*Organometallics* **2001,** *20,* 4080−4091

# $B(C_6F_5)_3$ as $C_6F_5$ Transfer Agent in Zirconium Chemistry: Borole Sandwich and Borole-Bridged Triple-Decker Complexes

Timothy J. Woodman,[†] Mark Thornton-Pett,[‡] David L. Hughes,[†] and
Manfred Bochmann*[,†]

*Wolfson Materials and Catalysis Centre, School of Chemical Sciences,*
*University of East Anglia, Norwich, U.K., NR4 7TJ, and School of Chemistry,*
*University of Leeds, Leeds, U.K., LS2 9JT*

*Received April 30, 2001*

Treatment of $Cp''Zr(C_6F_5)(OEt_2)\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ (**1H**, R = H; **1Me**, R = Me; $Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$) in toluene with nitriles R′CN gives rise to the adducts $Cp''Zr(C_6F_5)(NCR')\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ (**2H**, R = H, R′ = Me; **3H**, R = H, R′ = *t*Bu; **3Me**, R = Me, R′ = *t*Bu) in high yields. The reaction of **1H** and **1Me** with a 4-fold excess of *tert*-butylisocyanide in toluene at −20 °C leads to the formation of $Cp''Zr(C_6F_5)(CN\mathit{t}Bu)_2\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ (**4H**, R = H; **4Me**, R = Me), while warming to room temperature results in the insertion of one molecule of isocyanide into the zirconium−$C_6F_5$ bond to give the $\eta^2$-iminoacyl complexes $Cp''Zr\{\eta^2\text{-}(C_6F_5CN\mathit{t}Bu)\}(CN\mathit{t}Bu)\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ (**5H**, R = H; **5Me**, R = Me). The structures of **3H** and **5H** were confirmed by X-ray diffraction. The reaction of the diene complexes $Cp^RZr(\eta^3\text{-crotyl})(\eta^4\text{-butadiene})$ (**6a**, $Cp^R = C_5H_4SiMe_3$; **6b**, $C_5H_4Me$; **6c**, Cp; **6d**, Cp″) with $B(C_6F_5)_3$ in toluene solution at room temperature proceeds quantitatively with C−H activation, butene elimination, and $C_6F_5$ transfer to generate $Cp^RZr(C_6F_5)\{\eta^4\text{-}CH_2CHCHCHB(C_6F_5)_2\}$ (**7a−d**). These boryldiene complexes are thermally unstable and smoothly rearrange to give the triple-decker complexes $Zr_2(Cp^R)_2(C_6F_5)_2\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$ (**8a−d**). The formation of these complexes involves the complete transfer of all three $C_6F_5$ substituents of one $B(C_6F_5)_3$ molecule, as well as C−H activation and the loss of one $C_6F_5$ group as pentafluorobenzene. The triple-decker complexes feature a $Zr_2C_4B$ core, a zwitterionic structure, and an unusually strong Zr−F donor interaction. On activation with methylalumoxane (MAO), **8a−d** polymerize ethene.

## Introduction

Early transition complexes of the borole dianion $[C_4H_4BR]^{2-}$ have attracted attention as potential alkene polymerization catalysts.[1] Two general synthetic strategies have been employed: the dehydrogenation of 2,5-dihydro-1*H*-boroles with various transition metal compounds[2] and the reaction of metal halides with a preformed borole dianion.[3] We recently reported that half-sandwich zirconium 1,3-diene complexes such as $Cp''Zr(\eta^3\text{-crotyl})(\eta^4\text{-butadiene})$ and $Cp''Zr(\eta^3\text{-allyl})(\eta^4\text{-isoprene})$ react with $B(C_6F_5)_3$ to produce the borole complexes $Cp''Zr(C_6F_5)(OEt_2)\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ (**1H**, R = H; **1Me**, R = Me) as the products of successive C−H activation steps within the metal coordination sphere.[4] This reaction seems to be specific to bulky cyclopentadienyl ligands such as Cp″. As reported in a preliminary communication,[5] we subsequently found that under subtly different conditions **6d** follows a different reaction path, to give the zirconium triple-decker $Zr_2Cp''_2(C_6F_5)_2\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$, **8d**, featuring a novel *ansa*-borole-allyl ligand. We now report the synthesis of related triple-decker complexes with a variety of cyclopentadienyl ligands, as well as some stoichiometric and catalytic reactions of these borole complexes.

---

* Corresponding author. E-mail: m.bochmann@uea.ac.uk.

[†] University of East Anglia.

[‡] University of Leeds.

(1) (a) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489. (b) Pastor, A.; Kiely, A. F.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *528*, 65. (c) Bazan, G. C.; Donnelly, S. J.; Rodriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671. (d) Bazan, G. C.; Rodriguez, G. *Polyhedron* **1995**, *14*, 93. (e) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7791.

