Notes

Synthesis of Cyclopentadienyl Borate Ligands and Their Reactivity with Cp*Zr(CH_3)$_3$

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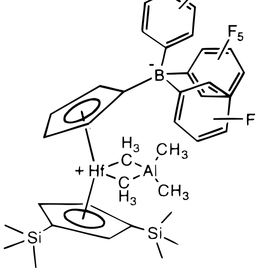
Summary: This paper describes the synthesis of the new anionic cyclopentadienyl ligands Li[1,3-$(CH_3)_3SiC_5H_4B(C_6F_5)_3$*] (**3**) and Li[*$C_5H_5B(C_6F_5)_3$*] (**4**), in which the tris(perfluorophenyl)boron moiety has been linked directly to the Cp ring. The structure of **3** has been confirmed by X-ray crystallography. The reaction of **3** with Cp*Zr(*CH_3*)*$_3$* produces the known sandwich complex [(*CH_3*)*$_3$*SiCp)(Cp*)Zr(*CH_3*)*$_2$*] via loss of Li[*$CH_3B(C_6F_5)_3$*]. In contrast, reaction of **4** with Cp*Zr(*CH_3*)*$_3$* produces the known complex (*CH_3*Cp)(Cp*)Zr(*CH_3*)*$_2$*.*

Introduction

The role of cationic group 4 alkylmetallocenes in Ziegler−Natta olefin polymerization is now well accepted.[1] In order to control ion pairing, synthesis of zwitterionic species has been a goal in our laboratory and in others.[2−4] The simplest strategy has been to link the anionic group, typically a borate group, to the Cp ring as reported by Bochmann et al. for **1**.[3] Borate precursors, namely, the tethered boron Lewis acids, have also been reported by Shapiro[5] and Piers.[6] In both the Erker and Piers systems, the boron atoms are separated from the Cp ring or the metal atom by an alkyl chain.



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Concurrent with the these reports, we have been working toward building stable zwitterionic metallocene systems. We find that $B(C_6F_5)_3$ can be attached directly to the Cp ring via simple reaction with base-free Li[Cp] or Li[$(CH_3)_3$Si-Cp] in aromatic hydrocarbon solvents. Herein, we report our results on the synthesis and reaction chemistry these ligands with Cp*Zr(CH_3)$_3$.

Experimental Section

General Procedures. All syntheses were performed under dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), benzene, and pentane were distilled from sodium benzophenone ketyl. THF-d_8 and C_6D_6 were dried over 4 Å molecular sieves prior to use. Zr[N(CH_3)$_2$]$_4$,[7] CpZr{N(^{i}Pr)$_2$}Cl_2,[8] Cp*Zr(CH_3)$_3$,[9] and $(CH_3)_3SiC_5H_5$[10] were synthesized according to literature procedures. Tris(perfluorophenyl)borane was purchased from Boulder Scientific Co. and used without further purification. ^{1}H NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a General Electric QE-300 (300 MHz) spectrometer.

Li[$(CH_3)_3SiC_5H_4B(C_6F_5)_3$] (3). A Schlenk tube was charged with 0.047 g of Li[$(CH_3)_3$Si-Cp] and 0.167 g of $B(C_6F_5)_3$, and 15 mL of toluene was added at room temperature. The two solids dissolved within 10 min to produce a clear yellow solution. The reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the remaining oily solid was washed with pentane (2 × 20 mL). A fine white solid was isolated in 82% yield. ^{1}H NMR (C_6D_6): δ −0.33 (s; 9H; Si(CH_3)$_3$), 2.92 (br s; 1H; methine), 6.17 (br s; 1H; Cp), 6.29 (br s; 1H; Cp), 6.48 (br s; 1H; Cp) Anal. Calcd: C, 47.5; H, 1.99. Found: C, 47.24; H, 2.20.

Li[$C_5H_5B(C_6F_5)_3$] (4). Compound **4** can be synthesized and isolated in the same manner as **3**. Typically, however, **4** was prepared just prior to use in the following manner: Base-free LiCp (0.003 g) and 0.025 g of $B(C_6F_5)_3$ were mixed in an NMR tube, and C_6D_6 was added at room temperature. The two solids dissolved within 5 min to produce a clear yellow solution. ^{1}H NMR (C_6D_6): δ 6.16 (d, 1H, J = 5.1 Hz), 5.90 (d, 1H, J = 5.1 Hz), 5.81 (s, 1H) and 2.51 (s, 2H).

