Synthesis and Properties of 1-Substituted 1-Boratanaphthalenes

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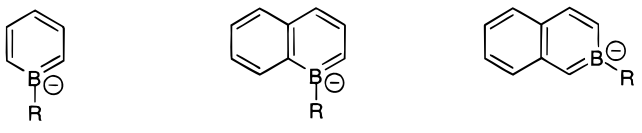
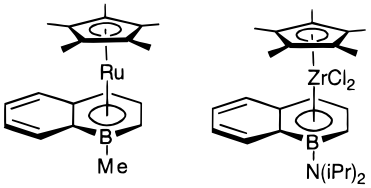
1,4-Dihydro-1,1-dimethyl-1-stannanaphthalene (**10**) has been prepared by a multistep synthesis starting from α,2-dibromotoluene (**6**). The reaction of **10** with $MeBBr_2$ followed by LDA afforded lithium 1-methyl-1-boratanaphthalene (**2a**). The reaction of **10** with BCl_3, followed by diisopropylamine and subsequent treatment with LDA, gave lithium *N*,*N*-diisopropyl-1-amino-1-boratanaphthalene (**2c**). The boratanaphthalenes have been characterized using ^{1}H NMR, ^{11}B NMR, and ^{13}C NMR spectroscopy. The pK_a of the conjugate acid of **2c** is close to that of indene. **2a** reacts with $[Cp^*RuCl]_4$ to form Ru sandwich compound **4a**, in which the boratanaphthalene is η^6 bound to Ru. **2c** reacts with Cp^*ZrCl_3 to form a Cp^*ZrCl_2 adduct **5c**, in which the boratanaphthalene unit is unsymmetrically bound to Zr.

Introduction

1-Substituted boratabenzenes **1** are six π-electron aromatic anions[1] which can serve as replacement ligands for the ubiquitous Cp in organometallic compounds.[2−4] In the same manner boratanaphthalenes **2** and **3** might be considered replacement ligands for indenyl. In fact Paetzold et al. have previously prepared several 2-boratanaphthalenes **3** and have shown that they can serve as ligands toward metals.[5] We report here on the first synthesis of 1-boratanaphthalenes **2**. The availability of **2** has allowed a comparison of **1**, **2**, and **3**.

However, boratabenzene metal complexes diverge from Cp metal complexes in that exocyclic π-donor substituents on boron may change the character of the ligand. This interaction is relatively small for electron-rich late transition metal complexes of 1-alkylboratabenzenes[2] but becomes dominant for electron-deficient early metal complexes of 1-aminoboratabenzenes.[4a] Thus it was of interest to prepare and examine metal complexes **4a** and **5c**. The crystal structure of **4a** shows that the C_5B ring of the 1-methyl-1-boratanaphthalene ligand is η^6 bound to Ru(II). In contrast the structure of **5c** shows the C_5B ring of the *N*,*N*-diisopropyl-1-amino-1-boratanaphthalene ligand is quite unsymmetrically bound to Zr(IV).





4a **5c**

Synthesis

Lithium boratabenzenes are usually prepared by deprotonation of the corresponding boracyclohexadienes, which are most generally available by B/Sn-exchange from the corresponding stannacyclohexadienes.[1b] Hence, the initial goal of our synthesis of 1-boratanaphthalenes involved the preparation of dihydrostannanaphthalene **10**. This tin heterocycle has been prepared via a multistep but high-yield sequence from commercially available α,2-dibromotoluene (**6**), as illustrated in Scheme 1.

The CuBr-catalyzed coupling of trimethylsilylacetylenemagnesium chloride with **6** gave a near quantitative yield of **7**. Diisobutylaluminum hydride reduction of **7** followed by hydrolysis gave a 62% yield of **8**, regrettably contaminated with 10% of its *Z*-isomer. Inversion/

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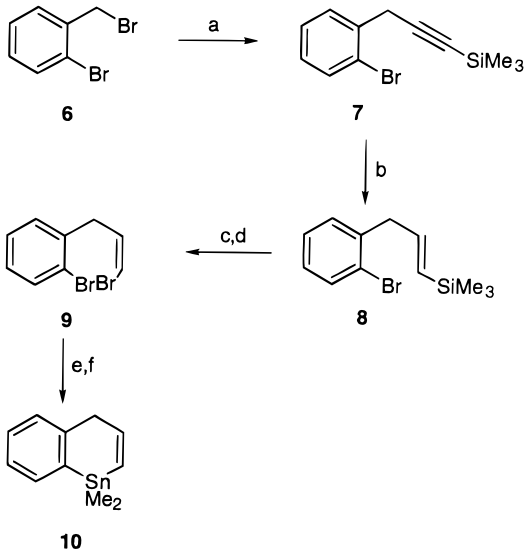
Scheme 1. Synthesis of 1,4-Dihydro-1,1-dimethyl-1-stannanaphthalene (10)[a]



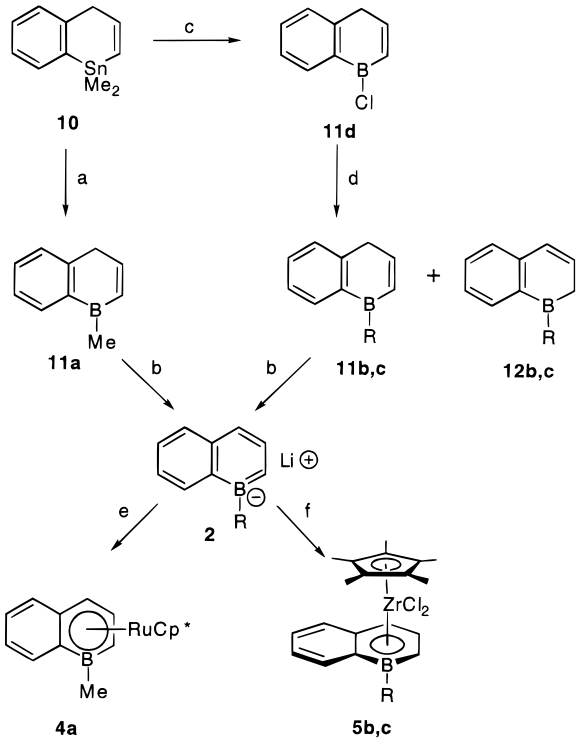
[a] Key: (a) Me_3SiC_2MgCl, CuBr; (b) $(i\text{-}Bu)_2AlH$; then H_2SO_4, H_2O; (c) Br_2; (d) NaOMe, HOMe; (e) t-BuLi; (f) Me_2SnCl_2.

substitution of **8** to **9** was accomplished using the procedure of Miller and McGarvey.[6] Bromination followed by elimination of [$BrSiMe_3$] with NaOMe afforded 94% of **9** (now contaminated with 10% of its *E*-isomer). Dilithiation of **9** in ether with *tert*-butyllithium followed by reaction with dimethyltin dichloride afforded a 49% yield of **10** as an air-sensitive colorless liquid. Since tin compounds analogous to **10** have been widely used in the preparation of main group element heterocycles,[7] we foresee that **10** will become a generally useful synthon for 1-heteronaphthalenes.[8]

As anticipated, 1,4-dihydro-1,1-dimethyl-1-stannanaphthalene **10** can be easily converted to 1-boratanaphthalenes **2**, as shown in Scheme 2. The exchange reaction of **10** with $MeBBr_2$ in pentane afforded **11a** and Me_2SnBr_2. The boracycle **11a** was converted to lithium 1-methyl-1-boratanaphthalene (**2a**) by treatment with LDA in ether. Removal of the ether followed by washing with pentane allowed isolation of pure **2a** as a pale yellow powder in 85% yield from **10**.

