Tricarbonylchromium Complexes of 1,2-Dihydro-1,2-benzazaborines

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1,2-Dihydro-2-phenyl-1,2-benzazaborine reacts with $Cr(CO)_3(CH_3CN)_3$ in THF at 140 °C to form complex **18**, in which the phenyl is η^6 -bound to chromium. 1,2-Dihydro-2-methyl-1,2-benzazaborine reacts with $Cr(CO)_3(CH_3CN)_3$ in THF at 60 °C to form complex **23**, in which the benzo ring is η^6 -bound to chromium. Treating **23** with potassium bis(trimethylsilyl)amide in THF forms the corresponding potassium salt **25**, which on heating undergoes haptotropic isomerization to complex **26**, in which the anionic heterocyclic ring is η^6 -bound to the chromium.

Introduction

Metal complexes of polycyclic aromatic compounds often undergo haptotropic migrations in which the metal migrates from one ring to another.¹ Chromium tricarbonyl complexes of naphthalenes (e.g., **1** and **2**) in which a Cr(CO)₃ group migrates across a ring fusion have been well studied experimentally and computationally.¹⁻⁵ Cr(CO)₃ migration across a single bond between two rings are also known, e.g. $3 \rightarrow 4$.^{6a} In most cases the migration of an electron withdrawing Cr(CO)₃ group from a neutral to an anionic ring is particularly favorable, e.g. $5 \rightarrow 6$.^{6,7} See Scheme 1.

We have been interested in haptotropic migrations involving boron-nitrogen analogues of benzocylic aromatics as shown in Scheme 2. The isomerization of $7 \rightarrow 8^8$ is closely analogous to that of $5 \rightarrow 6$.^{6b} However, reactions of boron-nitrogen heterocycles with acidic NH groups are potentially more complex. Thus, the reaction of 1,2-dihydro-2-phenyl-1,2-azaborine (9) with Cr(CO)₃(CH₃CN)₃ gives complex 10, which can

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be thermally isomerized to **11**. Complex **11** can then be deprotonated to form **12**, which on heating is isomerized to **13**. Protonation of **13** forms **10** again (see Scheme 2).⁹ This cycle of haptotropic migrations and acid/base steps is unique in that the $Cr(CO)_3$ groups can be switched to either the phenyl or the heterocyclic ring. In order to explore this phenomenon further, we have now examined the corresponding reactions of complexes of 1,2-dihydro-1,2-benzazaborines **15** and **16**, which are ring-fused analogues of **9**.



Scheme 1. Haptotropic Shifts of Cr(CO)₃ Complexes of Selected Carbocyclic Aromatic Compounds

Results and Discussion

2-Chloro-1,2-dihydro-1,2-benzazaborine (14) was originally prepared in 1959 by Dewar and Dietz by the reaction of BCl₃ with 2-aminostyrene.¹⁰The boron-bound chloro group of 14 can be easily replaced by nucleophiles to give 15-17, as illustrated in eq 1. More recently Paetzold and co-workers have reported on 14, 16, and several more highly substituted 1,2-dihydro-1,2-benzazaborines.¹¹ These compounds have now been more thoroughly characterized but are identical with those originally reported.¹⁰ Furthermore, we have obtained a crystal structure of the parent compound 17, which establishes its structure.

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Scheme 2. Haptotropic Shifts of Cr(CO)₃ Complexes of Boron-Nitrogen Heteroaromatic Compounds





The phenyl derivative **15** was of particular interest to us, since it is the benzo-fused analogue of **9**, which we had previously investigated in detail. Heating **15** with $Cr(CO)_3(CH_3CN)_3$ in THF to 140 °C for 40 h gave complex **18** as the sole product in 50% yield. The ¹H NMR spectrum of **18** in THF-*d*₈ is first order and can be readily assigned by inspection. The signals for the phenyl protons are shifted upfield relative to those of **15**, while those of the 1,2-dihydro-1,2-benzazaborine group are little effected by complexation. Therefore, π -complexation to the phenyl ring is indicated.¹² The regioselectivity of the $Cr(CO)_3$ complexation was confirmed by obtaining an X-ray structure of **18**, which is illustrated in Figure 1.

