

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-yl lithium reagents (**1c**, **1d**, and **1e**). The reaction of **1e** with $\text{Py}_3\text{Mo}(\text{CO})_3$ and $\text{BF}_3 \cdot \text{OEt}_2$ affords $\text{Mo}(\text{CO})_3$ complex **5e**, while the reaction of **1c** with $\text{Cr}(\text{CH}_3\text{CN})_3(\text{CO})_3$ affords $\text{Cr}(\text{CO})_3$ 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.

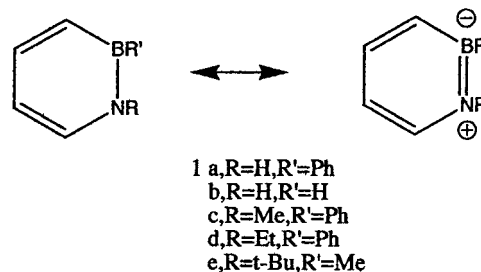
Introduction

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 1962¹ 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 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{Li}$ 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) Dewar, M. J. S.; Marr, P. A. *J. Am. Chem. Soc.* **1962**, *84*, 3782.
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 (3) Fritsch, A. J. *Chem. Heterocycl. Compd.* **1977**, *30*, 381.
 (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.
 (5) Gronowitz, S.; Ander, I. *Chem. Scr.* **1980**, *15*, 23, 145.
 (6) Kranz, M.; Clark, T. *J. Org. Chem.* **1992**, *57*, 5492.
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 (8) Ashe, A. J., III; Fang, X. *Org. Lett.* **2000**, *2*, 2089.
 (9) The systematic name for **4** is 2,3-dihydro-1*H*-1,2-azaborol-3-yl lithium.

(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.
 (11) (a) Burger, U.; Mazonod, F. *Tetrahedron Lett.* **1976**, 2881. (b) Burger, U.; Thorel, P. J.; Mentha, Y. *Chimica* **1987**, *41*, 26.
 (12) (a) Murata, I.; Nakasuji. *Tetrahedron Lett.* **1973**, 47. (b) Murata, I.; Tatsuoka, T.; Sugihara, Y. *Tetrahedron Lett.* **1973**, 4261. (c) Gandillon, G.; Bianco, B.; Burger, U. *Tetrahedron Lett.* **1981**, *22*, 51.
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 (14) Christl, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 529.
 (15) Burger, U.; Dreier, F. *Helv. Chim. Acta* **1979**, *62*, 540.
 (16) Nakadaira, Y.; Sato, R.; Sakurai, H. *J. Organomet. Chem.* **1992**, *441*, 411; *Organometallics* **1991**, *10*, 435.
 (17) Ashe, A. J., III; Klein, W.; Rousseau, R. *Organometallics* **1993**, *12*, 3225.

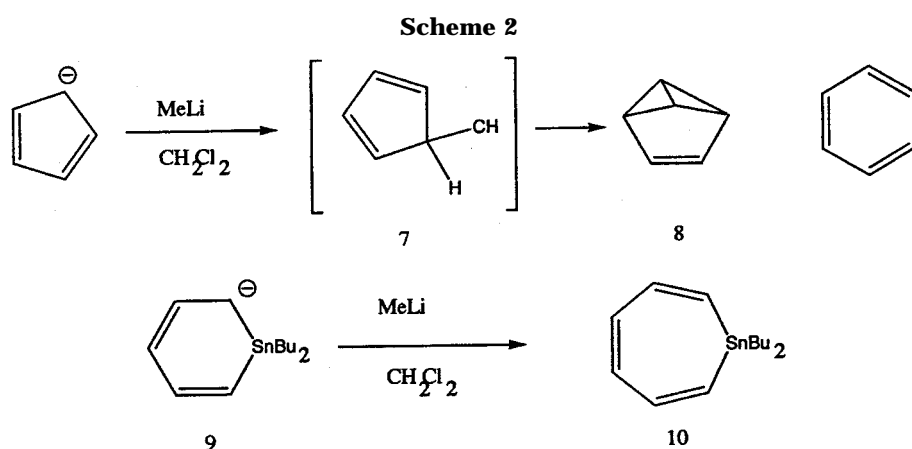
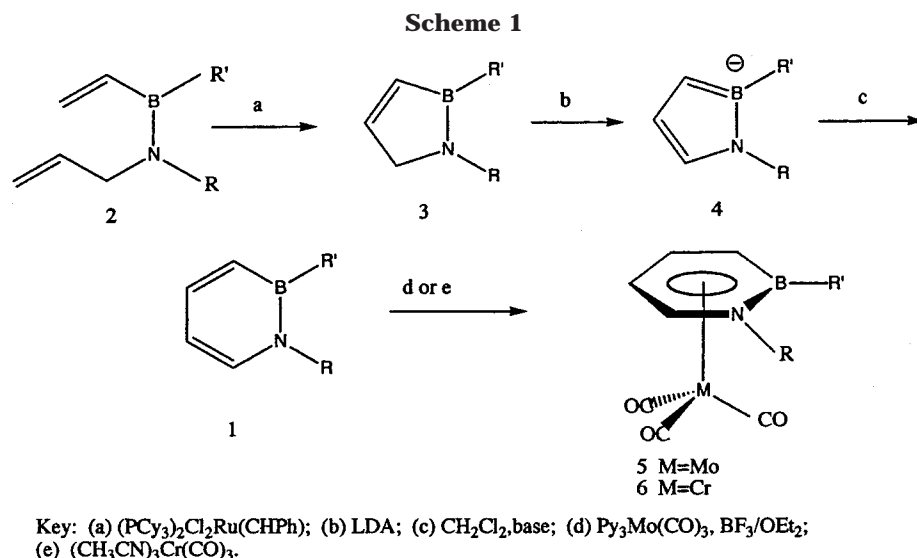