The reaction of **10** with BCl_3 in pentane afforded **11d**, which could be separated from Me_2SnCl_2 by distillation in 86% yield. The reaction of the chloride **11d** with 2 equiv of $HNEt_2$ in pentane afforded an oily mixture of conjugated and unconjugated aminoboranes **11b** and **12b**, which were separated from the insoluble amine hydrochloride in 61% yield. No attempt was made to separate the two isomers. Treating the mixture of **11b** and **12b** with LDA in ether gave a deep red solution of **2b**. After removal of the solvent the residue was washed with pentane, and on drying the pure **2b** was isolated in 95% yield as a yellow powder. **2c** was prepared in the same manner.

Scheme 2. Synthesis of 1-Boratanaphthalenes (2)[a]



[a] Key: (a) $MeBBr_2$; (b) LDA; (c) BCl_3; (d) $HNEt_2$ or $HN(i\text{-}Pr)_2$; (e) $[Cp^*RuCl]_4$; (f) Cp^*ZrCl_3. Cp* = pentamethylcyclopentadienyl.

The reaction of **2a** with $[Cp^*RuCl]_4$ afforded the (Cp*)-(1-methyl-1-boratanaphthalene)Ru **4a** as beautiful bright amber crystals in 81% yield. Similar reactions of **2c** with Cp^*ZrCl_3 gave bright red crystals of **5c** in 66% yield. We have obtained crystal structures of **4a** and **5c** which are discussed below.

NMR Spectra

The ^1H, ^{11}B, and ^{13}C NMR chemical shift values of lithium 1-boratanaphthalenes **2a** and **2c** are compared with those of the identically substituted boratabenzenes **1a** and **1c** in Figure 1. Data for Paetzold's lithium *N*,*N*-diisopropyl-2-amino-2-boratanaphthalene **3c** are also included.[5c] Also included are data for CpLi[10] and indenyllithium.[11] All spectra were recorded in THF-d_8. In this solvent it is likely that all species exist as contact ion pairs in which the Li cation resides preferentially over the anionic ring.[12] This geometry is explicitly shown in X-ray structures of indenyllithium,[13] **1**,[1c,14] and **3c**.[5]

The spectra of boratabenzenes have been discussed previously;[1b,9] however it is necessary to review their salient features in order to compare with the bora-

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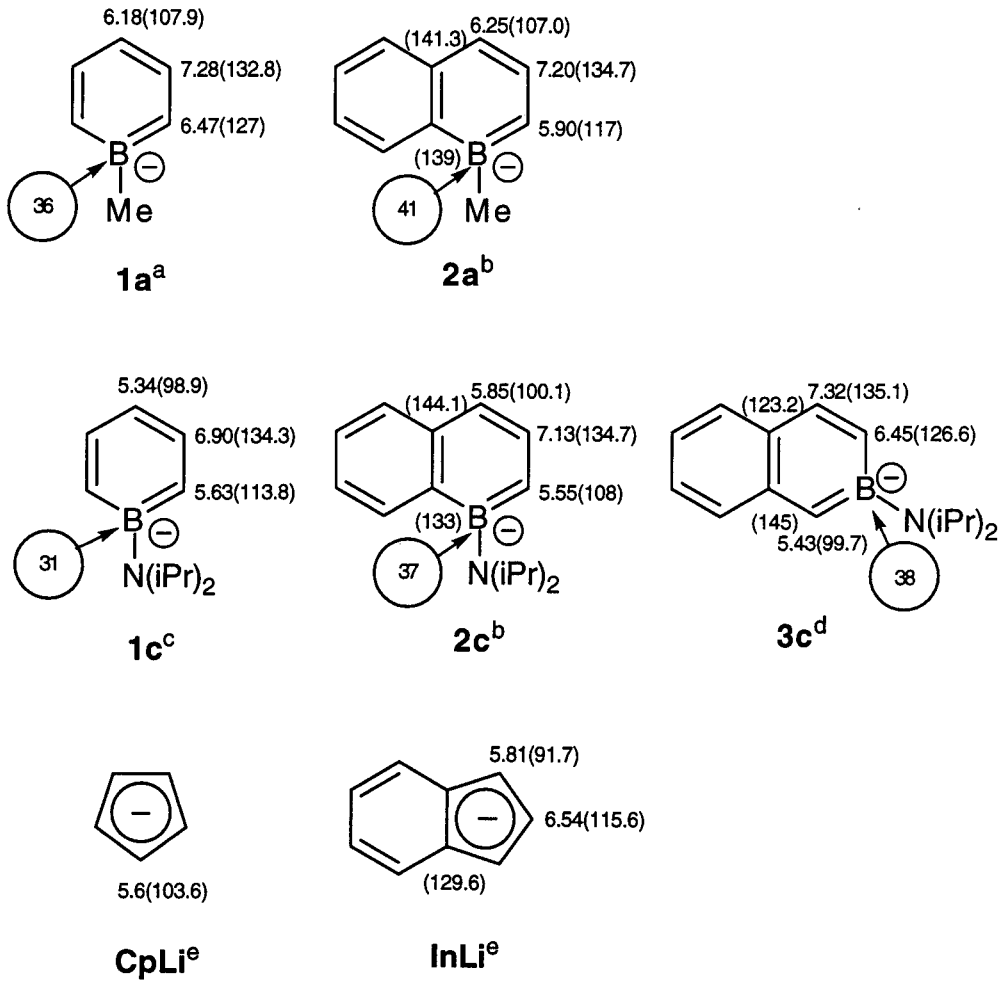

Figure 1. Comparison of the ^{1}H NMR, ^{13}C NMR (in parentheses), and ^{11}B NMR (in circles) chemical shift values of lithium boratabenzenes, lithium boratanaphthalenes, CpLi, and indenyllithium in THF(d_8). [a]Ref 9. [b]This work. [c]Ref 21. [d]Ref 50. [e]Ref 11.

tanaphthalenes. The ^{1}H NMR chemical shift values of boratabenzene ring protons which are β to boron, δ (H_3,H_5), are generally similar to those of benzene. In contrast δ (H_2, H_6) and δ (H_4) are upfield, which is consistent with their partial negative charge. The effect of donor substituents (e.g., NR_2) on boron is to enhance this upfield shift. The ^{1}H NMR signals for the CH groups on the C_5B rings of 1-boratanaphthalene closely conform to the pattern of boratabenzenes.

