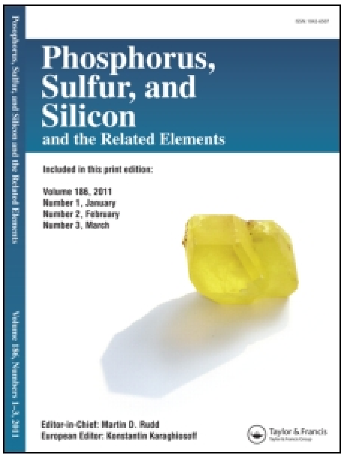

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NEW HETEROAROMATIC π -LIGANDS CONTAINING BORON

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NEW HETEROAROMATIC π-LIGANDS CONTAINING BORON

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*The heteroaromatic anions 2-(diisopropylamino)-1,2-thiaborolide(**2a**), 1-ethyl-2-phenyl-1,2-azaborolide(**2b**), and 2-(diisopropylamino)-1,2-oxaborolide(**2c**) have been prepared by a multi-step synthesis using the Grubbs ring-closing metathesis. Reactions of **2a**, **2b**, and **2c** with Cp*ZrCl$_3$ afforded the corresponding Zr(IV) complexes **3**.*

Keywords: Boron heterocycles; polymerization; zirconium complexes

Zirconocene dichlorides (**1**) have important uses as catalysts for the Ziegler-Natta polymerization of olefins.[1] We have been interested in preparing new derivatives of **1** in which the Cp groups are replaced by boron containing heterocycles.[2,3] Our goal is to adjust the electronic environment about the zirconium atom so that the reactivity of the catalyst can be tuned.

The 1,2-heteroborolides **2a**,[4] **2b**,[5–7] and **2c** are isoelectronic with Cp, but their electronic character should depend on the identity of the ring heteroatoms as well as the B-pendant group.[2] Extensive prior work by Schmid and coworkers[5] has demonstrated that 1,2-azaborolides **2b** can form Cp-like complexes with a variety of transition metals. However, previous to our work, 1,2-thiaborolide (**2a**)[4] and 1,2-oxaborolides were unknown. We report here on a general preparation of **2** and on their conversion to zirconium (**IV**) complexes **3**.

RESULTS AND DISCUSSION

The synthesis of the 1,2-heteroborolides is outlined in Scheme 1.[4,6] (Heteroallyl)-vinylboranes **6** are easily prepared in quantity from the

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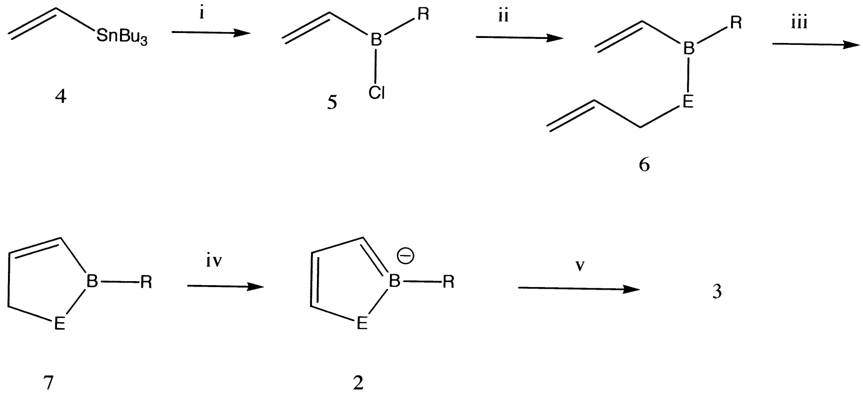
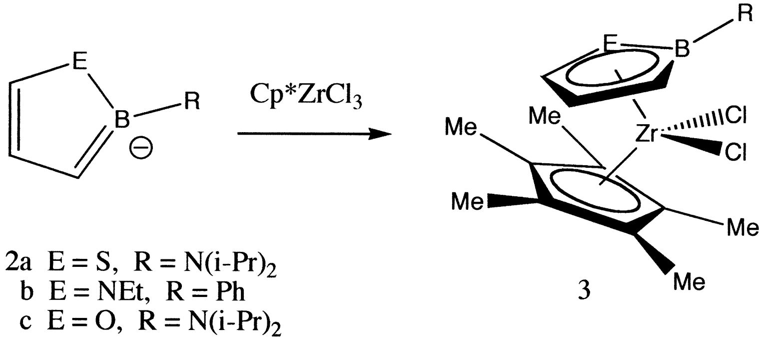


SCHEME 1 Synthesis Key: (i), $PhBCl_3$ or BCl_3 followed by $HN(i\text{-}Pr)_2$; (ii) C_3H_7EH, base; (iii) Grubbs catalyst ($RuCl_2(CHPh)[P(C_6H_{11})_3]_2$); (iv) LDA or t-Buli; (v) Cp^*ZrCl_3.

commercially available tributylvinylstannane (**4**). The key step in the synthesis involves a Grubbs ring-closing metathesis of **6** to **7**, which takes place in 80–95% yield using 1–5 mmol percent catalyst. Deprotonation of **7** with base affords the 1,2-heteroborolide. The NMR spectra of **2** are consistent with π-delocalized structures. The reaction of **2** with Cp^*ZrCl_3 affords the 1,2-diheterozirconocene dichlorides **3** as crystalline solids (Scheme 2).