Table 1. ^{11}B and ^{13}C NMR Chemical Shift Data for 1,2-Dihydro-1,2-azaborines ($\text{C}_4\text{H}_4\text{BR}'\text{NR}$) and Selected Other Compounds

R,R' (compd)	$\delta(^{11}\text{B})$	$\delta(\text{C}3)$	$\delta(\text{C}4)$	$\delta(\text{C}5)$	$\delta(\text{C}6)$	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, $\text{C}_4\text{D}_8\text{O}$. ^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}

(18) (a) Schulze, J.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 59. (b) Amirkhalili, S.; Boese, R.; Höhner, U.; Kampmann, D.; Schmid, G.; Rademacher, P. *Chem. Ber.* **1982**, *115*, 732. (c) Schmid, G.; Boltsch, O.; Bläser, D.; Boese, R. *Z. Naturforsch.* **1984**, *39b*, 1082. (d) Schmid, G.; Schultz, M. *J. Organomet. Chem.* **1995**, *492*, 185, and earlier papers in this series.

(19) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shin-kai, I., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 3, p 739.

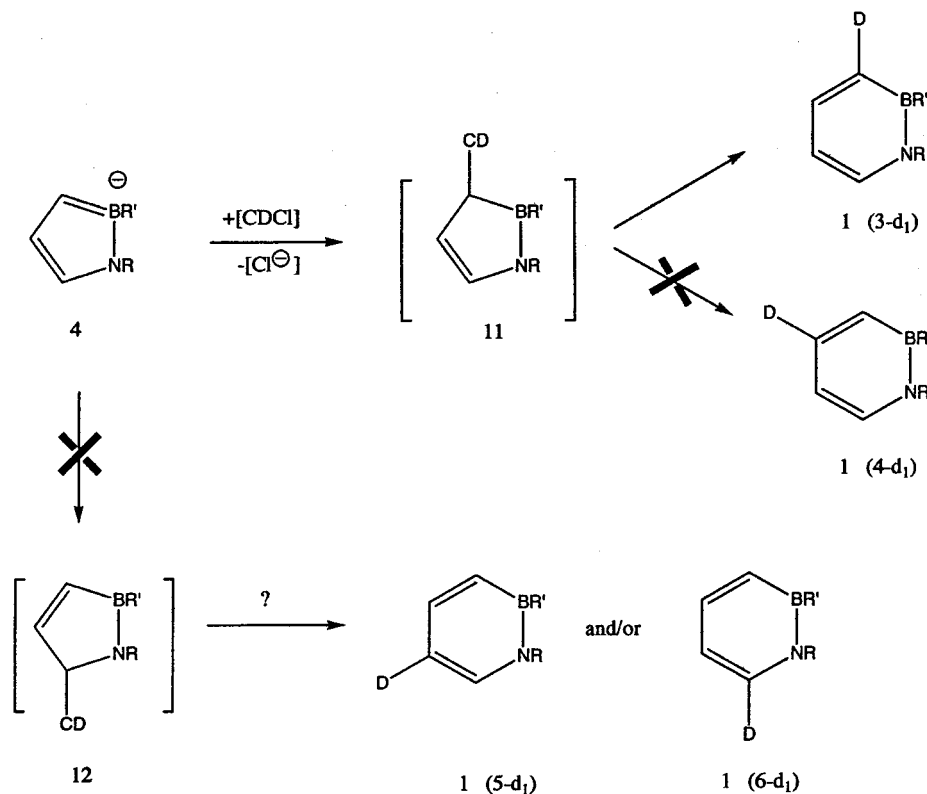
1,2-Azaborolides **4c** and **4d** can be prepared by LDA deprotonation of their conjugate acids (**3c** and **3d**), which in turn can be prepared by ring-closing metathesis on the appropriate B-vinyl, N-allyl aminoboranes **2**.⁸ This allows more general exploration of the ring expansion route to 1,2-dihydro-1,2-azaborines. 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

