Organometallics **2008,** *27,* 1345–1347

The Preparation and Crystal Structures of η^1-Derivatives of 2-Phenyl-1,2-azaboratabenzene

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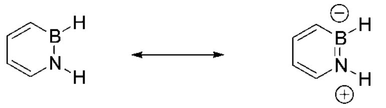
Received December 6, 2007

Summary: The reaction of potassium 2-phenyl-1,2-azaboratabenzene with Cp_2ZrCl_2 gave **5** *in which the heterocyclic rings are η^1-bound to zirconium.*

1,2-Dihydro-1,2-azaborine (**1**) is a 6 π-electron aromatic ring that is isoelectronic with benzene. Monocyclic derivatives of **1** were first prepared in very low yield by Dewar[1] and White[2] in the early 1960s. The Dewar group subsequently reported several fused-ring relatives of **1**[3] and more recently there has been renewed interest in these boron−nitrogen hetercycles for their potential application in optical and electronic devices.[4] In 2000–2001 we reported on two general syntheses of 1,2-dihydro-1,2-azaborines which make this heterocycle readily available for study.[5,6] Structural data on several 1,2-dihydro-1,2-azaborines show that the B−N ring is completely planar with intraring bond distances which are consistent with those of an aromatic ring.[7–9] Furthermore, derivatives of **1** undergo the most characteristic aromatic reaction, electrophilic substitution.[8]



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The coordination chemistry of **1** and its derivatives is of particular interest to us. 2-Phenyl-1,2-dihydro-1,2-azaborine (**1a**) forms arene-like $Cr(CO)_3$ complex **2**.[7] The removal of the NH proton from **1a** produces the conjugate base 1,2-azaboratabenzene (**3a**), which reacts with $[Cp^*RuCl]_4$ to form η^6 Ru complex **4**.[10] Since 2-phenyl-1,2-azaborabenzene (**3a**) can be N-methylated to form **1b** and N-silylated to form **1c**, it is nucleophilic at nitrogen. Therefore it seemed likely that it might form σ-metal complexes with the more electophilic metals. We report here on the preparation and crystal structure of **5**, the first η^1 metal complex of a 1,2-azaboratabenzene (Scheme 1).

Results and Discussion

Potassium 2-phenyl-1,2-azaboratabenzene (**3a**) was prepared by the reaction of **1a** with potassium bis(trimethylsilylamide) in toluene. After filtration **3a** was dissolved in THF and added to Cp_2ZrCl_2. The reaction gave a 56% yield of **5** that could be recrystallized from toluene. The ^1H NMR spectrum of **5** in $CDCl_3$ is first order and can be assigned by inspection. Aside from the absence of the NH signal and the presence of the Cp signal, the spectrum is very similar to that of **1a** and indeed shows only small changes in the chemical shifts of the corresponding signals. These data suggest that the 1,2-azaboratabenzene ligand is σ- rather than π-coordinated. This mode of coordination was confirmed by obtaining an X-ray crystal structure. The molecular structure of **5** is illustrated in Figure 1 and selected bond distances and angles are shown in Table 1.

The molecular structure of **5** is that of a bis(amido)zirconocene. The bulky, planar 1,2-azaboratabenzene groups are related to each other by an approximate C_2 axis bisecting the N−Zr−N angle. These ligands are inclined to the N−Zr−N plane by 31.22(6)° and 28.37(6)°, while the 2-phenyl groups are canted out of the 1,2-azaboratabenzene planes by 41.42(6)° and 58.60(5)°.

Inspection of the molecular structure of **5** shows that the ring nitrogen atoms are σ-bonded to zirconium. The 1,2-dihydro-1,2-azaborine rings of **5** are planar within 0.02 Å. The intraring distances of the C_4BN rings are identical (average difference, 0.01 Å) with those calculated for the parent heterocycle **1** at the MP2/6-31G* level.[11] They are also very similar to experimental distances found for several metal-free 1,2-dihydro-1,2-azaborines.[7–9] Thus the σ-bound zirconium does not significantly effect the electron delocalization of the 1,2-dihydro-1,2-azaborine heterocycle.

