Synthesis of 1,2-Dihydro-1,2-azaborines and Their Conversion to Tricarbonyl Chromium and Molybdenum Complexes

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1,2-Dihydro-1,2-azaborines (**1c**, **1d**, and **1e**) have been prepared by the reaction of the corresponding 2,3-dihydro-1*H*-1,2-azaborol-3-yllithium reagents (**1c**, **1d**, and **1e**). The reaction of **1e** with $Py_3Mo(CO)_3$ and $BF_3{\cdot}OEt_2$ affords $Mo(CO)_3$ complex **5e**, while the reaction of **1c** with $Cr(CH_3CN)_3(CO)_3$ affords $Cr(CO)_3$ complex **6c**. X-ray structures of **5e** and **6c** show that the metals are η^6-bound to the 1,2-dihydro-1,2-azaborine rings.

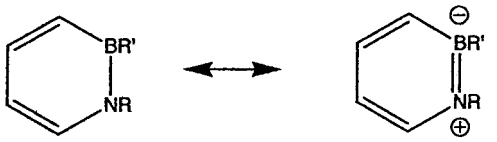
Introduction

The replacement of an adjacent pair of carbon atoms of benzene by boron and nitrogen yields the isoelectronic 1,2-dihydro-1,2-azaborine (**1**). Derivatives of **1** were first prepared in very low yield by Dewar in 1962[1] and White in 1963.[2] The original experimental characterization of **1** was modest and relied heavily on the "aromatic" UV spectrum of **1a**.[2,4b] Although a number of ring-fused derivatives of **1** have been prepared,[3] there have been few subsequent reports on monocyclic 1,2-dihydro-1,2-azaborines.[4,5] In 1992 Kranz and Clark carried out a thorough ab initio MO study of **1**, which allowed them to conclude that the electron delocalization of **1** is less than that of benzene due to electron localization by the B−N group.[6,7] We recently prepared 1,2-dihydro-1,2-azaborine **1d** via a DDQ oxidation of the corresponding 1,2,3,6-tetrahydro-1,2-azaborine.[8] The NMR spectra of **1d** are consistent with those of a weakly aromatic compound, as predicted by the computational work.[6]

We report here that 1,2-dihydro-1,2-azaborines may be generally prepared in good yield using a carbenoid ring expansion from lithium 1,2-azaborolides **4**.[9] The availability of **1** has allowed us to prepare metal carbonyl complexes **5** and **6**. Structural data show that the 1,2-dihydro-1,2-azaborine rings in these complexes are η^6-coordinated aromatic rings.

Results and Discussion

The reaction of lithium cyclopentadienide with CH_2Cl_2 and CH_3Li (the Katz reaction) gives benzvalene **8** and benzene in the ratio of 4:1.[10] Mechanistic studies have shown that the reaction proceeds through the intermediacy of chlorocarbene generated from CH_2Cl_2 and base.[11] The electrophilic chlorocarbene attacks the aromatic anion to give an exocyclic carbene intermediate **7**. 1,2-Addition of the carbene center to the adjacent double bond of **7** gives the bicyclo[1.1.0] butane product **8**, while 1,2-vinyl migration to the carbene center leads to ring expansion. Analogous reactions of in situ generated chlorocarbene with substituted cyclopentadienyl or cyclohexadienyl anions are important methods for producing the bicyclo[1.1.0]butane ring system.[12,13] Quite naturally major attention has focused on these interesting polycyclic products,[14] but in all cases simple ring expansion is also important. In certain cases the ring expansion products are major.[15] For example, the reaction of lithium stannacyclohexadienide (**9**) with CH_2Cl_2/CH_3Li gives predominately stannepin **10**.[16,17] We wished to explore whether this type of ring expansion could be used to convert 1,2-azaborolides (**4**) into 1,2-dihydro-1,2-azaborines (**1**). Certain 1,2-azaborolides are readily available. In 1980 Schmid prepared lithium 1-*tert*-butyl-2-methyl-1,2-azaborolide **4e**, which was converted to



1 a,R=H,R'=Ph
b,R=H,R'=H
c,R=Me,R'=Ph
d,R=Et,R'=Ph
e,R=t-Bu,R'=Me

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(4) (a) Culling, G. C.; Dewar, M. J. S.; Marr, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 1125. (b) Davies, K. M.; Dewar, M. J. S.; Rona, P. *J. Am. Chem. Soc.* **1967**, *89*, 6294.
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(10) (a) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782. (b) Katz, T. J.; Roth, R. J.; Acton, N.; Carnahan, E. J. *J. Org. Chem.* **1999**, *64*, 7663.
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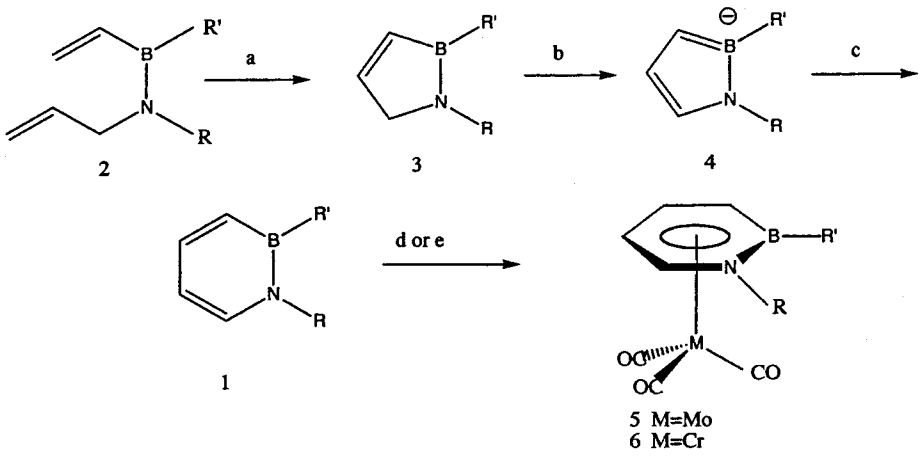
Scheme 1