The ^{11}B NMR chemical shift values of boratanaphthalenes are in the range found for aromatic boron anions but are 5−7 ppm downfield from the corresponding boratabenzenes. Relative to their uncharged conjugate acids, e.g., **11a** $\delta(^{11}B) = 62.6$, the upfield shifts on deprotonation are large (to $\delta(^{11}B) = 41$ for **2a**). Thus substantial π-donation of negative charge to boron is indicated for both boratabenzenes and boratanaphthalenes.

The ^{13}C NMR chemical shifts are particularly useful since they have been correlated with π-charge densities of carbanions[15,16] and heterocarbanions.[17] For boratabenzenes **1a** and **1c** the signals for CH groups which are β to boron are close to δ 134, indicating little negative charge at C(3), C(5). The signals for the CH groups at C(2), C(4), and C(6) are shifted upfield, reflecting their carbanionic character. In a qualitative way the π-charge distribution of boratabenzenes seems to be well represented by the classical resonance structures illustrated in Scheme 3. The 1-boratanaphthalene spectra completely conform to this pattern for the CH groups on the C_5B ring. However, the quaternary carbon atoms at the bridgeheads (C(4a), C(8a)) display relatively high-field signals (δ, 133−144). For comparison the bridgehead carbon atoms of indenyllithium also show high-field signals, which is consistent with their small π-charge density.[11] Thus the ^{13}C NMR shifts of 1-boratanaphthalenes indicate that the negative charge is localized to B(1), C(2), and C(4). Classical resonance structures for 1-boratanaphthalene show negative charge at B(1), C(2), and C(4). Only in the presumably less important quininoid structure **2‴** is the negative charge resident at C(8a). For comparison the ^{13}C NMR spectrum of **3c** shows only the signal for C(1) at high field. Therefore, the negative charge seems to be largely confined to C(1) and B(2), as would be anticipated from considering the lower energy resonance structures **3** and **3′**.

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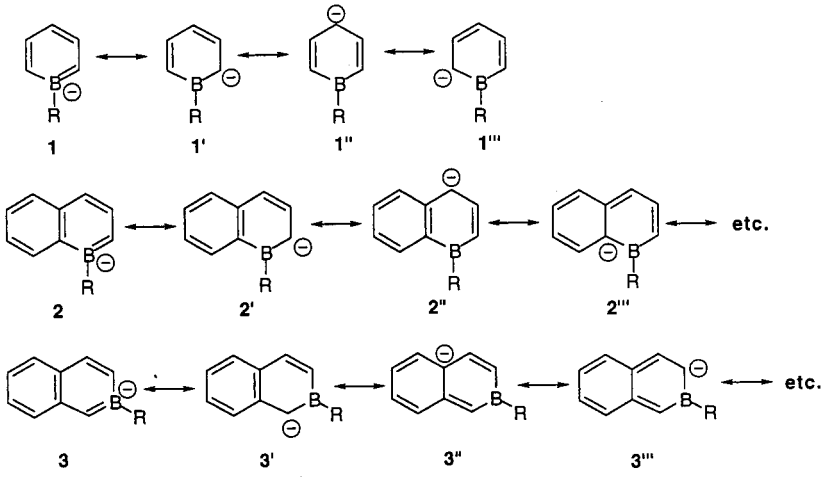
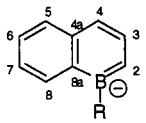
Scheme 3. Resonance Structures of Boratabenzenes, 1-Boratanaphthalenes, and 2-Boratanaphthalenes



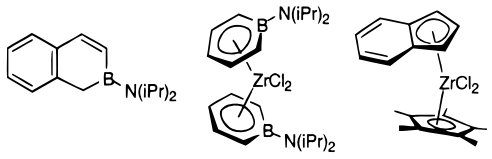


Acidity of the Conjugate Acids of Boratanaphthalenes

1-Methyl-1-boracyclohexa-1,4-diene is more acidic than cyclopentadiene in both the gas phase[18] and solution.[9,19] Treating **11a** with LiCp in DMSO leads to quantitative formation of **2a** and cyclopentadiene. Thus, the acidities of both 1-methyl-1-boracyclohexadiene and **11a** in DMSO are greater than that of cyclopentadiene (pK_a=18.0), which must derive from the aromatic stabilization of the corresponding aromatic anions **1a** and **2a**, respectively.

To obtain quantitative comparisons, we have chosen to measure the pK_a's of the less acidic dialkylaminodihydroboranaphthalenes. A large amount of data are available for acidities in DMSO.[20] For example, the conjugate acid of **1c**, *N*,*N*-diisopropyl-1-amino-1-boracyclohexa-1, 4-diene, has a pK_a (DMSO) = 17.8,[21] which is virtually identical to that of cyclopentadiene. Treating a DMSO-d_6 solution of **11c** and **12c** with CpLi gave no **2c** but partially isomerized **11c** to the more stable **12c** (equilibrium ratio 1:2.3). However treating a DMSO-d_6 solution of **11c** and **12c** with indenyllithium gave a complex mixture of indene, indenyllithium, **11c**, **12c**, and **2c**, which could be analyzed by ^{1}H NMR spectroscopy. On the basis of pK_a (DMSO) = 20.1 for indene,[20] the values pK_a = 19.7 for **11c** and 20.1 for **12c** have been determined. Since the pK_a's of diisopropylaminoboracyclohexadienes are similar to that of cyclopentadiene and the pK_a of **12c** is similar to that of indene, replacement of a double bond by a benzo group has a similar effect on the acidity in both the Cp and boratabenzene series. Thus it seems justified to view 1-boratanaphthalene as an electronic analogue of the indenyl anion.

For comparison we have also examined the acidity of **13c**, which we prepared by the method of Paetzold et al.[5] A DMSO-d_6 solution of **13c** remains unchanged when treated with indenyllithium. However treating **13c** with the more basic fluorenyllithium gives a mixture of **3c**, **13c**, fluorene, and fluorenyllithium. Analysis by ^{1}H NMR spectroscopy allowed evaluation of the pK_a (DMSO) = 21.5 for **13c** based on pK_a (DMSO) = 22.6 for fluorene.[20] Thus **13c** is approximately 25 times less acidic than its isomer **12c**. Relative acidities in DMSO solution depend on structural and solvent effects.[22] If the solvation energies of **2c** and **3c** in DMSO are similar, it may be that the higher acidity of **12c** reflects a greater stability of **2c** over **3c**. The greater delocalization of charge in **2** implied by considering resonance structures of **2** and **3** is consistent with a lower energy for **2**.



