Switchable Haptotropic Migrations of Tricarbonylchromium Complexes of 1,2-Dihydro-2-phenyl-1,2-azaborine

Jun Pan, Jeff W. Kampf, and Arthur J. Ashe III*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055

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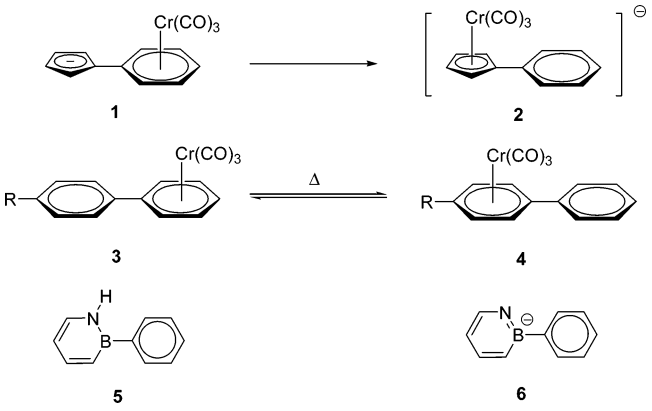
1,2-Dihydro-2-phenyl-1,2-azaborine (**5**) reacts with $Cr(CO)_3(CH_3CN)_3$ in THF at 50 °C to form the $Cr(CO)_3$ complex **7** in which the chromium is η^6-bound to the heterocyclic ring. Heating **7** in THF to 101 °C causes it to isomerize to complex **8**, in which the chromium is η^6-bound to the phenyl ring. The $Cr(CO)_3$ group of **8** may be switched back to the heterocyclic ring by base conversion to the anion **9**, followed by thermal isomerization to anion **10**. Protonation of **10** re-forms **7**. The X-ray structure of **8** shows that the uncoordinated 1,2-dihydro-1,2 azaborine ring is aromatic.

Introduction

π-Coordinated metals can undergo haptotropic migrations between the rings of certain polycyclic arene−metal complexes.[1] The best studied systems have been anionic chromium tricarbonyl complexes in which the $Cr(CO)_3$ group migrates from a neutral to an anionic ring:[2] e.g., **1** to **2**.[3] Haptotropic migrations



are also well-known for neutral systems in which the $Cr(CO)_3$ group equilibrates between two rings,[4] as in the biphenyl−$Cr(CO)_3$ complexes **3** and **4**.[5] Most noteworthy are the recent reports by Dötz and co-workers that a haptotropic $Cr(CO)_3$ migration in a naphthalene complex can be used as a molecular switch.[6]

Haptotropic migrations are much less common in heterocyclic systems, in part because many heterocycles are rather poor π ligands.[7] We recently prepared the boron−nitrogen heterocyclic analogue of biphenyl **5** and its conjugate base **6**.[8,9] Both **5** and **6** are excellent π ligands. Thus, it seemed desirable to explore possible haptotropic migrations of $Cr(CO)_3$ complexes of **5** and **6**. We wish to report here that **5** can form the $Cr(CO)_3$ complex **7**, which can be thermally isomerized to the more stable **8**. Deprotonation of **8** affords **9**, which can be isomerized to afford the more stable **10**. Protonation of **10** affords **7**. This cycle of reactions, which is summarized in Scheme 1, allows the $Cr(CO)_3$ group to be switched to either the benzocyclic or the heterocyclic ring.

Results and Discussion

Tricarbonylchromium complex **7** was prepared in 80% yield by heating **5** with $Cr(CO)_3(CH_3CN)_3$ in THF at 50 °C. By this method **7** is obtained regioselectively as the sole kinetic product of reaction. The ^{1}H NMR spectrum of **7** in THF-d_8 is first order and can be readily assigned by inspection. The signals for the 1,2-dihydro-1,2-azaborine ring protons are shifted upfield in comparison to the corresponding signals for the free ligand **5**, while the phenyl ring signals are little effected by complexation. Thus, π complexation to the heterocyclic ring is indicated. This regioselectivity of $Cr(CO)_3$ addition was confirmed by obtaining an X-ray crystal structure of **7**, which is illustrated in Figure 1.