Key: (a) $(PCy_3)_2Cl_2Ru(CHPh)$; (b) LDA; (c) CH_2Cl_2,base; (d) $Py_3Mo(CO)_3$, BF_3/OEt_2; (e) $(CH_3CN)_3Cr(CO)_3$.

Scheme 2

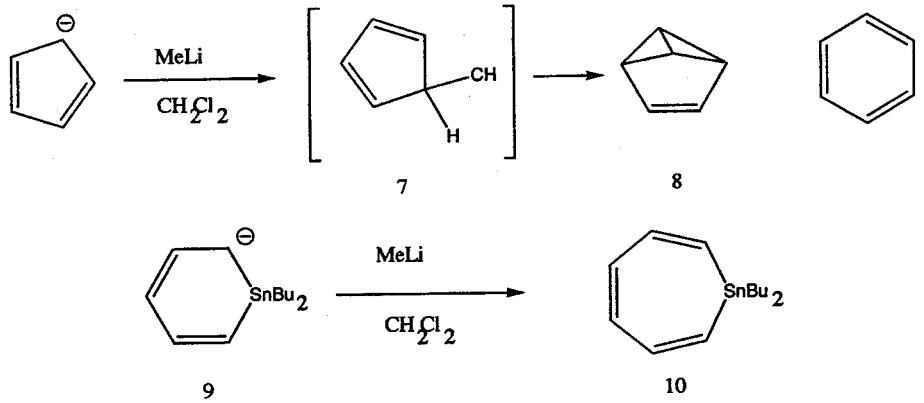


Table 1. ^{11}B and ^{13}C NMR Chemical Shift Data for 1,2-Dihydro-1,2-azaborines ($C_4H_4BR'NR$) and Selected Other Compounds

R,R′ (compd)	$\delta(^{11}B)$	δ(C3)	δ(C4)	δ(C5)	δ(C6)	R,R′
Me, Ph (**1c**)[a]	35.2	131.4	142.9	111.3	139.9	133.4, 127.8, 127.6 (Ph), 42.3 (Me)
Et, Ph (**1d**)[b]	35.4	132.0	142.9	111.8	138.0	133.0, 128.0, 127.6 (Ph), 48.1, 18.2 (Et)
t-Bu, Me (**1e**)[b]	37.7	n.o.[d]	141.5	109.9	135.2	31.8 (t-Bu), n.o. (BMe)[d]
t-Bu, Me (**5e**)[a]	26.6	n.o.[d]	103.9	82.3	107.1	31.7 (t-Bu), n.o. (BMe)[d]
Me, Ph (**6c**)[a]	22.9	86.4	104.4	82.5	107.3	134, 129.4, 128.2 (Ph), 45.5 (Me)
H, Ph (**13a**)[c,e]	32.2	123.5	133.5	107.7	133.5	
H, Me (**13b**)[c,f]	36	127	132.8	107.9	132.8	

[a] Solvent, $CDCl_3$. [b] Solvent, C_6D_6. [c] Solvent, C_4D_8O. [d] n.o., not observed. [e] Reference 21b. [f] Reference 22.

several Cp-like transition metal complexes.[18,19] In an initial experiment we added excess CH_2Cl_2 to **4e** at −78 °C. On warming to 25 °C followed by workup, 1-*tert*-butyl-1,2-dihydro-2-methyl-1,2-azaborine **1e** was isolated as a yellow oil in 25% yield. The ^1H, ^{11}B, and ^{13}C NMR spectra (Tables 1 and 2) and other spectroscopies are consistent with the 1,2-dihydroazaborine structure. It is interesting that the UV spectrum of **1e** in hexane shows bands at 223 and 283 nm. The low-energy band is only slightly blue shifted from the 289 nm band originally reported for **1a**.[2,4b]

1,2-Azaborolides **4c** and **4d** can be prepared by LDA deprotonation of their conjugate acids (**3c** and **3d**), which in turn can be prepared by ring-closing metathesis on the appropriate B-vinyl, N-allyl aminoboranes **2**.[8] This allows more general exploration of the ring expansion route to 1,2-dihydro-1,2-azaborines. The optimized method for conversion of **4c** to **1c** involves the addition of excess CH_2Cl_2 to solid **4c** at −78 °C followed by treatment with 1 equiv of LDA in ether at −78 °C. Reaction occurs during the slow warming to 25 °C. On workup **1c** was isolated as a yellow oil in 67% yield. In the same manner **4d** was converted to **1d** in 64% yield. The sample was identical to **1d** previously obtained by DDQ oxidation of 1-ethyl-1,2,3,6-tetrahydro-2-phenyl-1,2-azaborine.