(2) (a) Herberich, G. E.; Hessner, B.; Boveleth, W.; Lüthe, H.; Saive R.; Zelenka, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1024. (b) Herberich, G. E.; Negele, M.; Ohst, H. *Chem. Ber.* **1991**, *124*, 25. (c) Herberich, G. E.; Carstensen, T.; Klaff, N.; Neuschütz, M. *Chem. Ber.* **1992**, *125*, 1801. (d) Enders, M.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1992**, *125*, 1981. (e) Herberich, G. E.; Carstensen, T.; Englert, U. *Chem. Ber.* **1992**, *125*, 2351. (f) Braunstein, P.; Englert, U.; Herberich, G. E.; Neuschütz, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1010. (g) Herberich, G. E.; Carstensen, T.; Koffer, D. P. J.; Klaff, N.; Boese, R.; Hylakryspin, I.; Gleiter, R.; Stephan, M.; Meth, H.; Zenneck, U. *Organometallics* **1994**, *13*, 619. (h) Herberich, G. E.; Eckenrath, H. J.; Englert, U. *Organometallics* **1997**, *16*, 4292.

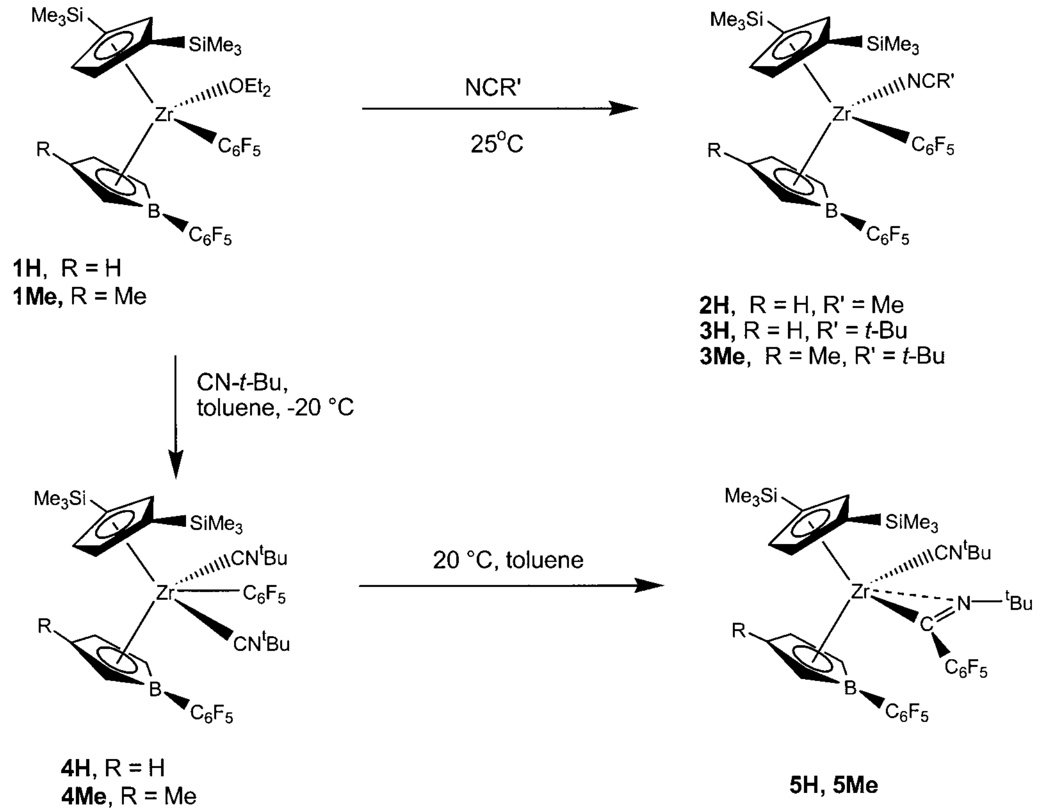
(3) (a) Herberich, G. E.; Hostalek, M.; Laven, R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 317. (b) Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17. (c) Herberich, G. E.; Eigendorf, U.; Englert, U. *Chem. Ber.* **1993**, *126*, 1397. (d) Herberich, G. E.; Marx, H. W.; Wagner, L. T. *Chem. Ber.* **1994**, *127*, 2135. (e) Herberich, G. E.; Wagner, T.; Marx, H. J. *J. Organomet. Chem.* **1995**, *502*, 67.

(4) Jiménez Pindado, G.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816.

(5) Woodman, T. J.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **2001**, 329.