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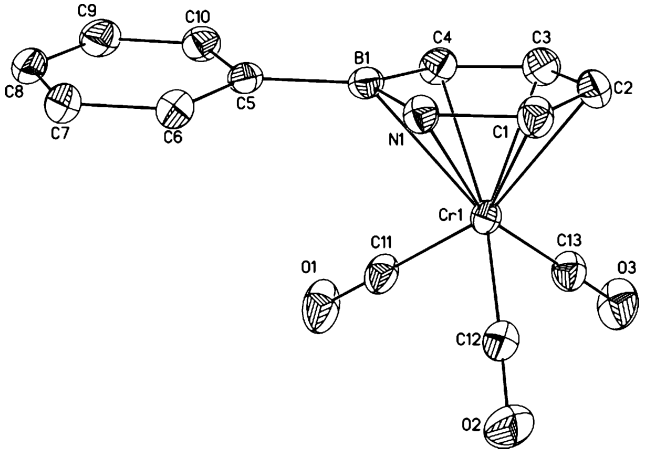
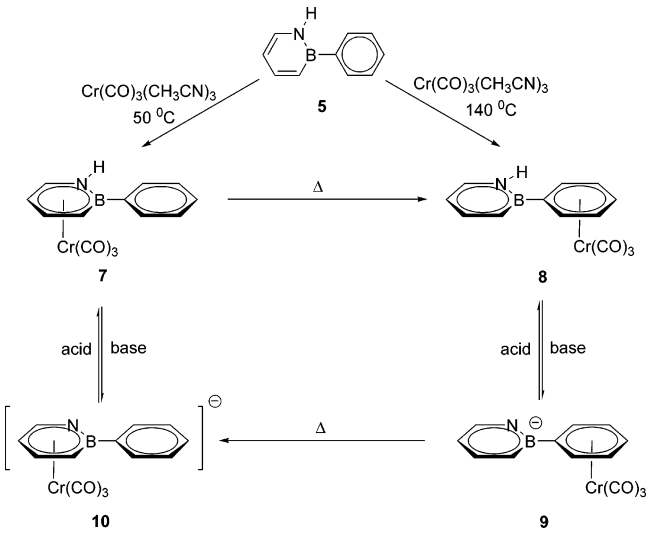


Figure 1. Solid-state structure of **7** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. A molecule of EtOAc hydrogen-bonded to N(1)H is not shown.

Scheme 1



7 can be quantitatively deprotonated by LDA or t-BuLi in THF to afford solutions of **10**. Alternatively, **10** can be isolated in 37% yield by precipitation by dioxane followed by washing with pentane and drying. The ^{1}H NMR spectrum of **10** in THF-d_8 shows a first-order pattern distinct from that of **7**. The major characteristic differences are the absence of the NH signal for **10** and the collapse of the C(6)H doublet of doublets of **7** to a broad doublet for **10**, due to the removal of the NH coupling. Alkylation of **10** with methyl iodide gave the known *N*-methyl derivative **7a**,[9] while the addition of protic acids regenerate **7**. Bracketing experiments in THF indicate that the acidity of **7** is comparable with that of pentaphenylcyclopentadiene (p$K_a \approx$ 12.5).[10,11] Since the acidity of **5** in THF is comparable with that of pentamethylcyclopentadiene (p$K_a \approx 26$),[10,11] there is a marked increase in acidity on complexation.[12]

Heating **7** in THF to 101 °C causes it to undergo a clean isomerization to its regioisomer **8**. Alternatively **8** may be prepared directly from **5** in 72% yield by heating with $Cr(CO)_3(CH_3CN)_3$ in THF to 140 °C. Like **7**, the ^{1}H NMR spectrum of **8** in DMSO-d_6 is first order. The ^{1}H NMR signals for the phenyl ring protons of **8** are shifted upfield relative to those of **5** and **7**, indicating Ph π complexation, while the signals for the uncomplexed 1,2-dihydro-1,2-azaborine ring protons of **5** and **8** are in the same range. The molecular structure of **8** (Figure 2) obtained from an X-ray diffraction study confirms the regioselectivity of the $Cr(CO)_3$ coordination.

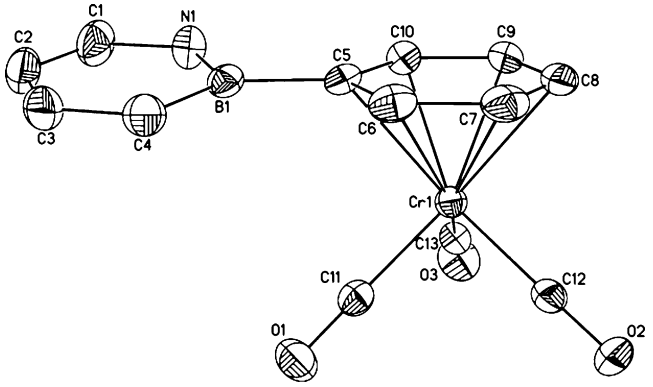
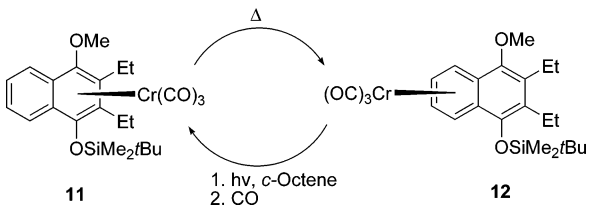


Figure 2. Solid-state structure of **8** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

8 can be deprotonated in THF using t-BuLi or LiTMP to afford solutions of **9** in the same manner as the conversion of **7** to **10**. **9** has been isolated as a yellow powder by precipitation with dioxane, followed by washing with pentane and drying. The ^{1}H NMR spectrum of **9** in DMSO-d_6 shows a first-order pattern, which is easily distinguished from that of **8** (and also from that of **10**).