Mechanism for the Formation of Azaborines. To probe the mechanism for the conversion of **4** to **1**, **4c** was treated with CD_2Cl_2 under conditions similar to

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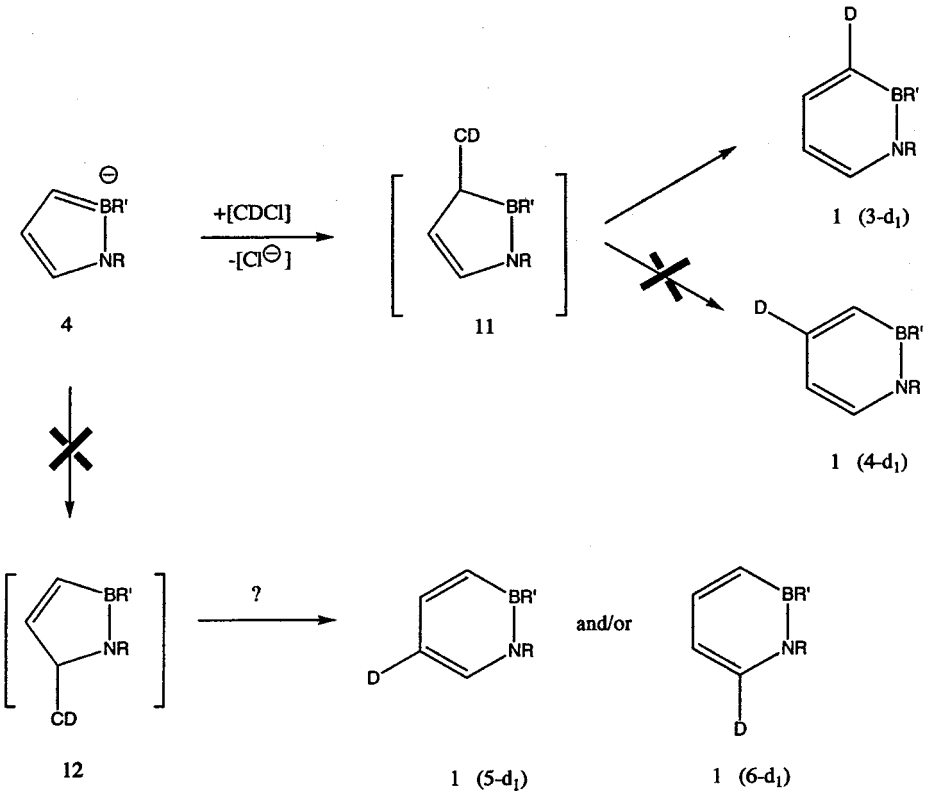
Table 2. ^{1}H NMR Parameters of 1,2-Dihydro-1,2-azaborines ($C_4H_4BR'NR$) and Selected Other Compounds

R,R′ (compd)	$\delta(H_3)$	$\delta(H_4)$	$\delta(H_5)$	$\delta(H_6)$	$^3J_{3,4}$Hz	$^3J_{4,5}$Hz	$^3J_{5,6}$Hz	R,R′
Me, Ph (**1c**)[a]	6.97	7.75	6.49	7.32	10.5	6.6	6.6	7.68 (oPh), 7.49 (mPh), 7.44 (pPh), 3.70 (Me)
Et, Ph (**1d**)[a]	6.90	7.71	6.48	7.35	10.8	6.8	6.8	7.60 (oPh), 7.45 (mPh), 7.41 (pPh), 3.92 (Et), 1.38 (Et)
t-Bu, Me (**1e**)[a]	6.61	7.41	6.15	7.53	10.6	6.6	7.0	1.61 (t-Bu), 1.00 (Me)
t-Bu, Me (**5e**)[a]	4.50	5.85	5.08	6.51	9.2	5.5	5.5	1.19 (t-Bu), 0.88 (Me)
Me, Ph (**6c**)[a]	4.79	5.88	5.32	6.11	9.2	6.2	5.1	7.68, 7.43 (Ph), 3.14 (Me)
H, Ph (**13a**)[b,c]	6.85	7.18	6.10	7.18	10.2	6.9	6.9	
H, Me (**13b**)[b,c,e]	6.47	7.28	6.18	7.28	9.8	7.0	7.0	

[a] Solvent, $CDCl_3$. [b] Solvent, C_4D_8O. [c] For consistency boron is numbered 2. [d] Reference 22. [e] Reference 21b.

Scheme 3



those described above. The 3-deuterioisomer of **1c** was obtained exclusively, and no other isomers were detected by NMR spectroscopy. In a similar manner **4e** was converted exclusively to the 3-deuterio isomer of **1e**. The exclusive formation of the 3-deuterio isomer of **1** is consistent with initial attack of chlorocarbene at C(3) of **4** followed by the loss of chloride to form intermediate **11**. Migration of boron to the carbene center of **11** would form the 3-deuterio isomer of **1** as illustrated in Scheme 3.