Structures

It was of considerable interest to obtain structures for metal complexes of 1-boratanaphthalenes. The molecular structure of **4a** is illustrated in Figure 2, while selected bond distances are listed in Table 1. **4a** appears to be a classical sandwich compound. The boratabenzene portion of **4a** is η^6 bound to Ru, while the noncoordinated portion of the benzo ring shows diene-like C−C bond alternation. The boratabenzene ring is completely planar (±0.01 Å) but unsymmetrically bound in that the Ru atom is closer to C(7) (2.195(3) Å) than to B(1) (2.35-(1) Å). Similar slip distortions away from boron are a

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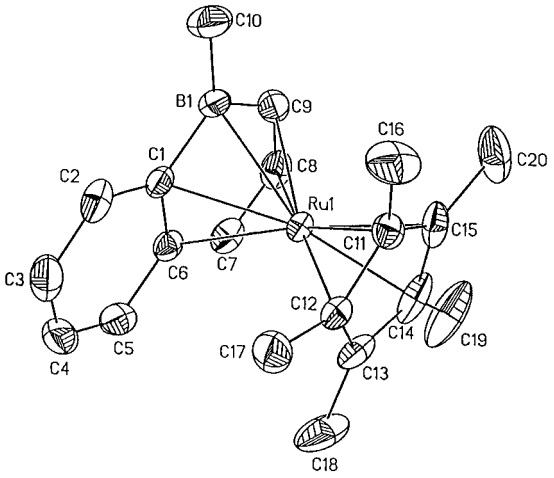

Figure 2. Solid-state structure of **4a** showing one of the two independent molecules.

Table 1. Selected Interatomic Distances (Å) for 4a

Ru(1)−C(14)	2.159 (3)	C(2)−C(3)	1.368 (4)
Ru(1)−C(15)	2.170 (2)	C(3)−C(4)	1.420 (5)
Ru(1)−C(13)	2.179 (3)	C(4)−C(5)	1.344 (4)
Ru(1)−C(12)	2.186 (2)	C(5)−C(6)	1.442 (4)
Ru(1)−C(11)	2.189 (2)	C(6)−C(7)	1.439 (4)
Ru(1)−C(7)	2.197 (2)	C(7)−C(8)	1.411 (4)
Ru(1)−C(8)	2.205 (3)	C(8)−C(9)	1.417 (4)
Ru(1)−C(9)	2.243 (3)	C(9)−B(1)	1.512 (5)
Ru(1)−C(6)	2.277 (2)	C(10)−B(1)	1.599 (4)
Ru(1)−C(1)	2.309 (2)	C(11)−C(12)	1.430 (3)
Ru(1)−B(1)	2.346 (3)	C(11)−C(15)	1.433 (4)
C(1)−C(2)	1.450 (4)	C(12)−C(13)	1.430 (3)
C(1)−C(6)	1.450 (3)	C(13)−C(14)	1.445 (5)
C(1)−B(1)	1.537 (4)	C(14)−C(15)	1.436 (5)

common feature of π-coordinated boron heterocycles.[2] The intra-ring bond distances conform to patterns shown by 1-methylboratabenzene late transition metal complexes[23] except that bonds involving the benzo fused ring are longer (av 0.03 Å), a pattern shown by other fused ring compounds.[24,25] It is notable that the intra-ring B−C bond lengths (1.51, 1.53 Å) are significantly shorter than the exocyclic B−CH_3 bond (1.60 Å). The shorter intra-ring B−C distance indicates B−C π-bonding. In summary, the boratabenzene portion of **4a** is an η^6 π-coordinated aromatic ring.

It is particularly interesting to compare structure **5c** with that of **4a**. A crystal of **5c** suitable for X-ray diffraction was obtained by recrystallization from pentane. The molecular structure of **5c** is illustrated in Figure 3, while selected bond distances are listed in Table 2. The Zr atom of **5c** shows pseudo-tetrahedral coordination which is typical of group 4 bent metallocenes. However Zr bonding to the *N*,*N*-diisopropyl-1-amino-1-boratanaphthalene ligand is very unsymmetrical. C(7), C(8), and C(9) are strongly bound, with Zr−C distances (2.53−2.56 Å) similar to those of the Cp* ring (2.53 Å). In contrast the distances between Zr and C(1) (2.77 Å), C(6) (2.81 Å), and B (2.955 Å) seem too long for effective bonding. Thus coordination approaches η^3. The carbon atoms of the C_5B ring are approximately

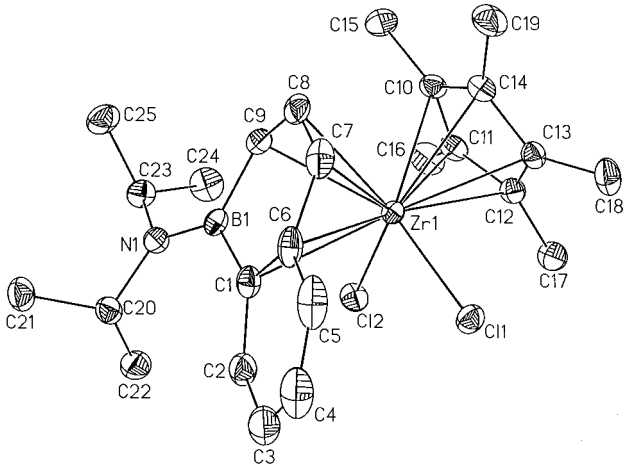

Figure 3. Solid-state structure of **5c**.

Table 2. Selected Interatomic Distances (Å) for 5c

B(1)−N(1)	1.424 (2)	Zr(1)−C(1)	2.8125 (14)
B(1)−C(9)	1.544 (2)	Zr(1)−B(1)	2.955 (1)
B(1)−C(1)	1.590 (2)	C(1)−C(2)	1.426 (2)
N(1)−C(20)	1.473 (2)	C(1)−C(6)	1.434 (2)
N(1)−C(23)	1.485 (2)	C(2)−C(3)	1.374 (2)
Zr(1)−Cl(2)	2.4394 (3)	C(3)−C(4)	1.403 (3)
Zr(1)−Cl(1)	2.4406 (3)	C(4)−C(5)	1.361 (3)
Zr(1)−C(12)	2.4928 (13)	C(5)−C(6)	1.426 (2)
Zr(1)−C(11)	2.5199 (14)	C(6)−C(7)	1.441 (2)
Zr(1)−C(13)	2.5225 (14)	C(7)−C(8)	1.388 (2)
Zr(1)−C(8)	2.5310 (14)	C(8)−C(9)	1.404 (2)
Zr(1)−C(9)	2.5314 (14)	C(10)−C(11)	1.414 (2)
Zr(1)−C(14)	2.5348 (14)	C(10)−C(14)	1.433 (2)
Zr(1)−C(10)	2.5425 (14)	C(11)−C(12)	1.422 (2)
Zr(1)−C(7)	2.5606 (14)	C(12)−C(13)	1.417 (2)
Zr(1)−C(6)	2.7776 (13)	C(13)−C(14)	1.417 (2)

coplanar (±0.026 Å), but the boron is displaced out of this plane away from Zr by 0.269(2) Å. Although the B atom is not coordinated to Zr, the relatively short B−N distance (1.42 Å) is consistent with π-bonding between these atoms.