The bonding in **5** appears to closely resemble that of bis(pyrrolyl)zirconocene **6a**[12a] and bis(2,5-dimethylpyrrolyl)zirconocene **6b**,[12b] the structures of which were reported by J. L. Atwood and co-workers. For all three compounds the Cp rings are π-bound while the aromatic nitrogen heterocycles are σ-bonded to Zr(IV). The Zr−N distances of **5** (2.238(1), 2.247(1) Å) and **6b** (2.22(2), 2.25(2) Å) are identical. However, the Zr−N distances of **5** and **6b** are somewhat larger than those of the less hindered **6a** (2.171(2), 2.167(2) Å). The N−Zr−N bond angles decrease with the size of the ligands: **5** (111.9(1)°) > **6b** (106.4(1)°) > **6a** (95.7(1)°). On the other hand, the Zr−N bond angles of **5** are much less symmetrical than those of **6a** and **6b**. For **5** the Zr−N−B angles (142.4(1)°, 136.4(1)°) average 36° greater than the Zr−N−C angles (99.9(1)°, 106.5(1)°). The corresponding differences for **6a** and **6b** are only 8° and 13°. The greater difference in the Zr−N bond angles

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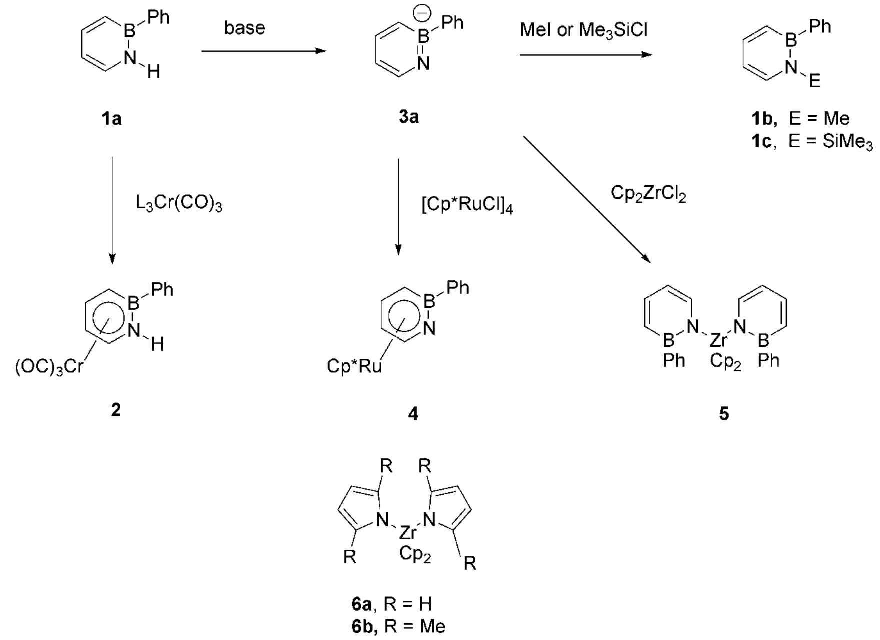
10.1021/om701224c CCC: $40.75

Scheme 1



of **5** is likely a consequence of the intrinsic lower symmetry of the 2-phenyl-1,2-azaboratabenzene ligand and the greater crowding in the metallocene wedge.

For comparison we have also obtained a crystal structure for **1c**, since it also has an electropositive substituent at nitrogen but is less crowded. The molecular structure of **1c** is illustrated in Figure 2 and selected bond distances and angles are shown in Table 1. The bond distances of the 1,2-azaboratabenzene groups of **1c** and **5** are not significantly different. The major difference between the two structures is that the exocyclic bond angles at nitrogen are more symmetrical for **1c**. The Si−N−B and the Si−N−C bond angles differ by only 9°.

In summary we have prepared and characterized **5**, the first η^1-coordinated 1,2-azaboratabenzene. Prior work had shown that 1,2-azaboratabenzene could form η^6-metal complexes. Thus this anionic heterocycle can form σ- or π-metal complexes depending upon the metal. In this respect 1,2-azaboratabenzene has a coordination chemistry similar to that