Table 2. ^1H NMR Parameters of 1,2-Dihydro-1,2-azaborines ($\text{C}_4\text{H}_4\text{BR}'\text{NR}$) and Selected Other Compounds

R,R' (compd)	$\delta(\text{H}_3)$	$\delta(\text{H}_4)$	$\delta(\text{H}_5)$	$\delta(\text{H}_6)$	$^3J_{3,4}\text{Hz}$	$^3J_{4,5}\text{Hz}$	$^3J_{5,6}\text{Hz}$	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, $\text{C}_4\text{D}_8\text{O}$. ^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 ^1H NMR spectra are summarized in Table 2. Data for the corresponding B-substituted boratabenzenes, lithium 1-phenylboratabenzene **13a**²¹ and lithium 1-methylboratabenzene²² **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-

(21) (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (b) Shu, P. Ph.D. Dissertation, University of Michigan, 1973. (c) Ashe, A. J., III; Kampf, J. W.; Müller, C.; Schneider, M. *Organometallics* **1996**, *15*, 387.

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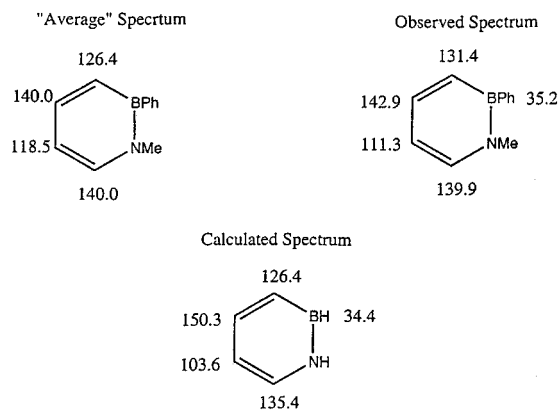


Figure 1. Observed ^{11}B and ^{13}C NMR chemical shifts of **1c** compared with averaged ^{13}C chemical shifts of **13** and **14** and the calculated ^{11}B and ^{13}C chemical shifts of **1b**.

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 boratabenzenes²² 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 $\text{BF}_3 \cdot \text{OEt}_2$ gave adduct **5e** in 51% yield as yellow crystals, which were recrystallized from hexane. The reaction of **1c** with tricarbonyltris(acetonitrile)chromium in THF

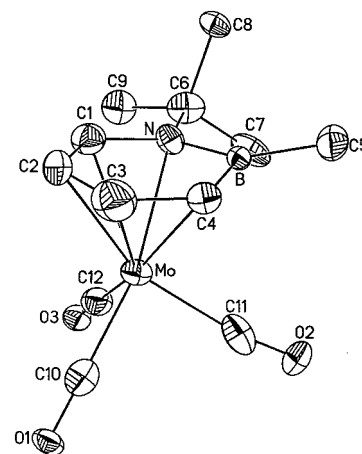


Figure 2. Molecular structure and atom labeling for **5e**.

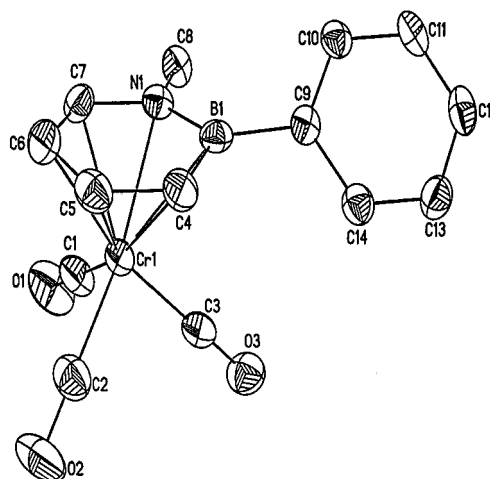


Figure 3. Molecular structure and atom labeling for **6c**.

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.

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 $\text{Cr}(\text{CO})_3$ 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– $\text{Mn}(\text{CO})_3$ complex **15**,²⁹ where one CO group

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(28) (a) Herberich, G. E.; Bauer, E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977**, *110*, 760. (b) Ashe, A. J., III; Kampf, J. W.; Nakadaira, Y.; Pace, J. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1255.

(29) Huttner, G.; Gartzke, W. *Chem. Ber.* **1974**, *107*, 3786.