The reaction of **15** with $Cr(CO)_3(CH_3CN)_3$ under milder conditions (25 °C) gave a mixture of **18** and an isomer tentatively identified as **19** in the ratio of 1:3. We have been unable to isolate pure **19** from the mixture, while heating it to 140 °C converted it to pure **18**. The structure of **19** was assigned on the basis of the ¹H NMR spectrum of the mixture. In particular signals for the fused benzocyclic ring of **19** were shifted markedly upfield from those of the uncoordinated ring of **15**. Similar π -coordination shifts are characteristic of $Cr(CO)_3$ coordinated arene rings.¹² Although the conversion of **19** to **18**



Figure 1. Solid-state structure of **18** (ORTEP). Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms have been omitted for clarity.

may involve the intermediacy of **20**, we have not been able to detect the formation of any **20**.

Complex 18 can be quantitatively deprotonated by LiTMP in THF to form solutions of 21. The ¹H NMR spectrum of 21 in THF- d_8 shows a first-order pattern which is distinct from the spectrum of 18. Quenching 21 with excess D₂O afforded 18-d, in which the deuterium was exclusively at N(1). Heating anion 21 to 110 °C in THF led to slow decomposition without giving any dectectable 22. This greater thermal lability of 21 relative to that of 12 prevented observation of Cr(CO)₃ migration from phenyl to the anionic heterocyclic ring which had been found for 12. See Scheme 3.

Our initial goal had been to examine possible "biphenyl-like" haptotropic migrations of complexes of **15** which might be analogous to those illustrated in Scheme 2. Since we were unable to prepare **20** and **22** and no $Cr(CO)_3$ migrations from **18** or **21** were found, this goal could not be achieved. Therefore, we decided to examine possible "naphthalene-type" migrations between the fused rings of the 1,2-dihydro-1,2-benzazaborine system. In order to limit metal coordination to the fused rings, we have examined the reactions of the methyl derivative **16**.

Treating **16** with Cr(CO)₃(CH₃CN)₃ in THF at 60 °C resulted in formation of complex **23** mixed with excess **16**. On heating to higher temperatures **23** decomposes to give **16** and unidentified chromium-containing materials. No complex **24** could be detected. Pure **23** was isolated in 39% yield using column chromatography on silica gel. The ¹H NMR spectrum of **23** in THF-*d*₈ is first order and can readily be assigned by inspection. The signals for the benzo-ring protons are shifted upfield in comparison with those of **16**, while the signals for the uncomplexed C₄BN ring are little changed. Therefore, π -complexation to the benzo ring is indicated, ¹² which was later confirmed by obtaining a crystal structure of **23**, shown in Figure 2.

Neutral complex 23 can be quantitatively deprotonated by treatment with potassium bis(trimethylsilyl)amide in THF to give a solution of potassium salt 25. The ¹H spectrum of 25 in THF- d_8 shows a first-order pattern, which is easily distinguished from that of 23. Quenching 25 with excess D₂O yielded N-deuterium-labeled 23-*d*. Heating 25 in THF- d_8 to 90 °C converted it to 26. Decomposition was approximately 25%. The conversion of 25 to 26 was monitored by ¹H NMR spectroscopy. In comparison to that of 25 the ¹H NMR spectrum of 26 showed that all of the signals of the benzo ring are shifted downfield and all of

Scheme 3. Reactions of 1,2-Dihydro-2-phenyl-1,2-benzazaborines



the signals for the C₄BN ring are shifted upfield. In addition, the ¹¹B NMR spectrum shows that the signal for **26** (δ 24.0) is shifted upfield relative to that of **25** (δ 40.8). This is consistent with a coordination shift of the Cr(CO)₃ group from the benzo ring to the heterocyclic ring.^{12,13}

Quenching **26** with methyl iodide in THF at 25 °C afforded the uncomplexed *N*-methyl derivative **28**.¹⁰ We suspect that the methyl iodide converted **26** to intermediate **27**, which must be highly labile at room temperature since it rapidly decomplexes to give **28**. See Scheme 4.