The x-ray structure of **3b** and **3c** are illustrated in Figures 1 and 2 respectively. The structure of a Me_2Si-bridged derivative of **3a** previously has been reported.[4] The structure of **3b** shows that the azaborolyl ring is η^5-coordinated to Zr, although the Zr–B distance (2.68 Å) is longer than the Zr–C and Zr–N distances (2.46–2.50 Å). In **3c** the differentiation



2a E = S, R = $N(i\text{-}Pr)_2$
b E = NEt, R = Ph
c E = O, R = $N(i\text{-}Pr)_2$

SCHEME 2

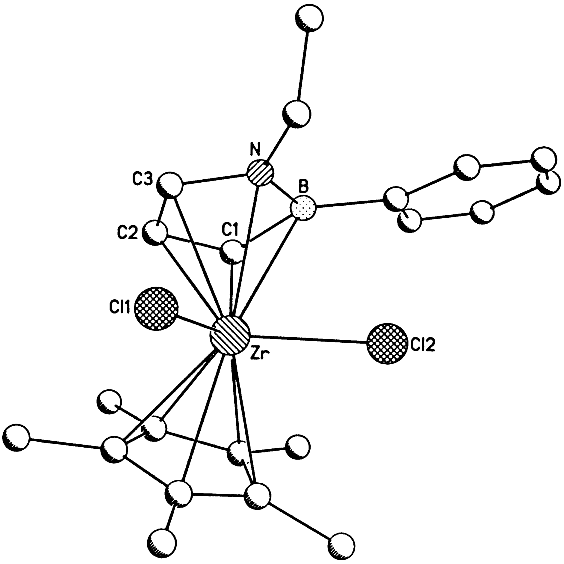


FIGURE 1 The molecular structure of **3b**. Selected distances (Å) to Zr: B, 2.681(2); N, 2.531(1); C(1), 2.479(2); C(2), 2.464(2); C(3), 2.491(2); C(Cp*), 2.486–2.524.

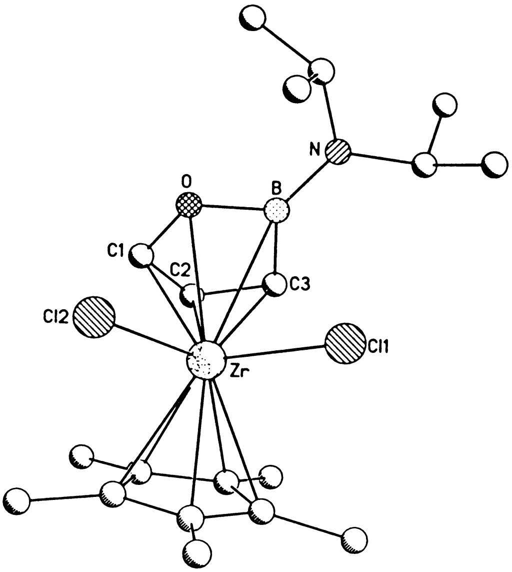


FIGURE 2 The molecular structure of **3c**. Selected distances (Å) to Zr: B, 2.802(3); O, 2.516(2); C(1), 2.402(1); C(2), 2.500(2); C3, 2.525(2); C(Cp*), 2.486–2.527.

between the Zr–B distance (2.80 Å) and the Zr–C and Zr–O distances (2.40–2.53 Å) is so great that the coordination to Zr approaches η.[4] In both cases, the metal slippage away from boron is probably due to the high electron demand of Zr(IV), which prefers to coordinate to the more electron rich ring atoms.[2]

On activation by excess methylaluminoxane **3a** and **3b** are active catalysts for the polymerization of ethylene. Under typical conditions[9] the activities of **3a** and **3b** were found to be 6.0×10^4 and 2.1×10^6 (g of polymer)/(mol of Zr) atm respectively. Although polymerizations have not been run with **3c**, yet, it is clear that the 1,2-heteroborolyl ligands can serve as a replacement ligand for Cp in useful catalysts.

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