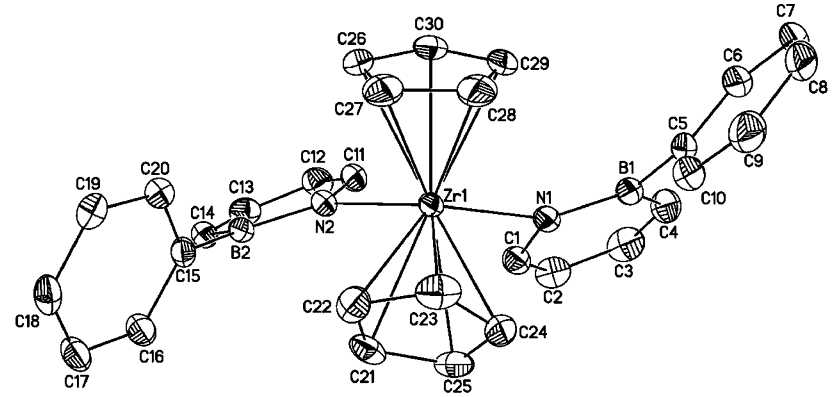


Figure 1. The solid-state structure of **5** (ORTEP). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) for 5 and 1c with the Calculated Bond Distances for 1[a]

bond, angle	**5** (M = Zr)[b]	**1c** (M = Si)[b]	**1** (M = H)[b]
B(1)−N(1); B(2)−N(2)	1.449(2); 1.445(2)	1.448(2)	1.433
B(1)−C(4); B(2)−C(14)	1.519(2); 1.521(2)	1.518(2)	1.510
C(4)−C(3); C(14)−C(13)	1.362(3); 1.360(2)	1.364(2)	1.510
C(3)−C(2); C(13)−C(12)	1.468(3); 1.409(2)	1.413(2)	1.417
C(2)−C(1); C(12)−C(11)	1.362(2); 1.364(2)	1.355(2)	1.370
C(1)−N(1); C(11)−N(2)	1.366(2); 1.372(2)	1.390(2)	1.367
B(1)−C(5); B(2)−C(15)	1.579(2); 1.586(2)	1.579(2)	
N(1)−M; N(2)−M	2.238(2); 2.247(2)	1.801(1)	
N(1)−Zr−N(2)	111.85(4)		
M−N(1)−B(1); M−N(2)−B(2)	142.4(1); 136.4(1)	125.4(1)	
M−N(1)−C(1); M−N(2)−C(11)	99.9(1); 106.5(1)	116.1(1)	
B(1)−N(1)−C(1); B(2)−N(2)−C(11)	117.1(1); 116.7(1)	118.4(1)	

[a] Reference 11. [b] M is the exocyclic substituent at N.

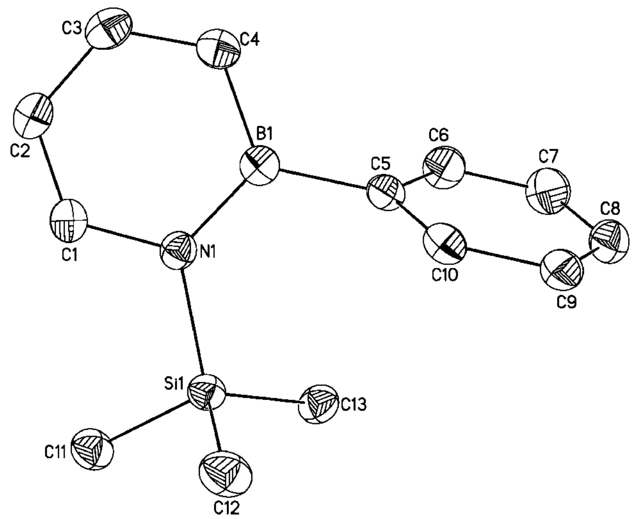


Figure 2. The solid-state structure of **1c** (ORTEP). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Crystal Data and Data Collection Parameters for 5 and 1c

	5	1c
empirical formula	$C_{30}H_{28}B_2N_2Zr$	$C_{13}H_{18}BNSi$
fw	529.38	227.18
temp, K	150(2)	150(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$
a, Å	14.737(16)	10.024(1)
b, Å	11.604(1)	15.631(2)
c, Å	15.199(2)	8.525(1)
β, deg	108.281(2)	96.184(2)
V, Å^3; Z	2470.9(5); 4	1327.8(3); 4
calcd density, Mg/m^3	1.423	1.136
abs coeff, mm^{-1}	0.467	0.150
F(000)	1088	488
cryst size, mm^3	0.50 × 0.26 × 0.20	0.32 × 0.26 × 0.21
limiting indices	$-19 \leq h \leq 18$	$-13 \leq h \leq 13$
	$-15 \leq k \leq 15$	$-20 \leq k \leq 20$
	$-20 \leq l \leq 20$	$-11 \leq l \leq 11$
no. of reflns collected/unique	22435/6139	12621/3304
abs cor	semiempirical from equivalents	
refinement method	full-matrix least squares on F^2	
no. of data/restrains/params	6139/0/316	3304/0/148
GOF on F^2	1.050	1.043
final R indices ($I > 2\sigma(I)$)	R1 = 0.0244	R1 = 0.0348
	wR2 = 0.0643	wR2 = 0.0923
R indices (all data)	R1 = 0.0280	R1 = 0.0424
	wR2 = 0.0667	wR2 = 0.0981
largest diff peak and hole, e/Å	0.402 and −0.321	0.338 and −0.214