The thermal conversion of **25** to **26** and the presumed lability of **27** suggest that the order of ligand strength toward Cr(CO)₃ is the anionic heterocyclic ring of 1,2-benzazaboratabenzene > the benzo ring of 1,2-benzazaboratabenzene > the neutral heterocyclic ring of 1,2-dihydro-1,2-benzazaborine. This order is analogous to that previously found for the monocyclic ring systems **10–13**, in which the order of ligand strength was 1,2azaboratabenzene > *B*-phenyl > 1,2-dihydro-1,2-azaborine. In both sets the anionic heterocyclic ring is the strongest ligand, while the neutral heterocyclic ring is the weakest ligand toward the electron-withdrawing Cr(CO)₃ group. Computational studies have indicated that the π -bonding of 1,2-dihydro-1,2-azaborine



Figure 2. Solid-state structure of **23** (ORTEP). Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms have been omitted for clarity.

is weaker than that of benzene due to localization of electrons by the B–N bond.¹⁴ This is consistent with the observed lower π -basicity of the heterocyclic ring toward Cr(CO)₃. Apparently deprotonation of NH of 1,2-dihydro-1,2-azaborine greatly enhances its π -basicity so that 1,2-azaboratabenzene is a stronger π -base toward Cr(CO)₃.

Our inability to prepare stable complexes in which the $Cr(CO)_3$ group is π -bound to the heterocyclic ring of 1,2dihydro-1,2-benzazborines implies that this ring system is a poorer ligand than the 1,2-dihydro-1,2-azaborine ring of **10**. Reduction in the π -ligand strength on benzannulation has a precedent in the observation that naphthalene is a poorer ligand than benzene toward $Cr(CO)_3$.¹⁵

It was of interest to examine the conversion of 25 to 26 in order to compare it with the formally similar Cr(CO)₃ migrations between the rings of η^6 -naphthalene complexes 1 and 2. The reaction of 25 to give 26 at 60 °C in THF-d₈ was monitored by ¹H NMR spectroscopy. Unfortunately, heating **25** led to unidentified products as well as 26. When the reaction was performed in the presence of the good π -donor hexamethylbenzene, no crossover products were observed. These data are consistent with a unimolecular reaction. The first-order rate constant for the loss of 25 was found to be $k = 2.80 \times 10^{-5}$ s^{-1} at 60 °C. For comparison the conversion of 1 to 2, where R = Me, is 34 times slower with an extrapolated $k = 8.2 \times 10^{-7}$ s⁻¹ at 60 °C.^{2a} Precise comparison is not warranted because of differences in charge type, solvent, and ring substituents. Nevertheless, the rates are qualitatively similar. It has been proposed that naphthalene $-Cr(CO)_3$ ring exchange occurs via an intramolecular stepwise decomplexation of the formal double

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Scheme 4. Reactions of 1,2-Dihydro-2-methyl-1,2-benzazaborines



bonds of one ring concomitant with or followed by complexation of the double bonds of the second ring.¹⁻⁵ It seems most reasonable to propose a similar mechanism for the conversion of **25** to **26**, although a mechanism involving intermediate complexation to the nucleophilic nitrogen cannot be excluded.⁹

Crystal Structures. An X-ray structure determination of **17** (in the Supporting Information) unambiguously identifies the compound. Since **17** is isostructural with naphthalene,¹⁶ the benzocyclic and heterocyclic rings are crystallographically identical. Thus, accurate bond distances could not be obtained. It is worth noting that the isomeric 4a,8a-azoniaboratanaphthalene **29**¹⁷ is also isostructural with naphthalene and that a similar isostructural relationship has been found for other boron–nitrogen heterocyclic compounds with their carbocyclic analogues.¹⁸ It has recently been proposed that this close structural similarity is a general and significant feature of boron–nitrogen heterocycles.¹⁹