Heating **9** in THF-d_8 to 93 °C cleanly converted it to **10**. Since protonation of **10** forms **7**, this series of reactions forms a cycle in which the $Cr(CO)_3$ group is transferred from the heterocyclic ring to phenyl and back again. The sequence of reactions (**7** to **8** to **9** to **10** to **7**) must be thermodynamically neutral. The thermal conversion of **7** to **8** is favorable, apparently because phenyl is a better ligand toward $Cr(CO)_3$ than is 1,2-dihydro-1,2-azaborinyl. Similarly the thermal reaction of **9** to **10** must be favorable, because the anionic 1,2-azaboratabenzene is a better ligand toward $Cr(CO)_3$ than is phenyl. The sequence is pushed back to thermodymanic neutrality by the acid/base steps **8** to **9** and **10** to **7**. Assuming that the pK_a of **8** is similar to that of **5** (p$K_a \approx 26$), the difference in acidity between **8** and **7** is approximately 13.5 pK_a units or 19 kcal/mol at 25 °C, which must energetically balance the thermal migration steps.

A molecular switch has been defined as any molecular-level system which can be reversibly interconverted by the application of an external stimulus.[13] By this definition the sequence **7** to **8** to **9** to **10** to **7** is a molecular switch. For comparison it is useful to review the Dötz molecular switch.[6] The naphthalene−$Cr(CO)_3$ complex **11** is thermally isomerized to **12**. Photolysis



of **12** in cyclooctene followed by CO addition gives **11** back. Obviously the photolysis provides the energy to reverse the

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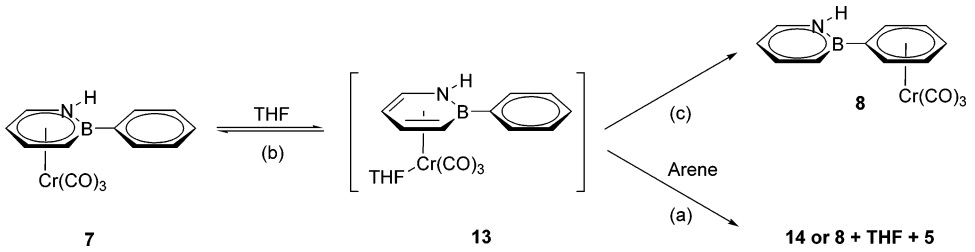
(11) The pK_a values in ethers are not thermodynamic values but are reasonably comparable with pK_a values determined in cyclohexylamine or DMSO. See: Streitweiser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, J., Eds.; Elsevier: Amsterdam, 1980; Part A, p 323.

(12) For a related case, see: Fraser, R. R.; Mansour, T. S. *J. Organomet. Chem.* **1986**, *310*, C60.

Scheme 2. Possible Mechanism for the Conversion of 7 to 8



favorable thermal reaction, while in present case the acid/base reactions provide the energy.

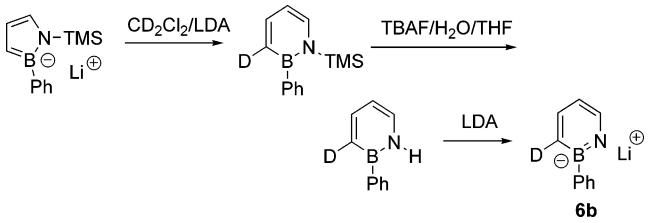
Possible Mechanisms. It was of interest to examine the thermal $Cr(CO)_3$ migrations **7** to **8** and **9** to **10** in more detail. The conversion of **7** to **8** is easily monitored by ^1H NMR spectroscopy. The first-order rate constant was found to be $k = 8.0 \times 10^{-5}$ s^{-1} at 101 °C in THF-d_8. Decomposition to **5** was less than 10% under these conditions. The reaction was much slower in noncoordinating solvents.[14] The approximate rate constant in cyclohexane-d_{12} at 160 °C was 1.9×10^{-4} s^{-1}. Decomposition to **5** now amounted to 30%.

The conversion of **7** to **8** can be partially diverted by the addition of extraneous substrates. The addition of 1 equiv of the strong π donor hexamethylbenzene to **7** in THF followed by heating for 1 half-life at 110 °C results in the formation of **8**, **5**, and (hexamethylbenzene)$Cr(CO)_3$ (**14**) in a ratio of 1:1:1, as measured by ^1H NMR spectroscopy. Similarly the addition of 1 equiv of **5**-*d*, specifically labeled at N(1), to **7** followed by heating to 110 °C resulted in 40% deuterium incorporation in **7** and **8**, as measured by mass spectroscopy.

The above data are consistent with the mechanism illustrated in Scheme 2. The faster rate of conversion of **7** to **8** in THF vs cyclohexane suggests that the THF is involved in the rate-determining step.[14,15] A THF molecule might slowly displace the B−N π bond (presumably the weakest π donor) of the η^6-coordinated 1,2-dihydro-1,2-azaborine ring of **7** to form the intermediate η^4-diene complex **13** (path b). Fast reaction of **13** with added hexamethylbenzene would give **14** and **5** (path a). This mechanism is analogous to those previously proposed for the donor-catalyzed exchange of (arene)$Cr(CO)_3$ complexes with extraneous arenes.[4b,14−16] Alternatively, reaction of **13** with labeled **5** would give labeled **7** and/or **8**. However, competitive intramolecular rearrangement of **13** to give **8** directly (path c) cannot be excluded.