of pyrrolyl, which is also know to form both σ-[12] and π-metal complexes.[13–15]

Experimental Section

General Methods. All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried using standard procedures. High-resolution mass spectra were recorded on a VG-250S spectrometer with an electron impact at 70 eV. The NMR spectra were obtained with a Varian INOVA 400 or 500 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4Si. The ^{11}B NMR spectra were referenced to external BF_3-OEt_2.

Bis(η^5-cyclopentadienyl)bis(η^1-2-phenyl-1,2-azaboratabenzene)zirconium(IV) (5). A 0.5 M solution of potassium bis(trimethylsilyl)amide (23 mL, 11.5mmol) in toluene was added gradually to a solution of **1a** (1.63 g, 10.5 mmol) in 20 mL of toluene at 0 °C. The mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature for 4 h. After filtration and removal of the solvent in vacuo, the residue was washed with 2 × 10 mL of toluene and 2 × 10 mL of pentane followed by drying in vacuo to give **3a** as a white powder (1.93 g, 95%). The ^{1}H, ^{11}B, and ^{13}C NMR spectra were as reported.[10] This material was taken up in 20 mL of THF and the resulting solution was added to a solution of Cp_2ZrCl_2 (1.30 g, 4.45 mmol) in 50 mL of THF at −78 °C. The mixture was stirred at −78 °C for 2 h and allowed to warm to room temperature for 10 h. The solvent was removed in vacuo and the residue was extracted with 3 × 25 mL of toluene. After filtration and removal of the solvent the residue was washed with 3 × 15 mL of hexanes. After drying the product (1.32 g, 56%) was an amber powder, which was recrystallized from toluene to give yellow needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06 (s, 10H, CpH), 6.20 (t, J = 6.2 Hz, 2H, C(5)H), 6.78 (d, J = 10.6 Hz, 2H, C(3)H), 7.09(d, J = 6.2 Hz, 2H,C(6)H), 7.38 (t, J = 7.6 Hz, 2H, ArH), 7.46 (t, J = 7.6 Hz, 4H, ArH), 7.57 (dd, J = 10.6, 6.2 Hz, 2H, C(4)H), 7.61 (d, J = 7.6 Hz, 4H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 109.1, 115.4, 127.3, 127.8, 131.8 (br), 132.7, 137.3, 142.4. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 39.8. HRMS (EI, m/z) calcd for $C_{30}H_{28}{}^{11}B_2N_2{}^{90}Zr$ [M − 2H] 526.1329, found 526.1327. Satisfactory CHN combustion analyses could not be obtained. However, the NMR spectra were consistent with a sample of high purity.

1,2-Dihydro-2-phenyl-1-(trimethylsilyl)-1,2-azaborine (1c). One equivalent of trimethylsilyl chloride was added to a THF solution of **3a** obtained as above. The ^{1}H NMR and mass spectra showed that **1c** was identical with previously obtained material.[10]

Single-Crystal X-ray Crystallography. Crystals of **1c** and **5** were obtained from crystallization from the melt and recrystallization from toluene, respectively. Crystallographic and data collection parameters are collected in Table 2. ORTEP drawings of **5** and **1c** showing the atom-numbering scheme used in refinement are given in Figures 1 and 2, respectively. Selected bond distances and angles are collected in Table 1. Additional crystallographic data are available in the Supporting Information.

Acknowledgment. Partial support of this research has been provided by NSF.

Supporting Information Available: CIF files giving X-ray characterization of **5** and **1c** and figures giving ^{1}H NMR spectra of **5** and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701224C

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