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$((CH_3)_3SiC_5H_4)(Cp^*)Zr(CH_3)_2$ (5). $Cp^*Zr(CH_3)_3$ (0.012 g) and 0.030 g of **3** were dissolved in C_6D_6 in an NMR tube at room temperature. No immediate reaction was observed by ^1H NMR spectroscopy. The sample was left at room temperature for 3 days. The known sandwich compound $((CH_3)_3Si$-$Cp)(Cp^*)Zr(CH_3)_2$ (**5**)[11] was observed as the major product. A minor unidentified species was also observed for which a singlet in the Cp region is apparent.

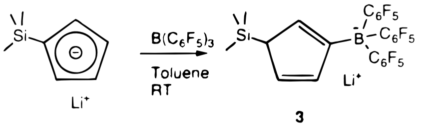
$(CH_3C_5H_4)(Cp^*)Zr(CH_3)_2$ (6). Compound **4** was prepared in C_6D_6 as described. To this solution, 0.020 g of $Cp^*Zr(CH_3)_3$ was added and the reaction was left at room temperature overnight. The ^1H NMR spectrum exhibits resonances for the known sandwich complex $(MeCp)(Cp^*)Zr(CH_3)_2$ (**6**).[12]

X-ray Experimental for 3. Single crystals of **3** were grown by slow evaporation of a DME solution of **3** under inert conditions. Data were collected at 173 K on a Siemens Smart Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). ψ-scan absorption corrections were applied based on the entire data set.

The structure was solved by the direct methods algorithm in SHELXTL5 and refined using full-matrix least squares on F_o^2. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were refined with isotropic thermal parameters. A total of 732 parameters were refined in the final cycle of refinement using 5043 reflections with $I > 2\sigma(I)$ to yield R1 and wR2 of 0.0458 and 0.0903, respectively.

Results and Discussion

The reaction of base free $Li[(CH_3)_3SiC_5H_4]$ with the strong Lewis acid $B(C_6F_5)_3$ in benzene or toluene results in an immediate reaction to give a yellow solution from which a fine white solid **3** can be isolated in high yield (eq 1). The reaction is somewhat surprising since base-



3

(1)

free $Li[(CH_3)_3SiC_5H_4]$ is extremely insoluble in aromatic solvents. Compound **3** is air-stable but hygroscopic and readily coordinates donor solvents such as Et_2O and THF. It is soluble in benzene and toluene and insoluble in pentane. Once it is exposed to ethereal solvents, it becomes insoluble in aliphatic and aromatic solvents. The ^1H NMR (C_6D_6) spectrum of **3** exhibits resonances at δ −0.33 (9H), 2.92 (2H), 6.17 (1H), 6.29 (1H), and 6.48 (1H) which are assigned to the $(CH_3)_3Si$, methylene, and three Cp ring protons, respectively.

The structure of **3** has been unambiguously identified by a single-crystal X-ray diffraction study. Unfortunately, we have not been able to obtain X-ray quality single crystals of **3** in the absence of coordinating solvents. However, slow evaporation of a DME solution of **3** gave single crystals of $[Li(DME)_3][(CH_3)_3SiC_5H_4B(C_6F_5)_3]$. A thermal ellipsoid plot of the anion of **3** is found in Figure 1. The crystal structure data for **3** is listed in Table 1, while selected bond lengths and angles are found in Table 2. The crystal structure of **3** is consistent with the structure of **3** that was proposed from ^1H NMR spectroscopy. The bond lengths within the cyclopentadiene ring display the expected variation with the boron and silyl groups occupying positions 1,3 relative to each other. The sum of the angles about C(1) is 325.4° and is considerably less than that expected for an sp^2-hybridized carbon atom, leading to the conclusion that the Me_3Si group is bonded to the methine carbon atom. The sum of the angles about C(3) is 358.1° as is consistent with sp^2 hybridization.