In principle the chlorocarbene might attack azaborolide **4** at either C(3) or C(5). However attack at C(5) would afford intermediate **12**, which might be expected to give the 5- and/or 6-deuterio isomers of **1**. It has been observed that other electrophiles attack azaborolides at C(3).[19] This regioselectivity is a likely consequence of the larger negative charge density at C(3), which is suggested by the higher field ^{13}C NMR signal of C(3) relative to C(5). The preferential migration of boron over carbon to the carbene center of **11** is analogous to the large migratory aptitude of boron found in other sigmatropic migrations.[20]

NMR Spectra of 1,2-Dihydro-1,2-azaborines. The ^{11}B and ^{13}C NMR spectra of 1,2-dihydro-1,2-azaborines (**1c**, **1d**, **1e**) are summarized in Table 1, and the ^{1}H NMR spectra are summarized in Table 2. Data for the corresponding B-substituted boratabenzenes, lithium 1-phenylboratabenzene **13a**[21] and lithium 1-methylboratabenzene[22] **13b**, are included for comparison.

The ^{13}C NMR spectra of 1,2-dihydro-1,2-azaborines show an alternating pattern in which the signals for ring carbon atoms that are α or γ to boron are shielded, while those that are α or γ to nitrogen are deshielded. An analogous pattern is shown by boratabenzene and pyridinium salts. Indeed the observed spectrum of **1c** can be approximately reproduced by averaging the appropriate signals for lithium 1-phenylboratabenzene **13a**[21] and 1-methylpyridinium **14**[23] as illustrated in Figure 1.

The ^{13}C NMR chemical shifts are particularly useful since they correlate with π-charge densities of aromatic and heteroaromatic rings.[24,25] Clark and Kranz have calculated ^{13}C NMR shifts of the parent 1,2-dihydro-

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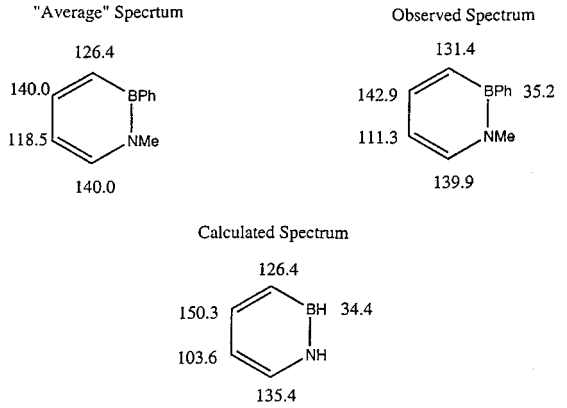

Figure 1. Observed ^{11}B and ^{13}C NMR chemical shifts of **1c** compared with averaged ^{13}C chemical shifts of **13** and **14** and the calculated ^{11}B and ^{13}C chemical shifts of **1b**.

1,2-azaborine **1b**[6] using the IGLO method.[25,26] Comparison of their calculated chemical shift values for **1b** (Figure 1) with the empirical values for **1c** shows that there is a reasonable level of agreement. In particular the alternating pattern of shielding and deshielding of adjacent atoms is nicely reproduced.

The ^{11}B NMR shift values of 1,2-dihydro-1,2-azaborines (δ 35.2−37.7) are in the normal range for boramines.[27] Clark and Kranz's calculated value for **1b** (δ 34.4) is in excellent agreement with the empirical values.

The ^1H NMR signals for the four nonequivalent ring protons of the three 1,2-dihydro-1,2-azaborines show a first-order pattern in the range δ 6.15−7.75. The chemical shift values of the protons that are α (H_3) and γ (H_5) to boron are approximately 1 ppm upfield from those β(H_4, H_6) to boron. The same relative separation of α and γ vs β proton signals is shown for boratabenzenes (**13**). For both types of compounds the upfield signals are consistent with partial negative charge at the α- and γ-positions. For the 1,2-dihydro-1,2-azaborines the values of the vicinal coupling constants $^3J_{3,4}$ (10.5−10.8 Hz) are much larger than $^3J_{4,5}$ and $^3J_{5,6}$. This effect must be due to boron since it is also shown by boratabenzenes[22] and borepins.[17,28b]

Tricarbonyl Chromium and Molybdenum Complexes. It was of interest to explore the coordination chemistry of 1,2-dihydro-1,2-azaborines. The reaction of **1e** with tricarbonyltris(pyridine)molybdenum and BF_3·OEt_2 gave adduct **5e** in 51% yield as yellow crystals, which were recrystallized from hexane. The reaction of **1c** with tricarbonyltris(acetonitrile)chromium in THF afforded a 32% yield of adduct **6c** as red needles. The ^1H, ^{11}B, and ^{13}C NMR signals of 1,2-dihydro-1,2-azaborine rings of **5e** and **6c** are shifted markedly upfield in comparison to those of the free ligands, which indicates π-complexation.[28] In the case of **6c** the ^1H and ^{13}C NMR signals of the phenyl ring are relatively little affected by complexation. Since there are no prior structural data on 1,2-dihydro-1,2-azaborines, it was of interest to obtain crystal structures.