The molecular structures of the 1,2-dihydro-1,2-benzazaborine-Cr(CO)₃ complexes **18** and **23** are illustrated in Figures 1 and 2, respectively. Selected bond distances of **18**, **11**, and **23** are compared in Table 1. Structure **18** consists of a near-planar

Table 1. Comparison of Selected Bond Distances (Å) for 18, 11,^{*a,b*} and 23^c

bond	18	11	23
C(1)-N(1)	1.391(2)	1.368(5)	1.376(4)
N(1) - B(1)	1.422(2)	1.430(5)	1.424(3)
B(1) - C(8)	1.526(2)	1.500(5)	1.534(4)
C(8) - C(7)	1.355(2)	1.370(6)	1.358(15)
C(7) - C(6)	1.439(2)	1.413(7)	1.447(6)
C(6) - C(1)	1.407(2)	1.353(6)	1.427(6)
B(1) - C(9)	1.576(2)	1.575(2)	1.583(5)
C(1) - C(2)	1.405(2)		1.420(4)
C(2) - C(3)	1.384(2)		1.399(12)
C(3) - C(4)	1.399(2)		1.412(3)
C(4) - C(5)	1.379(2)		1.411(11)
C(5) - C(6)	1.408(2)		1.428(4)

^{*a*} Reference 9. ^{*b*} The atom-numbering scheme for 11 corresponds to that of 18 and 23. ^{*c*} Average for two independent molecules.

uncoordinated 1,2-dihydro-1,2-benzazaborine ring which is bound to a *B*-phenyl, bearing an η^6 -bound Cr(CO)₃ unit. Structure **23** consists of a near planar 1,2-dihydro-2-methyl-1,2-benzazaborine ring which is η^6 -bound to a Cr(CO)₃ unit through the benzo-ring. In both cases the Cr(CO)₃ units are bound in typical piano-stool fashion.

Compound 18 is particularly notable, since it contains a noncoordinated 1,2-dihydro-1,2-benzazaborine group. This group is bound to the B-pendant $Ph-Cr(CO)_3$ unit in the same manner as is the parent 1,2-dihydro-1,2-azaborine ring of complex 11. Comparison of the boron-nitrogen heterocyclic rings of 18 and 11 shows that the bonds which are α - β to the ring fusion (N(1)-B(1)) and C(7)-C(8) are shorter while the other endocyclic bonds (C(1)-N(1), B(1)-C(8), C(7)-C(6), and C(6)-C(1)) are longer than the corresponding bonds of 11. Similar differentiation of the C-C bond distances is found for naphthalene¹⁵ vs benzene and generally for linearly fused arenes vs monocyclic arenes.¹⁹ It reflects a localization of π -bonding relative to monocyclic aromatics. However, the B-C bond lengths of 18 suggest that the 1,2-dihydro-1,2-benzazaborine ring has strong endocyclic π -bonding. The endocyclic B-C bond (1.526(2) Å) of **18** is significantly shorter than the exocyclic B-C bond (1.576(2) Å).

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 Table 2. Crystal and Data Collection Parameters for 18 and 23

	18	23
empirical formula	C ₁₇ H ₁₂ BCrNO ₃	C ₁₂ H ₁₀ BCrNO ₃
fw	341.09	279.02
temp, K	123(2)	123(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	11.8163(16)	15.212(4)
<i>b</i> , Å	10.9188(14)	10.730(3)
<i>c</i> , Å	12.0946(16)	16.259(4)
β , deg	104.151(2)	112.855(4)
$V, Å^3; Z$	1513.1(3); 4	2445.6(11); 8
calcd density, Mg/m ³	1.497	1.516
abs coeff, mm ⁻¹	0.768	0.932
F(000)	696	1136
cryst size, mm	$0.58 \times 0.22 \times 0.20$	$0.36 \times 0.32 \times 0.22$
limiting indices	$-15 \le h \le 15$	$-20 \le h \le 20$
	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-16 \le l \le 16$	$-21 \le l \le 21$
no. of rflns collected/unique	15 374/3762	39 806/26 502
abs cor	semiempirical from	equivalents
refinement method	full-matrix least squ	ares on F^2
no. of data/restraints/params	3762/0/208	
GOF on F^2	1.050	1.099
final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0304	R1 = 0.0583
	wR2 = 0.0865	wR2 = 0.1559
R indices (all data)	R1 = 0.0351	R1 = 0.0716
	wR2 = 0.0900	wR2 = 0.1627
largest diff peak and hole, e/Å ³	0.392 and -0.291	0.697 and -0.720