The conversion of **9** to **10** could also be monitored by ^1H NMR spectroscopy. The first-order rate constant at 93 °C in THF-d_8 was measured to be 5.8×10^{-5} s^{-1}. No decomposition products were noted after 3 half-lives. The addition of excess hexamethylbenzene to **9** in THF followed by heating for 3 half-lives resulted in no detectable formation of **14**. The lack of cross product suggests that the reaction is intramolecular. However, this conclusion rests on the undemonstrated assumption that hexamethylbenzene is a better ligand than **6**, which would favor the formation of **14** over **10**.

Scheme 3. Synthesis of 6b



To be certain about the intramolecularity of the conversion of **9** to **10**, **6b** specifically deuterium labeled at C(3) was prepared by the route illustrated in Scheme 3. This route is analogous to a prior preparation of 3-deuterio-2-methyl-1-phenyl-1,2-dihydro-1,2-azaborine.[9] When **9** was heated in the presence of 1 equiv of **6b** in THF-d_8, the position of deuterium could be easily followed by monitoring the ^2H NMR spectrum. After 3 half-lives less than 20% of the deuterium was incorporated into **10**. Thus, the conversion of **9** to **10** is predominately intramolecular.

The mechanisms which have been proposed for intramolecular haptotropic migrations in carbocyclic systems have involved stepwise π decomplexation of the double bonds of one ring followed by (or concomitant with) π complexation of the double bonds of the new ring.[1−4,17] Such a route for the conversion of **9** to **10** might involve intermediates such as **15** (Scheme 4), in which the $Cr(CO)_3$ group is π-bound to both rings. A simple alternative mechanism involving the possible intermediate **16** seems worthy of serious consideration. The proposed intermediate **16** might be formed by intramolecular nucleophilic attack by the nitrogen atom of the pendant 1,2-azaboratabenzene ring on the $Cr(CO)_3$ group with the concomitant release of a C−C double bond from the phenyl group. Rapid transfer of the $Cr(CO)_3$ group to the heterocyclic ring might follow. Semmelhack and co-workers have shown that similar pendant nucleophiles accelerate intermolecular arene exchange of arene−chromium carbonyl complexes.[16] Effectively **16** is an intramolecular variant of **13**. Available data do not allow a distinction to be made between routes involving **15** or **16**.

Crystal Structures. The molecular structures of the isomeric $(C_4BNH_5-C_6H_5)Cr(CO)_3$ complexes **7** and **8** are illustrated in Figures 1 and 2, respectively. Selected bond distances of **7** and **8** are compared in Table 1. The structure **7** consists of a near-planar C_4BNH_5 ring, which is η^6-bound to the $Cr(CO)_3$ unit in a typical piano-stool fashion. **7** crystallizes with one molecule of ethyl acetate (omitted from Figure 1) which hydrogen-bonds to the acidic NH group of the coordinated heterocycle. The

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(15) (a) Traylor, T. G.; Stewart, K. *Organometallics* **1984**, *3*, 325. (b) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445. (c) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *Organometallics* **1986**, *5*, 2062.

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Scheme 4. Possible Mechanism for the Conversion of 9 to 10

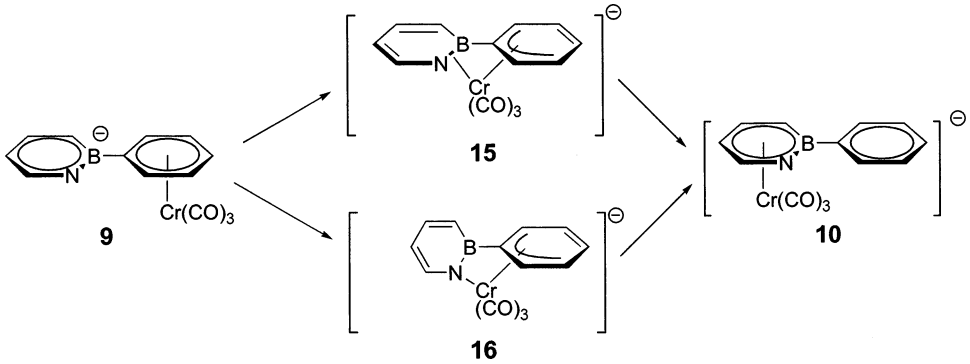

Table 1. Comparison of Selected Bond Distances (Å) for 7 and 8 and the Calculated Distances for 17