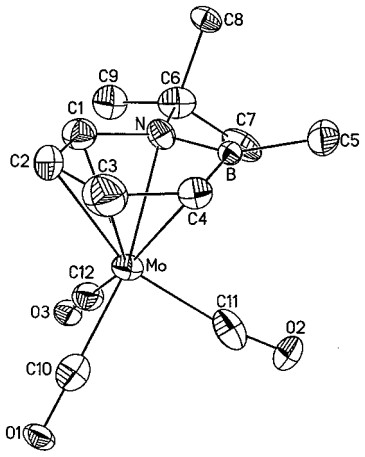

Figure 2. Molecular structure and atom labeling for **5e**.

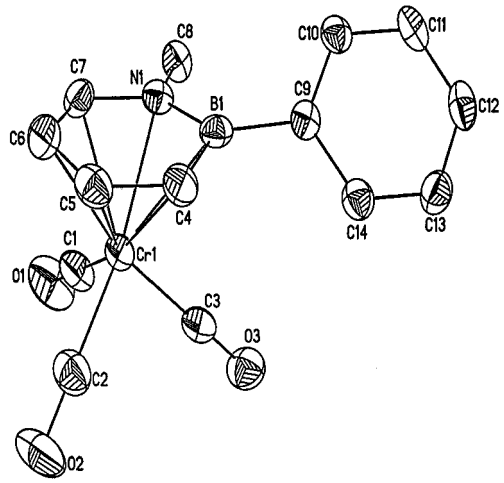

Figure 3. Molecular structure and atom labeling for **6c**.

Recrystallization of **5e** from hexane at −10 °C gave golden needles. Refinement showed that the crystals were pseudo-orthorhombic twins. Although the structure was solved, the quality of the structural parameters is relatively poorer than those subsequently obtained for **6c**. The molecular structure of **5e** is illustrated in Figure 2. A sample of **6c** suitable for X-ray diffraction was obtained by recrystallization from CH_2Cl_2/pentane. The molecular structure of **6c**, which is similar to that of **5e**, is illustrated in Figure 3, while selected bond distances are listed in Table 3.

The structure of **6c** consists of a near planar C_4BN ring which is η^6-bound to the $Cr(CO)_3$ unit in typical piano stool fashion. The B-phenyl ring is not coordinated and is canted relative to the C_4BN ring by 39°. The juxtaposition of the coordinated ring of **6c** relative to the metal carbonyl group resembles those of boratabenzene−$Mn(CO)_3$ complex **15**,[29] where one CO group

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Table 3. Selected Bond Distances (Å) for 6c

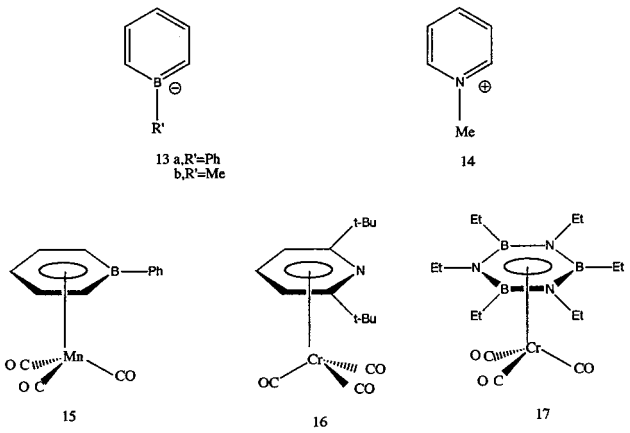
B(1)−N(1)	1.466(6)
B(1)−C(4)	1.510(6)
B(1)−C(9)	1.574(6)
B(1)−Cr(1)	2.366(5)
N(1)−C(7)	1.400(5)
N(1)−C(8)	1.479(5)
N(1)−Cr(1)	2.200(3)
Cr(1)−C(2)	1.840(4)
Cr(1)−C(3)	1.842(5)
Cr(1)−C(1)	1.848(5)
Cr(1)−C(7)	2.156(4)
Cr(1)−C(6)	2.201(4)
Cr(1)−C(5)	2.216(4)
Cr(1)−C(4)	2.254(4)
0(3)-C(3)	1.157(5)
0(2)-C(2)	1.151(5)
0(1)-C(1)	1.149(5)
C(4)−C(5)	1.394(6)
C(5)−C(6)	1.410(6)
C(6)−C(7)	1.375(6)
C(9)−C(14)	1.399(5)
C(9)−C(10)	1.402(5)
C(10)−C(11)	1.389(5)
C(11)−C(12)	1.379(6)
C(12)−C(13)	1.386(6)
C(13)−C(14)	1.377(6)

eclipses boron, and pyridine−$Cr(CO)_3$ complex **16**,[30] where one CO group is trans to nitrogen. This conformational feature has been found for metal carbonyl complexes of other boron and nitrogen heterocycles[31] and has been treated by MO studies.[32]