We propose that the distortion of the *N*,*N*-diisopropyl-1-amino-1-boratanaphthalene toward η^3-bonding is the consequence of the high electron demand of Zr(IV), which prefers coordination to the most electron-rich carbon atoms. A similar but less severe distortion has been previously observed for **14**, which distorts toward η^5-coordination.[4a] The benzofusion in **5c** appears to cause a further localization of electron density on the C_5B ring, which gives C(7), C(8), and C(9) an allyl anion character. Thus these atoms are strongly coordinated. A similar but less pronounced distortion toward η^3-bonding is found for **15**.[26] In this case the Zr atom slip distorts away from the two bridgehead atoms toward the electron-rich three-carbon bridge.

Summary

In summary the syntheses of the 1-substituted-1-boratanaphthalenes **2** have allowed comparison of their properties with the corresponding boratabenzenes and 2-boratanaphthalenes. The conjugate acids of **1**, **2**, and **3** are highly acidic, which must derive from the stabilization of the aromatic anions **1**, **2**, and **3**. 1-Boratanaphthalenes can serve as ligands toward early and

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late transition metals. A highly symmetrical η^6-bonding was found in the electron-rich Ru(II) adduct **4a**, while a highly unsymmetrical bonding that approaches η^3 was found to the electron-deficient Zr(IV) of **5c**.

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-70-S spectrometer, while the NMR spectra were obtained by using either a Bruker WH-400, WH-360, or AM-300 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me_4-Si. 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.

3-(2-Bromophenyl)-1-(trimethylsilyl)-1-propyne (7). Powdered CuBr (2.3 g, 16 mmol) was added to a solution of (trimethylsilyl)acetylenemagnesium chloride[27] (0.22 mol) in 230 mL of THF at 25 °C. After the mixture had been allowed to stir for 10 min, a solution of α,2-dibromotoluene (40 g, 0.16 mol) in 15 mL of THF was added rapidly with stirring, and the reaction mixture was heated to reflux for 24 h. After cooling to 25 °C 200 mL of cold saturated aqueous NH_4Cl and 200 mL of ether were added. The organic layer was separated, and the aqueous fraction was extracted with 4 × 200 mL of ether. The combined organic fractions were washed with a saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. The product (41 g, 100%) was isolated by distillation (bp, 65−70 °C/0.01 Torr). IR (film): cm^{-1}, 2181 (*C*≡*C*). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.66 (d, *J* = 7.6 Hz, 1H, *ArH*); 7.54 (d, *J* = 8.1 Hz, 1H, ArH); 7.34 (t, *J* = 7.6 Hz, 1H, *ArH*), 7.13 (t, *J* = 8.1 Hz, 1H, *ArH*); 3.74 (s, 2H, CH_2), 0.23 (s, 9H, $SiMe_3$). ^{13}C MNR ($CDCl_3$, 90.6 MHz): δ 135.9 (*ArC*), 132.6 (*ArCH*), 129.7 (*ArCH*), 128.5 (*ArCH*), 127.7 (*ArCH*), 124.0 (*ArCBr*), 103.1 (*C*≡*C*), 88.5 (*C*≡*C*), 27.4 (CH_2), 0.27 ($SiMe_3$). HRMS (EI, *m*/*z*): calcd for $C_{12}H_{15}{}^{79}BrSi$, 266.0126; found, 266.0117. Anal. Calcd for $C_{12}H_{15}BrSi$: C, 53.93; H, 5.66. Found: C, 53.89; H, 5.70.

(1*E*)-3-(2-Bromophenyl)-1-(trimethylsilyl)-1-propene (8). A solution of **7** (13.5 g, 50 mmol) in 22 mL of hexane was added to a solution of diisobutylaluminum hydride (7.1 g, 8.9 mL, 50 mmol) in 74 mL of hexane at −0 °C. The reaction mixture was allowed to stir at 0 °C for 2 h followed by 16 h at 25 °C. The reaction mixture was added to 20 mL of 10% H_2SO_4 and crushed ice. The layers were separated, and the aqueous fraction was extracted with 3 × 100 mL of ether. The combined organic layers were washed with saturated aqueous NaCl and dried over anhydrous Na_2SO_4. Distillation gave 8.3 g (62%) of **8**, bp 63−65 °C/0.01 Torr, which contained 10% of *Z*-isomer as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, 360 MHz): δ 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H, *ArH*), 6.96 (dd, *J* = 7.5, 1.7 Hz, 1H, *ArH*), 6.90 (td, *J* = 7.5, 1.7 Hz, 1H, *ArH*), 6.67 (td, *J* = 7.5, 1.5 Hz, 1H, *ArH*); 6.15 (dt, *J* = 18.1, 6.0 Hz, 1H, $CHCH_2$); 5.71 (dt, *J* = 18.1, 1.7 Hz, 1H, *CHSi*), 3.5 (dd, *J* = 6.0, 1.7 Hz, 2H, CH_2), 0.09 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 90.5 MHz): δ 145.3, 143.5, 139.7, 133.1, 132.4, 130.8, 127.5, 125.1 (*Ar, vinyl*), 43.3 (CH_2), 1.2 ($SiMe_3$). HRMS (EI, *m*/*z*): calcd for $C_{12}H_{17}{}^{79}BrSi$: 268.0283. Found: 268.0270. Anal. Calcd for $C_{12}H_{17}BrSi$: C, 53.53; H, 6.32. Found: C, 53.09; H, 6.56.

(2*Z*)-1-(2-Bromophenyl)-3-bromo-2-propene (9). To a solution of **8** (7.5 g, 27 mol) in CH_2Cl_2 (54 mL) at −78 °C was added a 3 M solution of Br_2 in CH_2Cl_2 until the bromine color persisted. After warming to 25 °C the solution was washed sequentially with 20 mL of a 10% aqueous solution of $Na_2S_2O_3$ and saturated aqueous NaCl. The organic fraction was dried over anhydrous Na_2SO_4. Removal of solvent gave 11.9 g of crude tribromide, which was dissolved in 14 mL of CH_2Cl_2 and cooled to 0 °C. A methanol solution of 1 N sodium methoxide (42 mL, 42 mmol) was added, and the reaction mixture was allowed to stir for 1 h at 0 °C and 2 h at 25 °C. The reaction mixture was partitioned between water (50 mL) and pentane (50 mL). The layers were separated, and the aqueous layer was extracted with 3 × 50 mL of pentane. The combined organic layers were washed with saturated aqueous NaCl and dried over anhydrous Na_2SO_4. Distillation gave 7.6 g (94%) of product, bp 65−67 °C/0.05 Torr. ^{1}H NMR spectra showed 10% of *E*-product. ^{1}H NMR (C_6D_6, 360 MHz): δ 7.32 (dd, *J* = 8, 1.3 Hz, 1H, *ArH*), 6.93 (dd, *J* = 7.5, 1.2 Hz, 1H, *ArH*), 6.84 (td, *J* = 7.5, 1.2 Hz, 1H, *ArH*), 6.65 (td, *J* = 8, 1.3 Hz, 1H, *ArH*), 5.86 (dt, *J* = 6.7, 1.3 Hz, 1H, *CHBr*), 5.81 (q, *J* = 6.7 Hz, 1H, $CHCH_2$), 3.52 (d, *J* = 6.7 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 134.9, 133.1, 132.2, 130.6, 128.4, 127.9, 124.7, 109.6 (*Ar, vinyl*), 36.8 (CH_2). HRMS (EI, *m*/*z*): calcd for $C_9H_8{}^{79}Br_2$, 273.8993; found, 273.8989. Anal. Calcd for $C_9H_8Br_2$: C, 39.17; H, 2.92. Found: C, 38.99; H, 3.04.