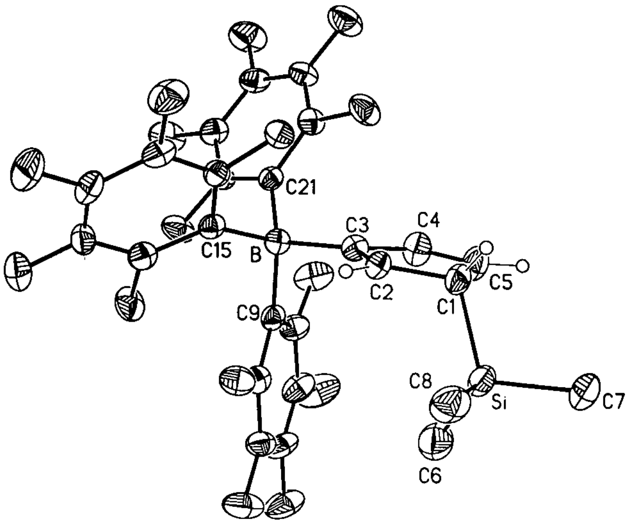


Figure 1. Thermal ellipsoid plot of the anion, $[(CH_3)_3SiC_5H_4B(C_6F_5)_3]$, of **3**.

Table 1. Crystal Data and Structure Refinement for 3

empirical formula	$C_{38}H_{43}BF_{15}LiO_6Si$	
formula weight	926.56	
temperature	173(2) K	
wavelength	0.710 73 Å	
crystal system	monoclinic	
space group	$P2_1/c$	
unit cell dimens	$a = 10.4853(2)$ Å	$\alpha = 90°$
	$b = 13.9717(2)$ Å	$\beta = 98.646(1)°$
	$c = 30.3971(1)$ Å	$\gamma = 90°$
volume, Z	4402.49(11) Å^3, 4	
density (calcd)	1.398 Mg/m^3	
absorption coeff	0.159 mm^{-1}	
$F(000)$	1904	
crystal size	0.06 × 0.28 × 0.42 mm	
θ range for data collctn	1.61−25.00°	
limiting indices	$-13 \le h \le 10$, $-15 \le k \le 18$, $-39 \le l \le 40$	
no. of reflctns collctn	22040	
no. of independent reflctns	7733 [R(int) = 0.0505]	
absorption correction	ψ scan	
max and min transm	0.990 and 0.945	
refinement method	full-matrix least squares on F^2	
data/restraints/params	7677/0/732	
goodness of fit on F^2	1.046	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0458, wR2 = 0.0903	
R indices (all data)	R1 = 0.0889, wR2 = 0.1121	
extinction coeff	0.0024(3)	
largest diff peak and hole	0.258 and −0.218 e Å^{-3}	

When the formation of **3** was followed by ^1H NMR (C_6D_6) spectroscopy, two intermediates were observed within 10 min of mixing at room temperature (Scheme 1). At these early reaction times, resonances for **1** are observed at δ 6.34 (1H; Cp), 5.97 (1H, Cp), 2.92 (2H, Cp methylene), and 0.01 (9H, $Si(CH_3)_3$) along with a set for **2** at δ 5.63 (2H, Cp), 5.67 (2H, Cp), and 0.14 (9H, Si-

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Scheme 1

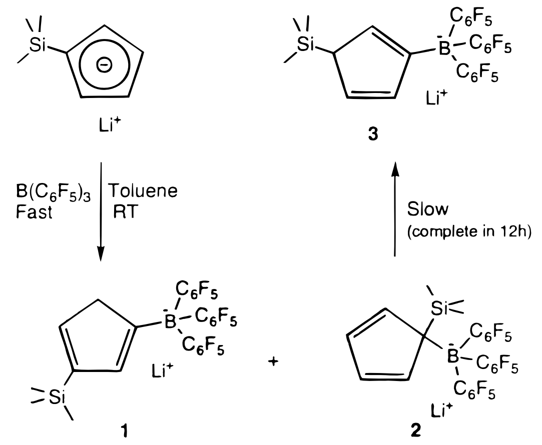


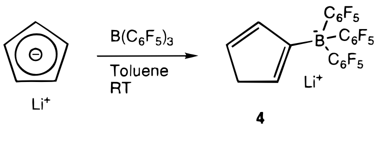
Table 2. Selected Bond Lengths and Angles for 3

