9$; $-13 \le l \le 13$
no. of reflns collected/unique	9633/1533
abs corr	none
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	1533/0/62
final R indices ($I > 2\sigma(I)$)	R1 = 0.0491, wR2 = 0.1247
largest diff peak and hole, e/Å^3	0.381 and −0.168

3a,7a-Azaborindenylpotassium (5). A 0.5 M toluene solution of potassium bis(trimethylsilyl)amide (41.0 mL, 20.5 mmol) was added dropwise to a solution of **14** (2.4 g, 20.5 mmol) in 15 mL of toluene at −78 °C. The mixture was stirred at −78 °C for 4 h and then 2 h at −20 °C. The solution was decanted, and the solid residue was washed first with toluene and then pentane. A yellow powder was obtained (2.7 g, 85%). ^{1}H NMR (500 MHz, C_6D_6 and 18-crown-6): δ 8.29 (dd, J = 6.4, 0.7 Hz, 1H, C(4)H); 7.70 (d, J = 11 Hz, 1H, C(7)H); 7.49 (dd, J = 11.1, 6.3 Hz, 1H, C(6)H; 7.38 (dd, J = 5.9, 2.2 Hz, 1H, C(2)H); 7.26 (t, J = 20 Hz, 1H, C(3)H; 6.49 (td, J = 6.3, 1.2 Hz, 1H, C(5)H; 5.70 (d, J = 5.9 Hz, 1H, C(1)H). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84 (d, J = 6.2 Hz, 1H, C(4)H); 6.65−6.76 (m, 4H); 5.90 (m, 1H); 4.77 (d, J = 5.9 Hz, 1H, C(1)H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 127.1, 123.0, 121.6, 104.5, 103.3, 88 br. C(7) not observed. ^{11}B NMR (115.5 MHz, C_6D_6): δ 25.8.

4a,8a-Azaboranaphthalene (6). Methylene chloride (25 mL) was added to 3a,7a-azaborindenylpotassium (**5**) (2.7 g, 17.41 mmol) at −78 °C. Then a solution of n-BuLi (6.70 mL, 17.50 mmol, 2.5 M in hexane) was added. The black mixture was stirred for 4 h at −78 °C and another 2 h at 25 °C. After removing the solvent, an orange liquid was obtained. The pure product was obtained by chromatography on silica gel using pentane as eluant. On concentration of the solution, pale yellow crystals of **6** were formed (1.22 g, 43%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.18 (d, J = 7.0 Hz, 2H, C(4)H); 7.67 (dd, J = 11.0, 7.0 Hz, 2H, C(2)H; 7.30 (d, J = 11.0 Hz, 2H, C(1)H); 6.81 (dt, J = 7.0, 1.5 Hz, 2H, C(4)H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 138.4 (C(2)); 134.1 (C(4)); 132.0 (br, C(1); 114.3 (C(3)). ^{11}B NMR (160.4 MHz, DMSO): δ 28.1. HRMS: calcd for $C_8H_8{}^{11}BN$ 129.0750, found 129.0749. Anal. Calcd for $C_8H_8{}^{11}BN$: C, 74.49; H, 6.26; N, 10.86. Found: C, 74.56; H, 6.42; N, 10.69.

Single-Crystal X-ray Crystallography. Crystals of **6** suitable for X-ray diffraction were obtained from recrystallization from pentane. Crystallographic and data collection parameters are collected in Table 3. An ORTEP drawing of **6** showing the atom-numbering scheme used in refinement is illustrated in Figure 1.

Selected bond distances are collected in Table 2. Additional crystallographic data are available in the Supporting Information.

DFT Calculations. DFT calculations at the B3LYP/6-31G* level were performed using Spartan (Wavefunction, Inc.).

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Supporting Information Available: X-ray characterization of **6**. Copies of the ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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