It is also interesting to compare the structure of the heterocyclic ring of **18** with that of B–O–B ether **30**, which was reported by Paetzold and co-workers.¹¹ The intra-ring distances of **18** and **30** were virtually identical, which indicates that the pendant oxygen makes only a small perturbation to the π -bonding of the ring. Finally, comparison of the structure of **23** with that of **18** shows that the C–C bonds of the benzocyclic ring expand by an average of 0.02 Å on complexation. This is a normal effect which is a consequence of partial removal of the π electrons by the Cr(CO)₃ group. On the other hand, bond distances in the heterocyclic rings of **23** and **18** differ by an average of only 0.01 Å, indicating that the coordination in **23** has little effect on the adjacent ring. It should also be noted that the corresponding bond distances in the more highly substituted **31**¹¹ are not appreciably different from those of **23**.

Experimental Section

General Considerations. Manipulations of air-sensitive compounds were performed under a nitrogen or argon atmosphere using standard Schlenk techniques or in a nitrogen-filled MBraun drybox. THF, ether, pentanes, and hexanes were dried and deoxygenated by distillation from sodium/benzophenone ketyl. THF-*d*₈ was dried over K/Na alloy before use. ¹H, ¹¹B, and ¹³C NMR spectra were recorded on a Varian Inova 400 or 500 NMR spectrometer operating at ambient temperature. The ¹H and ¹³C NMR chemical shifts were determined relative to internal solvent standards and are referenced to tetramethylsilane. The ¹¹B NMR chemical shifts were referenced to external boron trifluoride diethyl etherate. Combustion analyses were determined using a Perkin-Elmer 240 CHN analyzer by the analytical services department of the Department of Chemistry of the University of Michigan, Ann Arbor, MI.

1,2-Dihydro-2-methyl-1,2-benzazaborine (**16**) and 2-chloro-1,2dihydro-1,2-benzazaborine (**14**) were prepared by the route of Dietz and Dewar.¹⁰ NMR spectra of **14** and **16** were identical with those reported by Paetzold and co-workers.¹¹

1,2-Dihydro-2-phenyl-1,2-benzazborine (15). Compound 15 was prepared by the reaction of phenylmagnesium bromide with 14 as described by Dewar and Dietz¹⁰ and was isolated as a white

powder. ¹H NMR (400 MHz, THF- d_8): δ 7.12 (t, J = 8.1 Hz, 1H, (Benzo)H); 7.24 (d, J = 11.4 Hz, 1H, C(3)H); 7.38 (m, 4H, (Benzo)H, ArH); 7.52 (d, J = 8.1 Hz, 1H, (Benzo)H); 7.61 (d, J = 8.1 Hz, 1H, (Benzo)H); 7.96 (d, J = 8.1 Hz, 2H, ArH); 8.10 (d, J = 11.4 Hz, 1H, C(4)H); 9.62 (br, 1H, NH). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 118.8, 121.7, 128.8, 129.0, 129.9, 130.2, 133.2, 146.1; signals for C(ipso), C(3), C(4a), and C(8a) not observed. ¹¹B NMR (160.4 MHz, CD₂Cl₂): δ 33.9. HRMS (EI, m/z): calcd for C₁₄H₁₂¹¹BN (M⁺), 205.1063; found, 205.1062. Anal. Calcd for C₁₄H₁₂BN: C, 82.00; H, 5.90; N, 6.83. Found: C, 81.61; H, 5.84; N, 6.71.