	7	8	17[a]
B(1)−N(1)	1.450(2)	1.430(5)	1.433
N(1)−C(1)	1.383(2)	1.368(5)	1.367
C(1)−C(2)	1.389(2)	1.353(6)	1.370
C(2)−C(3)	1.421(2)	1.413(7)	1.417
C(3)−C(4)	1.395(2)	1.370(6)	1.380
C(4)−B(1)	1.524(2)	1.500(5)	1.510
B(1)−C(5)	1.564(2)	1.583(5)	
C(5)−C(6)	1.404(2)	1.432(5)	
C(6)−C(7)	1.389(2)	1.403(5)	
C(7)−C(8)	1.382(2)	1.415(6)	
C(8)−C(9)	1.388(2)	1.398(5)	
C(9)−C(10)	1.389(2)	1.420(5)	
C(10)−C(5)	1.401(2)	1.410(5)	
Cr(1)−B(1)	2.367(2)		
Cr(1)−N(1)	2.192(1)		
Cr(1)−C(av)	2.23(3)	2.23(1)	

[a] Reference 23b.

uncoordinated *B*-phenyl is close to being coplanar with the C_4BNH_5 ring. Structure **8** closely resembles structure **7**, except that the rings are interchanged. The phenyl is η^6-bound to the $Cr(CO)_3$ group, while the almost coplanar C_4BNH_5 ring is uncoordinated.

Compound **8** is particularly notable, since it contains a noncoordinated 1,2-dihydro-1,2-azaborine ring. 1,2-Dihydro-1,2-azaborine is isolectronic with benzene,[18−21] and there are no prior structural data on the ring system without potentially perturbing metal coordination. Thus, the structural data on **8** should be of great interest in terms of defining the possible aromaticity of this important ring system.

The 1,2-dihydro-1,2-azaborine ring of **8** is completely planar. The formal single bonds, N(1)−C(1), C(2)−C(3), and B(1)−C(4), are rather short, and the formal double bonds, B(1)−N(1), C(1)−C(2), and C(3)−C(4), are rather long, which suggests π-delocalized bonding. Thus, the CN bond length (1.37 Å) is identical with that of pyridine.[22] The B−C bond length (1.50 Å) is distinctly shorter than those found for nonconjugated B−C bonds (typical range 1.55−1.59 Å).[23] The B−N bond (1.43 Å) is longer than the usual values found for unconjugated aminoboranes (1.41 Å).[24] The range of C−C bond lengths (1.35−1.41 Å) is considerably smaller than is shown by sp^2-hybridized C−C bond lengths of 1,3-cyclohexadiene (1.33−1.46 Å).[25] This range is comparable with the range of C−C bond lengths found in naphthalene (1.37−1.42 Å)[27,28] and is consistent with those of an aromatic ring.

In 1992 Clark and Kranz carried out an ab initio MO study at the MP2/6-31G* level on the parent 1,2-dihydro-1,2-azaborine (**17**) which allowed them to conclude that the compound had a considerable degree of electron delocalization.[28a] Scheiner and co-workers have subsequently calculated the bond distances of **17**, which are also collected in Table 1.[28b] Comparison of the calculated bond distances of **17** with those experimentally found for **8** shows an excellent level of agreement (average ±0.007 Å).

The structure of **7** is nearly identical with that found for the *N*-methyl derivative **7a**.[9] The only important difference is that the *B*-phenyl group of **7a** is canted out of the $C_4BN(CH_3)H_4$ plane by 39°.[29] The corresponding bond distances of **7** and **7a** differ by an average of only ±0.012 Å.

Comparison of the structures of **7** and **8** clearly illustrates the structural changes which aromatic rings undergo on complexation. The bond distances of the coordinated C_4BN ring of **7** average 0.02 Å longer than those of the uncoordinated C_4BN ring of **8**. This change is consistent with the partial removal of π-electron density from the ring by the electron-withdrawing $Cr(CO)_3$ group.[30] A similar effect can be noted by comparing the coordinated Ph ring of **8** with the uncoordinated Ph ring of **7**. Again, bond distances expand by 0.02 Å on coordination.

Concluding Statements

The conjugate acid/base pair 1,2-dihydro-1,2-azaborine/1,2-azaboratabenzene are both good η^6-ligands. The thermal conversions of **7** to **8** and **9** to **10** rest on the relative ligand strengths of 1,2-azaboratabenzene > benzene > 1,2-dihydro-1,2-azaborine. The combination of thermal haptotropic migrations and acid/base steps allow the $Cr(CO)_3$ group to be transferred back and forth between the heterocyclic and phenyl rings of **7**−**10** so that the system functions as a molecular switch. Further

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investigations of haptotropic migrations of complexes of these boron−nitrogen heterocycles are in progress.

Experimental Section

General Procedures. Manipulations of air-sensitive compounds were performed under a nitrogen or argon atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. Tetrahydrofuran, dioxane, pentane, and hexanes were dried and deoxygenated by distillation from sodium/benzophenone ketyl. Tetrahydrofuran-d_8 was dried over potassium/sodium alloy before use. *t*-BuLi (Aldrich), hexamethylbenzene (Aldrich), and cyclohexane-d_{12} (Cambridge) were used without further purification. ^{1}H, ^{2}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian Inova 400 or 500 NMR spectrometer at ambient temperature. Chemical shifts are reported in parts per million (δ). Proton and carbon chemical shifts are relative to respective solvent internal standards shown as follows: cyclohexane-d_{12}, δ 1.38 (^{1}H), 26.43 (^{13}C); DMSO-d_6, δ 2.50 (^{1}H), 39.51 (^{13}C); THF-d_8, δ 3.58 (^{1}H), 67.57 (^{13}C). The coupling constants (J) are reported in Hertz. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All ^{13}C and ^{11}B NMR spectra were determined with complete proton decoupling. High-resolution mass spectra were recorded on a VG-250S spectrometer with electron impact at 70 eV. Elemental analyses were conducted on a Perkin-Elmer 240 CHN analyzer by the Analytical Service Department of the Chemistry Department at the University of Michigan, Ann Arbor, MI.