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)
O(3)–C(3)	1.157(5)
O(2)–C(2)	1.151(5)
O(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)

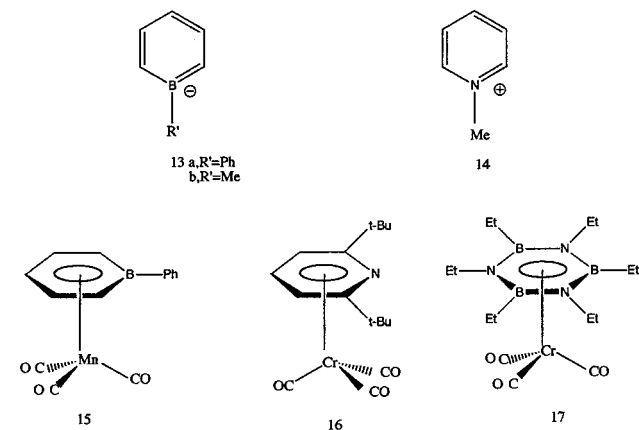
eclipses boron, and pyridine–Cr(CO)₃ complex **16**,³⁰ where one CO group is trans to nitrogen. This conformational feature has been found for metal carbonyl complexes of other boron and nitrogen heterocycles³¹ and has been treated by MO studies.³²

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 spectrometer, while the NMR spectra were obtained by using either a Bruker WH-400, WH-360, or AM-300 spectrometer. The ¹H NMR and ¹³C NMR spectra were calibrated by using signals from the solvents referenced to SiMe₄. The ¹¹B NMR spectra were referenced to external BF₃·OEt₂. 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-1H-1,2-azaborol-3-yl lithium (**4c**)⁸ (1.73 g, 10.6 mmol) in 20 mL of CH₂Cl₂ 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 C₁₁H₁₂¹¹BN(M⁺), 169.1063; found, 169.1065. Anal. Calcd for C₁₁H₁₂BN: 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 CD₂Cl₂ gave 66% of **11c** as a yellow oil. ¹H NMR (CDCl₃, 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 C₁₁¹H₁₁²H₁¹BN, 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 CH₂Cl₂ 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 $67\text{--}70^\circ\text{C}$ at 0.05 Torr. The ^1H NMR and ^{13}C NMR spectra are consistent with it existing as two B–N rotomers with a ratio of 1:1. ^1H 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, $=\text{CCH}_2$), 3.51 (dt, $J = 5.2$, 1.7 Hz, 2H, $=\text{CCH}_2$ '), 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 $\text{C}_{13}\text{H}_{18}^{11}\text{BN}$ (M^+), 199.1532; found, 199.1528. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{BN}$: 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-1H-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)benzylidene-ruthenium(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. ^1H 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, $\text{NCH}_2\text{CH}=\text{C}$), 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 ($\text{NCH}_2\text{C}=\text{C}$), 41.4 (Et), 16.7 (Et). ^{11}B NMR (C_6D_6 , 115.5 MHz): δ 39.4. HRMS (EI): m/z calcd for $\text{C}_{11}\text{H}_{14}^{11}\text{BN}$ (M^+), 171.1219; found, 171.1224. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{BN}$: 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-1H-1,2-borol-3-ylithium (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%). ^1H NMR ($\text{THF}-d_6$, 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 ($\text{THF}-d_6$, 100.6 MHz): δ 133.9, 123.8, 112.8, 111.9, 86.5 (br), 43.2 (Et), 19.6 (Et). ^{11}B NMR ($\text{THF}-d_6$, 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. ^1H 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 $\text{C}_{12}\text{H}_{14}^{11}\text{BN}$

(M^+), 183.1219; found, 183.1226. UV (pentane, nm): $\lambda(\epsilon)$ max 237 (2090), 282 (2610). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{BN}$: 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-1H-1,2-azaborol-3-ylithium in THF was prepared from 1-tert-butyl-2,3-dihydro-2-methyl-1H-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 ($3 \times$). 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. ^1H 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. ^1H NMR (360 MHz, C_6D_6): 6.16 (dd, 10.9, 5.9 Hz, H_5), 7.26 (d, $J = 5.9$ Hz, H_6), 7.57 (d, $J = 10.7$ Hz, H_4). 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). $\text{BF}_3\cdot\text{OEt}_2$ (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 ($3 \times$) 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). ^1H 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 $\text{C}_{12}\text{H}_{16}^{11}\text{B-MoNO}_3$, 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 $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (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 $\text{C}_{14}\text{H}_{12}^{11}\text{B}^{52}\text{CrNO}_3$ (M^+), 305.0315; found, 305.0323. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{-BCrNO}_3$: 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, anisotropic thermal parameters, and hydrogen atom coordinates of **5e** and **6c**. ^1H 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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