1,4-Dihydro-1,1-dimethyl-1-stannanaphthalene (10). A solution of **9** (16.9 g, 61.7 mmol) in 20 mL of ether was added dropwise with stirring to a solution of t-BuLi (246 mmol) in 145 mL of pentane and 60 mL of ether at −78 °C. The temperature of the reaction mixutre did not rise above −69 °C during the addition. The resulting white suspension was stirred at −78 °C for 3 h and then allowed to warm to 25 °C for 1 h before recooling to −78 °C. A solution of dimethyltin dichloride (13.5 g, 61.6 mmol) in 145 mL of ether was added, and the resulting reaction mixture was stirred for 2 h at −78 °C followed by 24 h at 25 °C. The white precipate was removed by filtration, and the solvent was removed in vacuo. The residue was extracted with 2 × 50 mL of pentane. The extracts were filtered, and the 8.0 g (49%) of product was isolated by distillation, bp, 50−52 °C/0.01 Torr. The product is a colorless liquid that is mildly sensitive to air and moisture. ^{1}H NMR (C_6D_6, 360 MHz): δ 7.41 (m, 1H, $^3J_{^{119}SnH}$ = 46 Hz, *ArH*), 7.13 (m, 2H, *ArH*), 7.05 (m, 1H, *ArH*), 6.87 (dt, *J* = 13.2, 4.6 Hz, $^3J_{^{119}SnH}$ = 133 Hz, 1H, $CHCH_2$), 6.42 (dt, *J* = 13.2, 1.2 Hz, $^2J_{^{119}SnH}$ = 92 Hz, 1H, *SnCH*), 3.37 (d, *J* = 4.6 Hz, 2H, CH_2), 0.22 (s, $^2J_{^{119}SnH}$ = 59 Hz, 6H, *Me*). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 146.0, 145.8, 139.6, 136.4, 129.8, 128.6, 128.5, 125.9 (*Ar, vinyl*), 39.6 (CH_2), −1.8 (Me). HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}{}^{120}Sn$ (M^+ − Me), 250.9883; found, 250.9877. Anal. Calcd for $C_{11}H_{14}Sn$: C, 48.05; H, 5.13. Found: C, 48.03; H, 5.18.

1,4-Dihydro-1-methyl-1-boratanaphthalene (11a). A solution of **10** (1.0 g, 3.8 mmol) in 8 mL of pentane was added to a solution of $MeBBr_2$ (1.06 g, 5.7 mmol) in 3 mL of pentane at −78 °C. A white precipate formed immediately. The reaction mixture was stirred at −78 °C for 1 h and then allowed to warm to 25 °C for 2 h. The color changed to yellow. Removal of solvent left a white solid mixture of Me_2SnBr_2 and **11a**, which was used as is. ^{1}H NMR (THF-d_8, 360 MHz): δ 8.01 (d, *J* = 7.2 Hz, 1H, ArH), 7.47−7.24 (m, 4H), 6.70 (dt, *J* = 11.7, 1.8 Hz, 1H, H(2)), 3.78 (br, 2H, H(4)), 1.09 (s, 3H, *Me*). ^{13}C NMR (THF-d_8, 90.6 MHz): δ 154.1 (C(3)), 135.1 (*ArH*), 131.9 (*ArH*), 128.9 (*ArH*), 126.3 (*ArH*), 38.0 (C(4)). ArC, BMe not observed. ^{11}B NMR (THF-d_8, 115.5 MHz): δ 62.6. HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}{}^{11}B$, 142.0954; found, 142.0961.

Lithium 1-Methyl-1-boratanaphthalene (2a). A solution of 3 equiv of LDA in 5 mL of ether was added to a solution of the above product in 5 mL of ether at −78 °C. The resulting yellow solution was allowed to warm to 25 °C. Solvent was removed in vacuo, leaving a yellow residue, which was washed with 4 × 30 mL of pentane. On drying 480 mg (85% from **10**) of **2a** was obtained as a pale yellow powder. ^{1}H NMR (THF-d_8, 360 MHz): δ 7.85 (d, *J* = 7.9 Hz, 1H, ArH), 7.22 (d, *J* = 7.9 Hz, 1H, ArH), 7.20 (dd, *J* = 9.6, 7.5 Hz, 1H, H(3)), 6.80 (t, *J* = 7.9 Hz, 1H, ArH), 6.55 (t, *J* = 7.9 Hz, 1H, ArH), 6.25 (d, *J* = 7.5 Hz, 1H, H(4)), 5.89 (d, *J* = 9.6, 1H, H(2)), 0.76 (s, 3H, Me). ^{13}C NMR (THF-d_8, 90.6 MHz): δ 144.1 (C(4a)), 139 (b, C(8a)), 134.7 (C(3)), 133.0 (*ArH*), 127.0 (*ArH*), 122.0 (*ArH*), 117

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Table 3. Crystal Data and Structure Refinement for 4a and 5c

	4a	5c
empirical formula	$C_{20}H_{25}BRu$	$C_{25}H_{36}BCl_2NZr$
formula weight	377.28	523.48
temp, K	158(2)	158(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)2(1)2(1)
unit cell dimensions	$a = 10.4714(3)$ Å $b = 23.0493(6)$ Å $c = 14.9480(4)$ Å $\beta = 102.5820(10)°$	$a = 7.96610(10)$ Å $b = 16.8351(3)$ Å $c = 18.7831(3)$ Å
volume, *Z*	3521.2(2) Å^3, 8	2519.00(7) Å^3, 4
density (calcd), Mg/m^3	1.423	1.380
abs coeff, mm^{-1}	0.884	0.661
F(000)	1552	1088
cryst size, mm	0.03 × 0.40 × 0.60	0.20 × 0.24 × 0.42
θ range for data collection, deg	2.18−29.40	2.42−28.28
limiting indices	$-13 \le h \le 14$, $-31 \le k \le 30$, $-19 \le l \le 20$	$-10 \le h \le 10$, $-22 \le k \le 22$, $-24 \le l \le 25$
no. of reflns collected	35 926	28 753
no. of ind reflns	8937 [*R*(int) = 0.0240]	6224 [*R*(int) = 0.0190]
abs corr	multiscan	none
max & min transmission	0.906 and 0.800	
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	8900/0/412	6221/0/417
goodness-of-fit on F^2	1.027	1.064
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0339, wR2 = 0.0840	R1 = 0.0168, wR2 = 0.0406
R indices (all data)	R1 = 0.0421, wR2 = 0.0893	R1 = 0.0180, wR2 = 0.0410
largest diff peak and hole, e/A^3	3.137 and −1.406	0.241 and −0.227

(br, C(2)), 114.9 (*ArH*), 107.0 (C(4)), 3.0 (br, Me). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 40.9.