Tricarbonyl[1,2-dihydro-2-phenyl-(η^6-1,2-azaborine)]chromium (7). 1,2-Dihydro-2-phenyl-1,2-azaborine (313 mg, 2.02 mmol) in 15 mL of THF was added to $Cr(CO)_3(CH_3CN)_3$ (522 mg, 2.01 mmol). The resulting red solution was heated to 50 °C for 24 h. The solvent was removed under reduced pressure. The residue was extracted by 3 × 15 mL of hot hexanes. After removal of the solvents, the crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexanes elution) to yield a pure sample of the product as an orange powder (470 mg, 80%). IR (benzene film): 1973, 1904, 1882 cm^{-1}. ^{1}H NMR (500 MHz, THF-d_8): δ 5.00 (d, J = 9.5 Hz, 1H, C(3)H); 5.40 (t, J = 5.8 Hz, 1H, C(5)H); 6.02 (dd, J = 9.5, 5.8 Hz, 1H, C(4)H); 6.43 (t, J = 5.8 Hz, 1H, C(6)H); 7.34 (m, 3H, Ar H); 7.67 (m, 2H, Ar H); 7.95 (br, 1H, NH). ^{13}C NMR (100.6 MHz, THF-d_8): δ 82.9, 85.0 (br), 100.9, 109.6, 128.7, 130.7, 133.6; the signal for C_{ipso} was not observed. ^{11}B NMR (160.4 MHz, THF-d_8): δ 19.9. HRMS (EI, *m*/*z*): calcd for $C_{13}H_{10}{}^{11}B^{52}CrNO_3(M^+)$, 291.0159; found, 291.0150. Anal. Calcd for $C_{13}H_{10}BCrNO_3$: C, 53.65; H, 3.46; N, 4.81. Found: C, 53.83; H, 3.62; N, 4.77.

Tricarbonyl[1,2-dihydro-2-(η^6-phenyl)-1,2-azaborine]chromium (8). 1,2-Dihydro-2-phenyl-1,2-azaborine (1.55 g, 10 mmol) in 50 mL of THF was added to $Cr(CO)_3(CH_3CN)_3$ (2.59 g, 10 mmol). The resulting red solution was heated at 140 °C for 24 h. The solvent was removed under reduced pressure. The residue was extracted by 4 × 60 mL of hot hexanes. After removal of the solvents, the crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexanes elution) to yield a pure sample of the product as a yellow powder (2.10 g, 72%). IR (benzene film): 1968, 1894 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.73 (t, J = 6.3 Hz, 2H, Ar H); 5.86 (t, J = 6.3 Hz, 1H, Ar H); 6.18 (d, J = 6.3 Hz, 2H, Ar H); 6.42 (t, J = 6.4 Hz, 1H, C(5)H); 6.92 (d, J = 11.2 Hz, 1H, C(3)H); 7.48 (t, J = 6.9 Hz, 1H, C(6)H); 7.71 (dd, J = 11.2, 6.4 Hz, 1H, C(4)H); 10.70 (br, 1H, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 94.6, 96.4, 99.5, 111.2, 125.9 (br), 135.3, 144.8; s the signal for C_{ipso} was not observed. ^{11}B NMR (160.4 MHz, THF-d_8): δ 32.7. HRMS (EI, *m*/*z*): calcd for $C_{13}H_{10}{}^{11}B^{52}CrNO_3$ (M^+), 291.0159; found, 291.0148. Anal. Calcd for $C_{13}H_{10}BCrNO_3$: C, 53.65; H, 3.46; N, 4.81. Found: C, 53.64; H, 3.21; N, 4.62.