It also seems useful to compare the overall structure of **6c** with those of **15** and **16**. The intra-ring distances of the 1,2-dihydro-1,2-azaborine ring are typical of those of similarly coordinated aromatic ligands. Thus the range of C−C bond distances of **6c** (1.38−1.41 Å) is identical to that of **16** and only slightly different from that of **15** (1.40−1.42 Å). The intra-ring C−N bond of **6c** (1.40 Å) is somewhat larger than those of **16** (1.36, 1.37 Å), which may be due to the higher coordination of the nitrogen atom of **6c**. The B−N bond of **6c** (1.46 Å) is considerably longer than the usual values found for unconjugated aminoboranes (1.41 Å),[33] which suggests that its B−N π-bonding is delocalized. Interestingly the B−N bonds of (hexaethylborazine)$Cr(CO)_3$ (**17**)[31a] (1.46−1.47 Å) are very similar. Finally the intra-ring B−C bond (1.51 Å) of **6c** is very close to those of **15** (1.52 Å). The exocyclic B−C bonds are significantly longer for both **6c** (1.57 Å) and **15** (1.58 Å), consistent with their single-bond character.

The 1,2-dihydro-1,2-azaborine ring of **6c** shows a small deviation from planarity. The B atom is displaced away from Cr out of the plane defined by N(1) C(4) C(5) C(6) C(7) by 0.049(3) Å. The structure of **15** and those of most coordinated boron heterocycles shows similar displacements of the boron atoms away from the transition metals.[29,33] The B−Cr distance of **6c** (2.366(5) Å) is somewhat longer than the C−Cr distances (2.16−2.25 Å) and the Cr−N distance (2.20 Å). This is consistent with the larger size of boron and conforms to the pattern shown by other heterocyclic boron ligands.[34]

In summary, the structural data clearly demonstrate that 1,2-dihydro-1,2-azaborine can serve as an aromatic ligand. It would be particularly interesting to obtain structural data for an uncomplexed 1,2-dihydro-1,2-azaborine so that a structural comparison can be made with **6c**.



Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. The mass spectra were determined by using a VG-70S spectometer, while the NMR spectra were obtained by using either a Bruker WH-400, WH-360, or AM-300 spectrometer. The ^1H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to $SiMe_4$. The ^{11}B NMR spectra were referenced to external BF_3−OEt_2. The combustion analyses were determined by the Analytical Services Department of the Department of Chemistry, University of Michigan.

1,2-Dihydro-1-methyl-2-phenyl-1,2-azaborine (1c). A solution of LDA (1.13 g, 10.6 mmol) in 12 mL of ether was added dropwise to a suspension of 2,3-dihydro-1-methyl-2-phenyl-1*H*-1,2-azaborol-3-yllithium (**4c**)[8] (1.73 g, 10.6 mmol) in 20 mL of CH_2Cl_2 at −78 °C. The mixture was stirred at −78 °C for 2 h and was allowed to warm to 25 °C for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with 30 mL of pentane. After filtration and removal of pentane the crude product was isolated as a yellow oil (1.20 g, 67%). A pure sample of the product was obtained by column chromatography on silica gel, hexane elution. HRMS (EI): *m/z* calcd for $C_{11}H_{12}{}^{11}BN(M^+)$, 169.1063; found, 169.1065. Anal. Calcd for $C_{11}H_{12}BN$: C, 78.16; H, 7.16; N, 8.29. Found: C, 78.09; H, 7.17; N, 8.23.

3-Deuterio-1,2-dihydro-1-methyl-2-phenyl-1,2-azaborine (11c). In the same manner as above the reaction of **4c** with CD_2Cl_2 gave 66% of **11c** as a yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, J = 7.0 Hz, 1H, H(4)), 7.60 (d, J = 8.0 Hz, 2H, ArH), 7.43 (t, J = 8.0 Hz, 2H, ArH); 7.39 (t, J = 8.0 Hz, 1H, ArH), 7.28 (dd, J = 7.0, 1.1 Hz, 1H, H(6)), 6.41 (t, J = 7.0 Hz, 1H, H(5)), 3.65 (s, 3H, NMe). HRMS (EI): *m/z* calcd for $C_{11}{}^1H_{11}{}^2H_1{}^{11}BN$, 170.1126, found, 170.1127.

(*N*-Allyl,*N*-ethylamino)phenylvinylborane (2d). A solution of *N*-allyl,*N*-ethylamine (3.61 g, 42.5 mmol) in 10 mL of CH_2Cl_2 was added to a solution of phenylvinylboron chloride