Bond Distances (Å)					
Si−C(6)	1.858(4)	B−C(21)	1.657(4)	C(2)−C(3)	1.347(3)
Si−C(7)	1.860(3)	B−C(9)	1.659(4)	C(3)−C(4)	1.465(4)
Si−C(8)	1.862(4)	B−C(15)	1.664(4)	C(4)−C(5)	1.339(4)
Si−C(1)	1.901(3)	C(1)−C(5)	1.482(4)		
B−C(3)	1.625(4)	C(1)−C(2)	1.493(3)		

Bond Angles (deg)			
C(6)−Si−C(7)	110.9(2)	C(9)−B−C(15)	113.5(2)
C(6)−Si−C(8)	110.3(2)	C(5)−C(1)−C(2)	102.0(2)
C(7)−Si−C(8)	109.5(2)	C(5)−C(1)−Si	111.3(2)
C(6)−Si−C(1)	110.3(2)	C(2)−C(1)−Si	112.1(2)
C(7)−Si−C(1)	107.9(2)	C(3)−C(2)−C(1)	112.1(2)
C(8)−Si−C(1)	107.8(2)	C(2)−C(3)−C(4)	105.3(2)
C(3)−B−C(21)	113.8(2)	C(2)−C(3)−B	131.3(2)
C(3)−B−C(9)	100.1(2)	C(4)−C(3)−B	122.5(2)
C(3)−B−C(15)	114.3(2)	C(5)−C(4)−C(3)	111.5(3)
C(21)−B−C(9)	112.0(2)	C(4)−C(5)−C(1)	108.9(3)
C(21)−B−C(15)	103.5(2)		

$(CH_3)_3$). Over the course of the reaction, the resonances assigned to **1** and **2** disappear while those for **3** begin to appear. Finally, after ~12 h, all of the material is converted to **3**, which displays resonances at δ 6.48 (1H; Cp), 6.29 (1H; Cp), 6.17 (1H; Cp), 2.92 (1H; methine), and −0.33 (9H; $-Si(CH_3)_3$). We believe that the Cp anion reacts with the Lewis acid to produce **1** and **2** initially with **1** predominating in a 4:1 ratio. We envision that **1** is converted to **3** via a simple proton migration to the carbon bearing the silyl group. Such sigmatropic rearrangements are well-known for substituted cyclopentadienes.[13] Formation of **3** from **2** requires silyl and proton migrations which are also well documented. The observed resonances for **3** sharpen dramatically and shift positions when Et_2O is added. Over time, a white solid precipitates from solution, presumably due to insolubility caused by ether complexation to the Li cation.

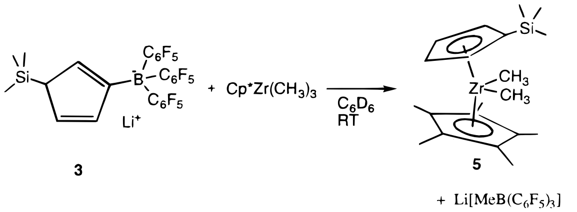
A similar yet simpler reaction is observed when base-free $Li(C_5H_5)$ reacts with $B(C_6F_5)_3$ in toluene (eq 2). A yellow solution of **4** is obtained within 5 min, from which a white solid can be isolated in a procedure identical to that for the isolation of **3**. Typically, we generate **4** in situ prior to use. When we followed this reaction by ^1H NMR spectroscopy, we observed that dissolution of $Li(C_5H_5)$ and $B(C_6F_5)_3$ in C_6D_6 initially produces a single species. Resonances at δ 6.16 (d, 1H, J = 5.1 Hz), 5.90 (d, 1H, J = 5.1 Hz), 5.81 (s, 1H), and 2.51 (s, 2H) are observed and can be attributed to three inequivalent Cp ring protons, two of which are coupled to one another while the fourth resonance is due to the Cp methylene group. Given these spectroscopic features, we propose the structure of **4** has the boron attached to a vinyl position (eq 2). Analysis of the NMR sample of **4** after 24 h revealed that the initial species, **4**, had disappeared and at least two new species containing methine protons were present. We have not characterized these products further, though given the propensity for substituted cyclopentadienes to undergo rearrangement, it is likely that they are the other isomers of **4**.