Tricarbonyl[1,2-dihydro-1-lithio-2-phenyl-(η^6-1,2-azaborine)]chromium (10). In the NMR-scale reaction, a mixture of **7** (12 mg, 41 μmol) and LDA (5 mg, 47 μmol) was dissolved in 0.75 mL of THF-d_8. The resulting NMR spectrum showed that **10** was formed quantitatively. After quenching with CH_3I (8 mg, 56 μmol), it formed the known compound tricarbonyl[1,2-dihydro-1-methyl-2-phenyl-1,2-azaborine]chromium[9] was formed. To isolate **10**, the following large-scale experiment was performed. A 1.7 M solution of *tert*-butyllithium (1.5 mL, 2.55 mmol) in pentane was added slowly to a solution of **7** (582 mg, 2 mmol) in 10 mL of dioxane at 0 °C. As the mixture was stirred at 0 °C for 1 h and at room temperature for 4 h, a yellow precipitate was formed. After filtration, the precipitate was washed with 2 × 10 mL of pentane and dried in vacuo to give the product as a yellow powder (350 mg, 37%). The ^{1}H NMR showed that the product contained 2 equiv of dioxane. ^{1}H NMR (500 MHz, THF-d_8): δ 4.48 (d, J = 9.3 Hz, 1H, C(3)H); 5.08 (t, J = 5.9 Hz, 1H, C(5)H); 5.66 (dd, J = 9.3, 5.9 Hz, 1H, C(4)H); 6.48 (br, 1H, C(6)H); 7.16 (t, J = 7.1 Hz, 1H, Ar H); 7.21 (t, J = 7.1 Hz, 2H, Ar H); 7.69 (d, J = 7.1 Hz, 2H, Ar H). ^{13}C NMR (125.7 MHz, THF-d_8): δ 84.8, 88.2 (br), 110.7, 117.4, 127.6, 127.7, 134.1; the signal for C_{ipso} was not observed. ^{11}B NMR (160.4 MHz, THF-d_8): δ 21.6.

Tricarbonyl[1,2-dihydro-1-lithio-2-(η^6-phenyl)-1,2-azaborine]chromium (9). In the NMR-scale reaction, a mixture of **8** (13 mg, 45 μmol) and LTMP (8 mg, 54 μmol) was dissolved in 0.75 mL of THF-d_8. The resulting NMR spectrum showed that **9** was formed quantitatively. To isolate **9**, the following large-scale experiment was performed. A 1.7 M solution of *tert*-butyllithium (0.8 mL, 1.36 mmol) in pentane was added slowly to a solution of **8** (305 mg, 1.05 mmol) in 10 mL of dioxane at 0 °C. After the mixture was stirred at 0 °C for 1 h and at room temperature for 4 h, a yellow precipitate was formed. After filtration, the precipitate was washed with 2 × 10 mL of pentane and dried in vacuo to give the product as a yellow powder (205 mg, 41%). The ^{1}H NMR showed that the product contained 2 equiv of dioxane. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.61 (m, 3H, Ar H); 6.07 (t, J = 5.4 Hz, 1H, C(5)H); 6.24 (m, 2H, Ar H); 6.33 (d, J = 10.5 Hz, 1H, C(3)H); 7.23 (dd, J = 10.5, 5.4 Hz, 1H, C(4)H); 8.00 (d, J = 4.1 Hz, 1H, C(6)H). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 94.7, 95.3, 99.9, 111.4, 118.8 (br), 139.4, 148.3; the signal for C_{ipso} was not observed. ^{11}B NMR (160.4 MHz, THF-d_8): δ 34.4.

1,2-Dihydro-1-deuterio-2-phenyl-1,2-azaborine (5-*d*). To a solution of (1,2-dihydro-2-phenyl-1,2-azaborin-1-yl)potassium (295 mg, 1.53 mmol) in 10 mL of THF at −78 °C was slowly added 2 mL of CD_3COOD. The mixture was warmed to room temperature and stirred for 2 h. The volatiles were removed in vacuo, and the residue was extracted with 3 × 10 mL of hexanes. The solution was concentrated and crystallized at −30 °C to give the product as white crystals (200 mg, 84%). The isotopic purity determined by the mass spectroscopy was 80%.

(1,2-Dihydro-2-phenyl-3-deuterio-1,2-azaborin-1-yl)lithium (6b). The procedure for preparing **6b** was identical with that for (1,2-dihydro-2-phenyl-1,2-azaborin-1-yl)lithium, except CD_2Cl_2 was used in place of CH_2Cl_2[9] (see Scheme 3). ^{1}H NMR (500 MHz, THF-d_8): δ 6.02 (dd, J = 6.5, 5.0 Hz, 1H, C(5)H); 7.00 (t, J = 7.3 Hz, 1H, Ar H); 7.13 (t, J = 7.8 Hz, 2H, Ar H); 7.32 (d, J = 6.5 Hz, 1H, C(4)H); 7.70 (d, J = 7.8 Hz, 2H, Ar H); 7.95 (d, J = 5.0 Hz, 1H, C(6)H). ^{2}H NMR (76.7 MHz, THF-d_8): δ 6.55 (br, C(3)D). The isotopic purity determined by ^{1}H NMR was 90%.

Haptotropic Migration from 7 to 8. 1. In THF. In a sealed NMR tube, a solution of **7** (13 mg, 45 μmol) in 0.75 mL of THF-d_8 was heated to 101 °C and the migration was monitored by ^{1}H NMR spectroscopy. The percent conversion was determined by monitoring the signal of C(3)H of **7** and that of the corresponding proton of **8**. The resulting rate constant k is 8.0×10^{-5} s^{-1}. The decomplexed product 1,2-dihydro-2-phenyl-1,2-azaborine was less than 10% of the amount of product.