1,2-Dihydro-1,2-benzazaborine (17). The reaction of **14** with LiAlH₄ gave **17** as a white powder.¹⁰ ¹H NMR (500 MHz, DMSO- d_6): δ 5.02 (br, 1H, BH); 6.92 (d, J = 11.2 Hz, 1H, C(3)H); 7.19 (t, J = 8.0 Hz, 1H, (Benzo)H); 7.46 (t, J = 8.0 Hz, 1H, (Benzo)H); 7.54 (d, J = 8.0 Hz, 1H, (Benzo)H); 7.70 (d, J = 8.0 Hz, 1H, (Benzo)H); 8.11 (d, J = 11.2 Hz, 1H, C(4)H); 10.68 (br, 1H, NH). ¹³C NMR (100.6 MHz, DMSO- d_6): δ 118.4, 120.9, 125.2, 128.2, 129.2, 129.4 (br), 140.5, 144.7. ¹¹B NMR (160.4 MHz, DMSO- d_6): δ 31.5. HRMS (EI, m/z): calcd for C₈H₈¹¹BN (M⁺), 129.0750; found, 129.0747.

Tricarbonyl[1,2-dihydro-2-(η^6 -phenyl)-1,2-benzazaborine]chromium (18). 1,2-Dihydro-2-phenyl-1,2-benzazaborine (15) (600 mg, 2.93 mmol) and Cr(CH₃CN)₃(CO)₃ (800 mg, 3.09 mmol) were dissolved in 25 mL of THF. The resulting solution was heated to 140 °C with stirring for 60 h in a Teflon screw-stoppered thickwalled glass reaction tube. After the solvent was removed in vacuo, the residue was washed with hexanes $(3 \times 30 \text{ mL})$ at 0 °C. The residue was purified by column chromatography on silica gel (25%) ethyl acetate in hexanes elution) to give a pure sample of the product (494 mg, 49%) as a yellow powder. IR (benzene film): 1968, 1895 cm⁻¹. ¹H NMR (500 MHz, THF- d_8): δ 5.50 (t, J = 6.3 Hz, 2H, ArH); 5.70 (t, J = 6.3 Hz, 1H, ArH); 6.10 (d, J = 6.3 Hz, 2H, ArH); 7.05 (d, J = 11.5 Hz, 1H, C(3)H); 7.15 (t, J = 8.1 Hz, 1H, (Benzo)H); 7.40 (t, J = 8.1 Hz, 1H, (Benzo)H); 7.46 (d, J = 8.1Hz, 1H, (Benzo)H); 7.63 (d, J = 8.1 Hz, 1H, (Benzo)H); 8.11 (d, J = 11.5 Hz, 1H, C(4)H); 9.60 (br, 1H, NH). ¹³C NMR (100.6 MHz, THF-*d*₈): δ 93.5, 96.1, 99.8, 119.4, 122.1, 127.0 (br), 129.4, 130.3, 146.9; signals for C(ipso), C(4a), C(8a), and CO not observed. ¹¹B NMR (160.4 MHz, THF-*d*₈): δ 32.9. HRMS (EI, *m/z*): calcd for C₁₇H₁₂¹¹BNO₃⁵²Cr (M⁺), 341.0315; found, 341.0327. Anal. Calcd for C₁₇H₁₂BNO₃Cr: C, 59.86; H, 3.55; N, 4.11. Found: C, 60.23; H, 3.49; N, 4.14.

When the starting materials were stirred at 25 °C for 18 h, the ¹H spectrum indicated a mixture of **15**, **18**, and another product tentatively identified as **19**. ¹H NMR for **19** (500 MHz, THF-*d*₈): δ 5.06 (t, J = 7 Hz); 5.72 (t, J = 7 Hz); 5.88 (d, J = 7 Hz); 6.19 (d, J = 7 Hz) for the coordinated benzocyclic ring protons. Other peaks were obscured by peaks from **15** and **18**. Heating the mixture to 140 °C converted it to **18**.