(η^6-1-Methyl-1-boratanaphthalene)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (4). A solution containing a slight excess of **2a** in 4 mL of THF was added slowly to a solution of $[Cp^*RuCl]_4$ (0.15 g, 0.55 mmol) in 5 mL of THF at −78 °C. The mixture was allowed to stir at −78 °C for 2 h and then at 25 °C for 8 h. Solvent was removed, and the residue was extracted with 2 × 30 mL of pentane. After filtration and removal of solvent the residue was a yellow solid. Recrystallization from pentane gave 176 mg (81%) of **12** as amber crystals, mp 184 °C. ^{1}H NMR (C_6D_6, 360 MHz): δ 7.73 (d, J = 8.1 Hz, 1H, ArH), 7.02 (m, 2H, ArH), 6.91 (d, J = 7.4 Hz, 1H, ArH), 5.13 (d, J = 5.6 Hz, 1H, H(4)), 5.02 (dd, J = 8.0, 5.6 Hz, 1H, H(3)), 4.46 (d, J = 8.0 Hz, 1H, H(2)), 1.36 (s, 15H, Cp*Me), 1.22 (s, 3H, BMe). ^{13}C NMR (C_6D_6, 90.6 MHz): δ 136.9 (*ArH*), 127.0 (*ArH*), 122.7 (*ArH*), 102.9 (*ArC*), 92.9 (C(3)), 85.0 (C(*Cp*)), 77.2 (C(4)), 9.8 (*CpMe*), 1.3 (*BMe*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 17.8. HRMS (EI, *m*/*z*): calcd for $C_{20}H_{25}{}^{11}BRu$, 378.1093; found, 378.1087.

1-Chloro-1,4-dihydro-1-boratanaphthalene (11d). A solution of **10** (4.0 g, 15.1 mmol) in 10 mL of pentane was added to a solution of BCl_3 (2.54 g, 30 mmol) in 15 mL of pentane at −78 °C. A white solid formed immediately. The mixture was stirred at −78 °C for 1 h and at room temperature for 3 h. Excess BCl_3 and solvent were removed by distillation under reduced pressure. Me_2SnCl_2 was removed by vacuum distillation (the oil bath temperature was kept between 47 and 52 °C). The product was obtained as a brown liquid, which solidified to form colorless crystals (mp 38−39 °C) (2.12 g, 86% yield). ^{1}H NMR (360 MHz, C_6D_6): δ 8.40 (d, 1H, J = 7.6 Hz, ArH), 7.24 (dt, 1H, J = 7.2, 1.8 Hz, ArH), 7.18 (m, 2H, ArH & H_3), 6.96 (d, 1H, J = 7.2 Hz, ArH), 6.92 (td(broad), 1H, J = 12, 2.8 Hz, H(3)), 6.67 (td, 1H, J = 12, 1.8 Hz, H(2)), 3.14 (m, 2H, H_4). ^{13}C NMR (90.6 MHz, C_6D_6): δ 157.6, 148.4, 135.0, 132.7, 128.3, 126.7, 37.4 (C(4)). ^{11}B NMR (115.5 MHz, C_6D_6): δ 53.6. HRMS (EI, *m*/*z*): calcd for $C_9H_8{}^{11}B^{35}Cl$, 162.0408; found, 162.0416.

***N*,*N*-Diethyl-1-amino-1,4-dihydro-1-boranaphthalene (11b) and *N*,*N*-Diethyl-1-amino-1,2-dihydro-1-boranaphthalene (12b).** Diethylamine (1.26, 17.2 mmol) was added via a syringe to a solution of **11d** (1.4 g, 8.6 mmol) in 15 mL of pentane at 25 °C. A white solid was formed immediately. The mixture was stirred at room temperature for 10 h. The solvent was removed after filtration to give the product (1.04 g, 61% yield) as a yellow oil. NMR spectra were consistent with a mixture of **11b** and **12b** in the ratio 6:1. ^{11}B NMR (155 MHz, C_6D_6): δ 40.8 (minor), 33.6 (major). HRMS (EI, *m*/*z*): calcd for $C_{13}H_{18}{}^{11}BN$, 199.1532; found, 199.1533.

***N*,*N*-Diisopropyl-1-amino-1,4-dihydro-1-boranaphthalene (11c) and *N*,*N*-Diisopropyl-1-amino-1,2-dihydro-1-boranaphthene (12c).** In the same manner as above a mixture of **11c** and **12c** was obtained from treating a solution of **11d** (2.12 g, 13.0 mmol) in 20 mL of pentane with 2 equiv of $HN(i\text{-}Pr)_2$. The product was obtained as a yellow oil (2.04 g, 69%). ^{11}B NMR (155 MHz, C_6D_6): δ 42.4 (minor), 34.6 (major). HRMS (EI, *m*/*z*): calcd for $C_{15}H_{22}{}^{11}BN$, 227.1845; found, 227.1855.

Lithium *N*,*N*-Diethyl-1-amino-1-boratanaphthalene (2b). A solution of LDA (1.1 equiv) in 15 mL of ether was gradually added to a mixture of **11b** and **12b** (1.04 g, 5.23 mmol) in 8 mL of ether at −78 °C. The mixture was stirred at −78 °C for 2 h and allowed to warm to 25 °C for 10 h. The solvent was removed in vacuo, and the residue was washed with 3 × 30 mL of pentane. On drying in high vacuum, **2b** was obtained as a pale yellow powder (1.02 g, 95%). ^{1}H NMR (400 MHz, THF-d_8): δ 7.95 (d, J = 8.1 Hz, 1H, ArH); 7.16 (m, 2H, ArH, H(3)), 6.82 (t, J = 8.1 Hz, 1H, ArH); 6.51 (t, J = 8.1 Hz, 1H, ArH); 5.83 (d, J = 7.3 Hz, 1H, H(4)); 5.19 (d, J = 10.3 Hz, 1H, H(2)); 3.33 (q, J = 7.0 Hz, 4H, CH_2); 1.19 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (100.6 MHz, THF-d_8): δ 144.0 (C(4a)); 135.7 (C(3)), 133.4, 130.5 (br, C(8a)), 126.6, 122.4, 113.5, 101.3 (br, C(2)), 100.1 (C(4)), 45.5 (CH_2), 16.1 (CH_3). ^{11}B NMR (155.5 MHz, THF-d_8): δ 35.6.