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(6.4 g, 42.7 mmol) in 20 mL of CH_2Cl_2 at −78 °C with stirring. After the mixture had stirred for 1 h trimethylamine (4.3 g, 42.6 mmol) was added, causing a white precipitate to form. The reaction mixture was allowed to warm to 25 °C for 3 h. The solid was removed by filtration, and the solvent was removed in vacuo. The product was obtained by vacuum distillation as a clear colorless liquid (84%), bp 67−70 °C at 0.05 Torr. The ^{1}H NMR and ^{13}C NMR spectra are consistent with it existing as two B−N rotomers with a ratio of 1:1. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.42 (d, J = 8.0 Hz, 4H, ArH), 7.31−7.19 (m, 6H, ArH), 6.64 (dd, J = 19.0, 13.2 Hz, 1H, BCH), 6.57 (dd, J = 19.0, 13.2 Hz, BCH′), 6.02 (bt, J = 13.2 Hz, 2H, alkene), 5.80−5.50 (m, 4H, alkene), 5.12−4.91 (m, 4H, alkene), 3.68 (dt, J = 5.2, 1.7 Hz, 2H, =CCH_2), 3.51 (dt, J = 5.2, 1.7 Hz, 2H, =CCH_2′), 3.12 (q, J = 7.1 Hz, 2H, Et), 2.93 (q, J = 7.1 Hz, 2H, Et′), 0.99 (t, J = 7.1 Hz, 3H, Et), 0.81 (t, J = 7.1 Hz, 3H, Et′). ^{13}C NMR (C_6D_6, 100.6 MHz): shows two sets of signals. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.4. HRMS (EI): m/z calcd for $C_{13}H_{18}{}^{11}BN$ (M^+), 199.1532; found, 199.1528. Anal. Calcd for $C_{13}H_{18}BN$: C, 78.42; H, 9.11; N, 7.03. Found: C, 78.28; H, 8.59; N, 6.50.

1-Ethyl-2,5-dihydro-2-phenyl-1*H*-1,2-azaborole (3d). A solution of **2d** (17.2 g, 86.4 mmol) in 120 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (Grubbs' catalyst) (3.55 g, 4.31 mmol) in 40 mL of CH_2Cl_2 at 25 °C. The mixture was stirred at 25 °C for 10 h, after which the color had changed from purple-red to dark brown. The solvent was removed in vacuo, and the product (12.6 g, 85%) was obtained as a clear colorless liquid, bp 60 °C at 0.05 Torr. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.75 (d, J = 8.0 Hz, 2H, ArH), 7.33 (t, J = 8.0 Hz, 2H, ArH), 7.25 (t, J = 8.0 Hz, 1H, ArH), 6.93 (d, J = 8.1 Hz, 1H, vinyl), 6.60 (d, J = 8.1 Hz, 1H, vinyl), 3.51 (m, 2H, NCH_2CH=), 3.26 (q, J = 7.0 Hz, 2H, Et), 0.94 (t, J = 7.0 Hz, 3H, Et). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 148.5, 134.1, 132.1, 128.9, 128.1, 127.6, 60.3 (NCH_2C=), 41.4 (Et), 16.7 (Et). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 39.4. HRMS (EI): m/z calcd for $C_{11}H_{14}{}^{11}BN$ (M^+), 171.1219; found, 171.1224. Anal. Calcd for $C_{11}H_{14}BN$: C, 77.24; H, 8.25; N, 8.19. Found: C, 77.83; H, 8.45; N, 7.68.

1-Ethyl-2,3-dihydro-2-phenyl-1*H*-1,2-borol-3-yllithium (4d). A solution of LDA (3.13 g, 29.2 mmol) in 15 mL of ether was added to a solution of **3d** (5.0 g, 29.2 mmol) in 15 mL of ether at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 10 h. After removal of the solvent the residue was washed with 3 × 20 mL of pentane. The residue was dried under vacuum to give the product as a light yellow powder (3.9 g, 77%). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.05 (t, J = 8.0 Hz, 2H, ArH), 6.87 (t, J = 8.0 Hz, 1H, ArH), 5.91 (m, 1H, H_4), 5.86 (m, 1H, H_5), 4.16 (m, 1H, H_3), 3.78 (1, J = 7.0 Hz, 2H, Et), 1.27 (t, J = 7.0 Hz, 3H, Et). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 133.9, 123.8, 112.8, 111.9, 86.5 (br), 43.2 (Et), 19.6 (Et). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 29.4.

1-Ethyl-1,2-dihydro-2-phenyl-1,2-azaborine (1d). Solid **4d** (2.6 g, 14.7 mmol) was mixed with 20 mL of CH_2Cl_2 and cooled to −78 °C. A solution of LDA (1.57 g, 14.7 mmol) in 10 mL of ether was added to the above solution. The solid gradually dissolved. The mixture was stirred at −78 °C for 1 h and gradually warmed to 25 °C, during which time a fine precipitate formed. The mixture was stirred at 25 °C for 10 h. After removal of the solvent, the residue was extracted with 2 × 20 mL of pentane. After filtration and removal of pentane, the product was obtained as a yellow oil. A pure sample of the product (1.71 g, 64%) was collected by column chromatography on silica gel, hexane elution. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.52 (dd, J = 10.0, 7.0 Hz, 1H, H_4), 7.50 (d, J = 8.0 Hz, 2H, ArH), 7.21 (t, J = 8.0 Hz, 2H, ArH), 7.16 (t, J = 8.0 Hz, 1H, ArH), 7.00 (d, J = 10.0 Hz, 1H, H_3), 6.66 (d, J = 7.0 Hz, 1H, H_6), 6.18 (t, J = 7.0 Hz, 1H, H_6), 3.35 (q, J = 7.2 Hz, 2H, Et), 0.78 (t, J = 7.2 Hz, 3H, Et). HRMS (EI): m/z calcd for $C_{12}H_{14}{}^{11}BN$ (M^+), 183.1219; found, 183.1226. UV (pentane, nm): $\lambda(\epsilon)$ max 237 (2090), 282 (2610). Anal. Calcd for $C_{12}H_{14}BN$: C, 78.73; H, 7.71; N, 7.65. Found: C, 78.59; H, 7.65; N, 7.48.