Tricarbonyl[1,2-dihydro-1-lithio-2-(n⁶-phenyl)-1,2-benzazaborine]chromium (21). A mixture of LiTMP (6 mg, 0.041 mmol) and 18 (13 mg, 0.038 mmol) was dissolved in 0.75 mL of THF- d_8 . The ¹H NMR spectrum showed that **21** was formed quantitatively. Quenching the mixture with 10 μ L of D₂O resulted in the formation of 18-d, which was confirmed by ¹H spectroscopy (absence of the NH signal) and HRMS (HRMS (EI, m/z): calcd for C₁₇H₁₁²H¹¹BNO₃⁵²Cr (M⁺), 342.0378; found, 342.0376). Heating a sample of 21 in THF- d_8 resulted in slow decomposition to unidentified products. Data for 21 are as follows. ¹H NMR (500 MHz, THF- d_8): δ 5.38 (t, J = 6.3 Hz, 2H, ArH); 5.44 (t, J = 6.3Hz, 1H, ArH); 6.05 (d, *J* = 6.3 Hz, 2H, ArH); 6.76 (t, *J* = 8.0 Hz, 1H, (Benzo)H); 6.88 (d, J = 11.1 Hz, 1H, C(3)H); 7.10 (t, J = 8.0Hz, 1H, (Benzo)H); 7.31 (d, J = 8.0 Hz, 1H, (Benzo)H); 7.40 (d, J = 8.0 Hz, 1H, (Benzo)H); 7.86 (d, J = 11.1 Hz, 1H, C(4)H). ¹³C NMR (100.6 MHz, THF-d₈): δ 93.9, 94.8, 100.8, 117.0, 125.9,

126.4, 128.0 (br), 130.0, 142.9; signals for C(ipso), C(4a), and C(8a) not observed. ¹¹B NMR (160.4 MHz, THF- d_8): δ 34.8.

Tricarbonyl[(4a,5,6,7,8,8a-\eta)-1,2-dihydro-2-methyl-1,2-benzazaborine]chromium (23). 1,2-Dihydro-2-methyl-1,2-benzazaborine (16; 1.70 g, 11.89 mmol) and Cr(CH₃CN)₃(CO)₃ (5.80 g, 22.4 mmol) were dissolved in 80 mL of THF. The resulting solution was heated to 60 °C with stirring for 14 h. After the solvent was removed in vacuo, a ¹H NMR spectrum of the residue indicated that it was a mixture of 16 and 23 in a 1:3 ratio. Heating the reaction mixture to higher temperature resulted in the destruction of 23, but 16 survived. The residue was extracted with ethyl ether (4×20) mL). Ethyl ether was removed in vacuo, and the residue was washed with pentane $(3 \times 15 \text{ mL})$. The residue was purified by column chromatography on silica gel (30% CH₂Cl₂ in hexanes elution) to give a pure sample of the product (1.30 g, 39%) as an orange powder. IR (hexanes film): 1975, 1908 cm⁻¹. ¹H NMR (500 MHz, benzene- d_6): δ 0.45 (s, 3H, CH₃); 4.09 (t, J = 6.3 Hz, 1H, (Benzo)H); 4.35 (d, J = 6.3 Hz, 1H, (Benzo)H); 4.76 (t, J = 6.3Hz, 1H, (Benzo)H); 5.14 (d, J = 6.3 Hz, 1H, (Benzo)H); 5.86 (br, 1H, NH); 6.37 (d, *J* = 11.5 Hz, 1H, C(3)H); 6.96 (d, *J* = 11.5 Hz, 1H, C(4)H). ¹³C NMR (125.7 MHz, benzene-*d*₆): δ 80.5, 85.9, 94.5, 95.6, 131.6 (br), 144.9; signals for C(ipso), C(4a), C(8a), Me, and CO not observed. ¹¹B NMR (160.4 MHz, benzene- d_6): δ 39.9. HRMS (EI, m/z): calcd for $C_{12}H_{10}^{11}BNO_3^{52}Cr$ (M⁺), 279.0159; found, 279.0152. Anal. Calcd for C12H10BNO3Cr: C, 51.66; H, 3.61; N, 5.02. Found: C, 51.84; H, 3.73; N, 4.96.