Lithium *N*,*N*-Diisopropyl-1-amino-1-boratanaphthalene (2c). In the same manner the reaction of **11c** and **12c** (2.04 g, 9.0 mmol) with LDA afforded 1.0 g (48%) of **2c** as a pale yellow powder. ^{1}H NMR (400 MHz, THF-d_8): δ 7.94 (d, J = 8.1 Hz, 1H, ArH); 7.13 (m, 2H, ArH + H(3)); 6.77 (dt, J = 8.1, 1.5 Hz, 1H, ArH); 6.46 (dt, J = 8.1, 1.5 Hz, 1H, ArH); 5.85 (d, J = 7.3 Hz, 1H, H(4)); 5.55 (d, J = 10.7 Hz, H(2)); 3.91 (sept, J = 7.0 Hz, 2H, i-Pr); 1.30 (d, J = 7.0 Hz, 12H, i-Pr). ^{13}C NMR (100.6 MHz, THF-d_8): δ 144.1 (C(4a)), 134.7 (C(3)), 134.1, 133 (br, (C8a)), 126.9, 122.8, 114.3, 108 (br, C(2)), 99.7 (C(4)); 48.7 (NCH), 25.0 (CH_3). ^{11}B NMR (155.5 MHz, THF-d_8): δ 37.

[*N,N*-Diethyl-1-amino-1-boratanaphthalene][pentamethylcyclopentadienyl]zirconium dichloride (5b). Cold toluene (25 mL) was added to a mixture of **2b** (0.5 g, 2.44 mmol) and Cp*$ZrCl_3$ (0.89 g, 2.68 mmol) at −78 °C. The yellow suspension was stirred at −78 °C for 2 h before warming to −25 ° for 10 h. The color changed to red-orange and fine precipitates formed on warming. Removal of the solvent under vacuum gave a bright red residue. Recrystallization was performed by slow diffusion of pentane into a CH_2Cl_2 solution of this residue at −15 °C. The product (0.96 g, 80%) was obtained as red crystals (mp 180 °C). ^{1}H NMR (400 MHz, $CDCl_3$, $T = -30$ °C): δ 8.09 (d, 1H, $J = 8.0$ Hz, ArH); 7.57 (t, 1H, $J = 8.0$ Hz, ArH); 7.36 (t, 1H, $J = 8.0$ Hz, ArH); 7.27 (d, 1H, $J = 8.0$ Hz, ArH); 6.57 (dd, 1H, $J = 10.7$, 7.7 Hz, H(3)); 5.73 (d, 1H, $J = 7.7$ Hz, H(4)); 4.52 (d, 1H, $J = 10.7$ Hz, H(2)); 3.68 (sextet, 1H, $J = 7.0$ Hz, NCH); 3.14 (m, 3H, 3NCH); 2.07 (s, 15H, Cp*CH_3); 1.43 (t, 3H, $J = 7.0$ Hz, $CHCH_3$); 1.14 (t, 3H, $J = 7.0$ Hz, $CHCH_3$). ^{11}B NMR (115.5 MHz, $CDCl_3$): δ 34.8. ^{13}C NMR (100.6 MHz, $CDCl_3$, $T = -30$ °C): δ 144.0 (C(5)); 138.0 (C(3)), 136.5, 131.8, 130.6, 127.5, 125.0 (Cp*), 123.5 (b, C(8a)), 102.2 (C(4)), 98.3 (b, C(2)), 44.0 (NC), 43.5 (NC), 16.3 (CH_3), 14.7 (CH_3), 13.0 (C_5Me_5). HRMS *(EI):* calcd for $C_{23}H_{32}{}^{11}B^{35}Cl_2NZr$, 493.1052; found, 493.1041. Anal. Calcd for $C_{23}H_{32}BCl_2NZr$: C, 55.76; H, 6.51; N, 2.83. Found: C, 54.77; H, 6.60; N, 2.77.

[*N,N*-Diisopropyl-1-amino-1-boratanaphthalene][pentamethylcyclopentadienyl]zirconium Dichloride (5c). 5c was prepared in the same manner as **5b** in 66% yield as red crystals, mp, 230−232 °C. ^{1}H NMR (400 MHz, $CDCl_3$, $T = -35$ °C): δ 8.01 (d, 1H, $J = 8.0$ Hz, ArH); 7.50 (t, 1H, $J = 8.0$ Hz, ArH); 7.30 (t, 1H, $J = 8.0$ Hz, ArH); 7.18 (d, 1H, $J = 8.0$ Hz, ArH); 6.49 (dd, 1H, $J = 11$, 7.3 Hz, H(3)); 5.61 (dd, 1H, $J = 7.3$, 1.4 Hz, H(4)); 4.68 (dd, 1H, $J = 11$, 1.4 Hz, H(2)); 4.35 (septet, 1H, $J = 6.6$ Hz, NCH); 3.47 (septet, 1H, $J = 7.3$ Hz, NCH); 2.03 (s, 15H, Cp*Me); 1.39 (d, 3H, $J = 6.6$ Hz, Me); 1.32 (d, 3H, $J = 7.3$ Hz, Me); 1.29 (d, 3H, $J = 7.3$ Hz, Me); 1.05 (d, 3H, $J = 6.6$ Hz, Me). ^{11}B NMR (155.5 MHz, $CDCl_3$): δ 35.3. ^{13}C NMR (100.6 MHz, $CDCl_3$, $T = -35$ °C): δ 143.8, 137.9, 136.9, 131.5, 130.0, 126.7, 124.7 (C_5Me_5), 122.1 (b, C(8a)); 101.8 (C(4)); 98.9 (b, C(2)); 48.9 (NCH); 44.9 (NCH); 23.8 (CH_3); 23.5 (CH_3); 22.6 (CH_3); 22.0 (CH_3); 12.7 (C_5Me_5). HRMS (EI): calcd for $C_{25}H_{36}{}^{11}BN^{35}Cl_2Zr$, 521.1365; found, 521.1383. Anal. Calcd for $C_{25}H_{36}BNCl_2Zr$: C, 57.36; H, 6.93; N, 2.68. Found: C, 56.24; H, 6.82; N, 2.66.

Relative Acidities in DMSO-d_6. (a) 11a and CpLi. A solution of 10 mg of **11a** in 0.5 mL of dry DMSO-d_6 was placed in an NMR tube. Addition of excess CpLi gave CpH and **2a**, which were detected by ^{1}H NMR spectroscopy.

(b) 11c, 12c, and CpLi. In the same manner addition of CpLi to mixtures of **11c** and **12c** gave an equibrium mixture of **11c** and **12c** in the ratio of 1:2.3 as determined by integration of appropriate signals in the ^{1}H NMR spectra and ^{11}B NMR spectra.

(c) 11c and 12c and Indenyllithium. In the same manner a solution of **11c**, **12c**, and indenyllithium gave indene, indenyllithium, **11c**, **12c**, and **2c**.

(d) 13c and Fluorenyllithium. In the same manner a solution of **13c** and fluorenyllithium gave a solution of **13c**, **3c**, fluorene, and fluorenyllithium.

X-ray Structure Determinations. Crystals of **4a** and **5c** suitable for X-ray diffraction were obtained by recrystallization from pentane. Crystallographic data are collected in Table 3. ORTEP drawings of **4a** and **5c** showing the numbering scheme used in refinement are presented in Figures 2 and 3, respectively. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: Tables of bond distances, angles, positional parameters, anisotropic thermal parameters, and hydrogen atom coordinates of **4a** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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