(2)

Efforts to attach these anionic Cp ligands **3** and **4** intact to a zirconium center have proven unsuccessful. We have been unable to remove the acidic methine proton by simple deprotonation in the absence of coordinating solvents. Thus, a mixture of products was isolated when deprotonation was attempted with a mixture of *n*-BuLi in toluene. Alternatively, a commonly used and milder route to Cp complexes involves the reaction of the desired cyclopentadiene with a transition metal amide via the elimination of an amine.[14] We find that **3** or **4** reacts with $Zr[N(CH_3)_2]_4$ or $CpZr\{N(^iPr)_2\}Cl_2$, giving complicated mixtures of products. Although resonances in the ^1H NMR spectra of the products indicate that new Cp complexes are formed, we have not been able to unequivocally identify the products. Furthermore, the complexity of the spectra in the Cp region suggests that B−C bond cleavage may also be occurring.

Because the reaction between cyclopentadienes and $Zr[N(CH_3)_2]_4$ is an equilibrium process,[14] we investigated the use of alkane elimination from Zr alkyl complexes and **3** and **4** as a possible route to the desired complexes because alkane elimination should not be reversible. When the known trialkyl complex $Cp^*Zr(CH_3)_3$[9] is mixed with complex **3** in an NMR tube, no immediate reaction was observed by ^1H NMR spectroscopy. After the sample had been left at room temperature for 3 days, the known sandwich compound $((CH_3)_3SiCp)(Cp^*)Zr(CH_3)_2$ (**5**)[11] was observed as the major product along with a broad resonance at 0.5 ppm that was assigned to $[CH_3B(C_6F_5)_3]^-$ (eq 3).



(3)

As expected, reaction of the less sterically encumbered complex **4** with $Cp^*Zr(CH_3)_3$ proceeds to completion

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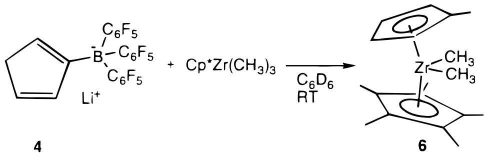
more rapidly. Quite surprisingly, the reaction does not proceed in a fashion analogous to eq 3. Instead, the ^{1}H NMR spectrum exhibits resonances for the known sandwich complex (MeCp)(Cp*)Zr(CH_3)$_2$ (**6**)[12] as the major product (>95%) of this reaction (eq 4). We have



4 **6** (4)

no mechanistic details concerning this transformation, and we have not identified the boron-containing product, but we presume it is Li[HB(C_6F_5)$_3$]. There is ample literature precedent for B−C bond cleavage as well as other unusual rearrangements in reactions involving [RB(C_6F_5)$_3$]$^-$ or B(C_6F_5)$_3$ in the presence of electrophilic Zr centers.[15]

Conclusions

The synthesis of Cp borates is quite facile when base-free LiCp reagents are reacted with B(C_6F_5)$_3$ in aromatic hydrocarbon solvents. The solubility of these base-free Li salts must be due to strong interactions between the Li$^+$ and the F atoms of the borate group, which presumably form a strong contact ion-paired species. Unfortunately, we have not yet been able to obtain X-ray quality crystals of **3** or **4** in the absence of coordinating solvents. The reaction between **3** or **4** and Cp*ZrMe$_3$ involves rupture of the B−Cp bond in both cases. These observations suggest that the Cp−B bond may not be robust enough to remain present during the use of zwitterionic group 4 metallocene complexes as catalysts for the polymerization of α-olefins if the borate group is bound directly to a cyclopentadienyl ring of the catatlyst. Thus, while Cp-B cleavage will not result in catalyst deactivation as long as a Zr alkyl or hydride cation remains, Cp−B cleavage could cause changes in the properties of the resultant polymer as the catalyst changes from a zwitterion to an ion-paired structure.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1** (9 pages). Ordering information is given on any current masthead page.

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