2. In Cyclohexane. In a sealed NMR tube, a solution of **7** (saturated at room temperature) in 1 mL of cyclohexane-d_{12} was heated at 160 °C and the migration was monitored by ^{1}H NMR spectroscopy. The percent conversion was determined by monitoring the signal of C(3)H of **7** and the signal for the corresponding proton of **8**. The resulting rate constant k is approximately 1.9×10^{-4} s^{-1}. The decomplexed product 1,2-dihydro-2-phenyl-1,2-azaborine was around 30% of the total product.

3. Crossover Reaction. In a sealed NMR tube, a mixture of **7** (13 mg, 45 μmol) and **5**-*d* (7 mg, 45 μmol, % D = 80%) was dissolved in 0.75 mL of THF-d_8. This solution was heated to 110 °C for 115 min. The amount of deuterium exchange product detected from the mass spectrum was around 40%. Also, in the sealed NMR tube, a mixed solution of **7** (9 mg, 31 μmol) and hexamethylbenzene (5 mg, 31 μmol) in 0.75 mL of THF-d_8 was heated to 110 °C for 115 min; the cross product **14** and **8** and **5** were detected in a ratio of approximately 1:1:1.

Haptotropic Migration from 9 to 10. 1. In THF. In a sealed NMR tube, a solution of **9** (15 mg, 51 μmol) in 0.75 mL of THF-d_8 was heated to 93 °C and the migration was monitored by ^{1}H NMR spectroscopy. The percent conversion was determined by monitoring the signal of C(5)H of **9** and the signal for the corresponding proton of **10**. The resulting rate constant k is approximately 5.8×10^{-5} s^{-1}. No decomplexed product was observed by NMR spectroscopy.

2. Crossover Reaction. In a sealed NMR tube, a mixture of **9** (9 mg, 30 μmol) and hexamethylbenzene (6 mg, 37 μmol) was dissolved in 0.75 mL of THF-d_8. This solution was heated at 110 °C for 180 min (approximately 3 half-lives). No crossover product was detected by NMR spectroscopy.

In a sealed NMR tube, a mixture of **9** (16 mg, 54 μmol) and **6b** (9 mg, 56 μmol) was dissolved in 0.75 mL of THF-d_8. This solution was heated at 110 °C for 150 min. ^{2}H NMR spectroscopy indicated that less than 20% of the deuterium was incorporated into **10**. Thus, the conversion of **9** to **10** is predominately intramolecular.

Determination of the pK_a Value of 7. In the NMR tube, 7 mg of (pentaphenylcyclopentadienyl)lithium (15 μmol) was added to a solution of **7** (5 mg, 17 μmol) in 0.75 mL of THF-d_8. The resulting NMR spectrum showed the peaks of pentaphenylcyclopentadiene as well as of (pentaphenylcyclopentadienyl)lithium. This indicates that the acidity of **7** is comparable with that of pentaphenylcyclopentadiene.

Single-Crystal X-ray Crystallography. Crystals of **7** and **8** suitable for X-ray diffraction were obtained by recrystallization from hexane/ethyl acetate. Crystallographic and data collection parameters are collected in Table 2. ORTEP drawings of **7** and **8** showing the atom-numbering scheme used in refinement are given in Figures 1 and 2, respectively. Selected bond distances are collected in Table 1. Additional crystallographic data are available in the Supporting Information.

Table 2. Crystal Data and Data Collection Parameters for 7 and 8

	7	**8**
empirical formula	$C_{13}H_{10}BCrNO_3 \cdot C_4H_8O_2$	$C_{13}H_{10}BCrNO_3$
fw	379.13	291.03
temp, K	118(2)	150(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	7.5897(13)	9.9188(15)
b, Å	9.9787(17)	17.330(3)
c, Å	13.252(2)	7.2858(11)
α, deg	68.342(3)	90
β, deg	75.790(3)	90.348(3)
γ, deg	75.134(3)	90
V, Å^3; Z	888.0(3); 2	1252.3(3); 4
calcd density, Mg/m^3	1.417	1.544
abs coeff, mm^{-1}	0.670	0.913
F(000)	392	592
cryst size, mm	$0.44 \times 0.30 \times 0.12$	$0.36 \times 0.32 \times 0.16$
limiting indices	$-9 \le h \le 10$ $-12 \le k \le 13$ $-17 \le l \le 17$	$-13 \le h \le 13$ $-23 \le k \le 23$ $-9 \le l \le 9$
no. of rflns collected/ unique	8792/4330	12 085/3081
abs cor	semiempirical from equivalents	
refinement method	full-matrix least squares on F^2	
no. of data/restraints/ params	4330/0/229	3081/0/173
GOF on F^2	1.041	1.094
final R indices ($I > 2\sigma(I)$)	R1 = 0.0298 wR2 = 0.0821	R1 = 0.0468 wR2 = 0.1270
R indices (all data)	R1 = 0.0340 wR2 = 0.0842	R1 = 0.0555 wR2 = 0.1347
largest diff peak and hole, e/Å^3	0.420 and −0.241	0.587 and −0.597

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Supporting Information Available: CIF files giving X-ray characterization data for **7** and **8** and figures giving ^{1}H NMR spectra of **7**−**10** and rate data for the conversions of **7** to **8** and **9** to **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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