1-*tert*-Butyl-1,2-dihydro-2-methyl-1,2-azaborine (1e). A solution of 1-*tert*-butyl-2,3-dihydro-2-methyl-1*H*-1,2-azaborol-3-yllithium in THF was prepared from 1-*tert*-butyl-2,3-dihydro-2-methyl-1*H*-2-methyl-1,2-azaborole (0.74 g, 5.40 mmol) and an excess of lithium 2,2,6,6-tetramethylpiperidide. The solvents were removed under reduced pressure, the residue was cooled to −78 °C, and CH_2Cl_2 (3 mL) was slowly added at −78 °C. The resulting mixture was warmed to room temperature and stirred for 30 min. After solvent was removed, residue was extracted with pentane (3×). The pentane was then removed, and the residue was distilled under full vacuum to give a mixture of product **1e** (0.20 g, 25%) and tetramethylpiperidine as a colorless liquid, which could not be further separated by distillation. A small amount of pure sample was obtained by running the mixture through a silica gel column eluted with hexane. ^{1}H NMR (360 MHz, C_6D_6): δ 1.13 (s, 3H), 1.24 (s, 9H), 6.14 (dt, J = 6.6, 1.8 Hz, 1H, H_5), 6.92 (d, J = 10.7 Hz, 1H, H_3), 7.26 (d, J = 7.4 Hz, 1H, H_6), 7.50 (dd, J = 10.7, 1.3 Hz, 1H, H_4). MS (EI) m/z, relative intensity: 149 (M^+, 39), 93 (100). UV (hexane, $\lambda(\epsilon)$): 283 (4182, 223 (2440). When CD_2Cl_2 was used instead of CH_2Cl_2, the 3-deuterio isomer was obtained. ^{1}H NMR (360 MHz, C_6D_6): 6.16 (dd, 10.9, 5.9 Hz, H5), 7.26 (d, J = 5.9 Hz, H6), 7.57 (d, J = 10.7 Hz, H4). MS (EI) m/z (relative intensity): 150 (M+, 22), 94 (100).

Tricarbonyl(η^6-1-*tert*-butyl-1,2-dihydro-2-methyl-1,2-azaborine)molybdenum (5e). $BF_3{\cdot}OEt_2$ (0.76 mL, 6.04 mmol) was added to a mixture of **1e** (0.98 g, 0.60 mmol) and (tricarbonyltrispyridine)molybdenum (0.63 g, 1.51 mmol) in ether (12 mL). The mixture was stirred 15 h at room temperature to give a black suspension. Solvent was removed, and the residue was extracted with hexane (3×) and filtered. The hexane solution was concentrated and cooled to −78 °C to give product (0.10 g, 51%) as a yellow solid: mp, 138 °C (dec). ^{1}H NMR (360 MHz, C_6D_6): δ 0.79 (s, 3H), 0.84 (s, 9H), 4.23 (dd, J = 9.0, 1.7 Hz, 1H), 4.28 (dt, J = 5.7, 1.8 Hz, 1H), 5.31 (dd, J = 9.0, 5.7 Hz, 1H), 5.71 (d, J = 5.4 Hz, 1H). IR (hexane): 1977, 1909, 1893 cm^{-1}. HRMS (EI): m/z calcd for $C_{12}H_{16}{}^{11}BMoNO_3$, 331.0277; found 331.0270.

Tricarbonyl[η^6-1,2-dihydro-1-methyl-2-phenyl-1,2-azaborine]chromium (6c). 1,2-Dihydro-1-methyl-2-phenyl-1,2-azaborine (**1c**) (1.53 g, 9.05 mmol) in 20 mL of THF was added to $Cr(CO)_3(CH_3CN)_3$ (2.34 g, 9.05 mmol). The resulting dark red solution was heated at 50 °C for 24 h. The solvent was removed under reduced pressure. The residue was washed with 30 mL of pentane at 25 °C, and the brown extract was discarded. The dark residue was further extracted with 4 × 60 mL of hot hexane until no orange red color was observed in the extracts. The solution was concentrated and crystallized at −30 °C. The product was obtained after repeated recrystallization at 25 °C in CH_2Cl_2/pentane as needlelike red crystals (0.88 g, 32%), mp 125 °C. IR (hexane, film): 1979, 1916, 1900 cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_{12}{}^{11}B^{52}CrNO_3$ (M^+), 305.0315; found, 305.0323. Anal. Calcd for $C_{14}H_{12}BCrNO_3$: C, 55.12; H, 3.96; N, 4.59. Found: C, 55.24; H, 3.91; N, 4.42.

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Supporting Information Available: Tables of bond distances, angles, positional parameters, aniosotropic thermal parameters, and hydrogen atom coordinates of **5e** and **6c**. ^{1}H NMR spectra of **1c**, **1d**, **1e**, **5e**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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