Conversion of 23 to 25. A mixture of KHMDS (8 mg, 0.040 mmol) and **23** (10 mg, 0.036 mmol) was dissolved in 0.75 mL of THF-*d*₈. The resulting NMR showed that **25** was formed quantitatively. Quenching the mixture with 10 μ L of D₂O resulted in the formation of **23-***d*, which was confirmed by HRMS (HRMS (EI, *m/z*): calcd for C₁₂H₉²H¹¹BNO₃⁵²Cr (M⁺), 280.0222; found, 280.0229). Data for **25** are as follows. ¹H NMR (500 MHz, THF-*d*₈): δ 0.54 (s, 3H, CH₃); 4.92 (t, *J* = 6.3 Hz, 1H, (Benzo)H); 5.51 (t, *J* = 6.3 Hz, 1H, (Benzo)H); 5.59 (d, *J* = 6.3 Hz, 1H, (Benzo)H); 6.05 (d, *J* = 6.3 Hz, 1H, (Benzo)H); 5.59 (d, *J* = 11.1 Hz, 1H, C(3)H); 7.34 (d, *J* = 11.1 Hz, 1H, C(4)H). ¹³C NMR (100.6 MHz, THF-*d*₈): δ 84.0, 92.1, 97.4, 100.7, 133.8(br), 142.7; signals for C(ipso), C(4a), C(8a), CO, and Me not observed. ¹¹B NMR (160.4 MHz, THF-*d*₈): δ 40.8.

Conversion of 25 to 26. A solution of 25 was prepared from 23 (12 mg, 0.043 mmol) and KHMDS (10 mg, 0.05 mmol) in 0.75 mL of THF- d_8 . After the resulting solution was heated to 90 °C

for 4 h, the ¹H NMR spectrum indicated the formation of **26** along with 25% of unidentified products. After the reaction mixture was cooled to room temperature, it was quenched with excess MeI to give **28** and other unidentified materials. The ¹H NMR and mass spectra showed that **28** was identical with previously obtained material.¹⁰ Data for **26** are as follows. ¹H NMR (500 MHz, THF*d*₈): δ 0.56 (s, 3H, CH₃); 4.36 (d, *J* = 9.5 Hz, 1H, C(3)H); 6.30 (d, *J* = 9.5 Hz, 1H, C(4)H); 6.95 (t, *J* = 7.8 Hz, 1H, (Benzo)H); 7.13 (d, *J* = 7.8 Hz, 1H, (Benzo)H); 7.22 (t, *J* = 7.8 Hz, 1H, (Benzo)H); 7.47 (d, *J* = 7.8 Hz, 1H, (Benzo)H). ¹³C NMR (125.7 MHz, THF*d*₈): δ 95.0 (br), 110.3, 129.0, 129.9, 133.1, 133.9; signals for C(ipso) C(3), C(4a), C(8a), CO, and C(Me) not observed. ¹¹B NMR (160.4 MHz, THF-*d*₈): δ 24.0.

Kinetics of the Haptotropic Migration of 25. The reaction was carried out on solutions of 25 prepared as described above and sealed in NMR tubes. The reaction was monitored by ¹H NMR spectroscopy. The integrals of various proton multiplets of 25 were normalized against that of the signal of cyclohexane used as an internal standard. Use of the first-order rate equation gave satisfactory plots ($R^2 = 0.998$) for up to 2 half-lives. The rate constant was found to be $2.80 \times 10^{-5} \text{ s}^{-1}$ at 333 K. No crossover products were found when the reaction was performed in the presence of hexamethylbenzene.

Single-Crystal X-ray Crystallography. Crystals of **17**, **18**, and **23** suitable for X-ray diffraction were obtained by recrystallization at room temperature from pentane/CH₂Cl₂, benzene/ethyl acetate, and ethyl acetate, respectively. All crystallographic data for **17** are available in the Supporting Information. Crystallographic and data collection parameters for **18** and **23** are collected in Table 2. ORTEP drawings of **18** and **23** showing the atom-numbering schemes 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.

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Supporting Information Available: CIF files giving X-ray characterization data for **17**, **18**, and **23** and figures giving ¹H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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