10.1021/om010348i CCC: $20.00

**Scheme 1**



## Results and Discussion

**Reactivity of Borole Complexes.** Mixtures of mononuclear borole complexes of type **1** with trimethylaluminum show good activity as ethene polymerization catalysts, and the formation of zirconium methyl species following $C_6F_5/CH_3$ exchange has been suggested.[4] The propensity of the Zr-$C_6F_5$ ligand to undergo exchange with alkylating agents was therefore explored further, in an effort to generate isolable 14-electron zirconium alkyl complexes that might be suitable as single-component catalysts for olefin polymerizations. While $SnMe_4$, Sn(allyl)$_4$, and B(allyl)$_3$ failed to react with **1H** and **1Me**, Grignard reagents such as benzyl- and allylmagnesium chloride led to a color change from dark red to yellow-orange. These reactions were accompanied by a change in the borole $^{11}B$ NMR chemical shift from $\delta$ 40 to 25, indicative of an exchange of the B-$C_6F_5$ as well as the Zr-$C_6F_5$ substituents. With methyllithium or $ZnMe_2$ there was evidence for preferential methylation on zirconium to give yellow solids. However, none of these reactions allowed the isolation of clean products.

In an effort to further elucidate the reactivity of the Zr−$C_6F_5$ bond, the reactions of complexes **1** with nitriles and isocyanides were examined. Treatment of toluene solutions of **1H** with acetonitrile and of **1H** and **1Me** with pivalonitrile produces rapid color changes from red to deep purple or blue. Removal of the volatiles from these solutions and recrystallization from light petroleum or toluene provides Cp″Zr($C_6F_5$)(NCR′){$\eta^5$-(3-$RC_4H_3BC_6F_5$)} (**2H**, R = H, R′ = Me; **3H**, R = H, R′ = *t*Bu; **3Me**, R = Me, R′ = *t*Bu) as purple to blue solids (Scheme 1). $^1H$ and $^{13}C$ NMR data for all new complexes are collected in Table 1, and $^{19}F$ NMR data (where applicable) in Table 2. Unlike the ether adducts, where the diethyl ether ligand readily dissociates in benzene solution, the nitrile ligands remain coordinated. All three complexes are chiral. As in the case of **1Me**, the methyl substituent on the borole ligand in **3Me** leads to the formation of two diastereomers in an approximate ratio of 1:0.6 at room temperature. It is of note that this ratio is very similar to that observed for **1Me** at −50 °C; however, since the ether ligand in this complex undergoes rapid exchange at room temperature, it seems likely that any correlation is merely coincidental and does not provide information concerning a possible reaction mechanism. The $^{19}F$ NMR spectra at room temperature show two peaks for the *ortho*-F of the zirconium-$C_6F_5$ ligand, indicative of hindered rotation. By contrast, the borole-$C_6F_5$ group shows only one *o*-F peak at this temperature. As with **1H** and **1Me**, the $^{11}B$ NMR spectra of the complexes show broad peaks around $\delta$ 30−40, which are low-field shifted by some 10−20 ppm compared to $C_6H_5$-substituted boroles,[2a,c,e,g,h] possibly a reflection of the stronger electron-withdrawing characteristics of the perfluorophenyl substituent, although it should be noted that these examples are all $d^6$ to $d^{10}$

---

(6) A reviewer suggested that a comparison of $^{11}B$ NMR chemical shifts with $d^0$ complexes featuring "innocent" organic boron substituents such as B-Me might be more appropriate than with 1-phenylborole complexes of $d^6$−$d^{10}$ metals. However, due to the lack of $\pi$-conjugation, B-Me compounds tend to be found at lower field than related B-Ph and even B-$C_6F_5$ compounds and represent an electronically different environment. For complexes with methyl-substituted boroles and boratabenzenes see for example: Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981. Herberich, G. E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751.

(7) (a) Durfee, D. L.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (b) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (c) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: London, 1982; Vol. 8, Chapter 38.4.

**Table 1. $^1$H and $^{13}$C NMR Data for New Complexes$^a$**

| | $^1$H NMR | | $^{13}$C NMR | |
|---|---|---|---|---|
| complex | $\delta$ | assgnt | $\delta$ | assgnt |
| Cp″Zr(C$_6$F$_5$)(NCMe) | -0.02, 0.11 (s, 9 H each) | SiMe$_3$ | −0.90, −0.47 | both SiMe$_3$ |
| {$\eta^5$-C$_4$H$_4$BC$_6$F$_5$}, **2H** | 0.99 (s, 3 H) | NCMe | 0.88 | NCMe |
| (C$_6$D$_6$, 1,2-difluorobenzene, 20 °C) | 5.87 (m, 1 H) | *o*-C$_4$H$_4$B | 115.09 | *m*-C$_4$H$_4$B |
| | 6.07 (m, 1 H) | *o*-C$_4$H$_4$B | 117.72 | *m*-C$_4$H$_4$B |
| | 6.28 (m, 1 H) | *m*-C$_4$H$_4$B | 120.04 | 4,5-Cp″ |
| | 6.31 (m, 1 H) | 4,5-Cp″H | 121.99 | 4,5-Cp″ |
| | 6.37 (t, 1 H, $J = 1.89$) | 2-Cp″H | 129.42 | 2-Cp″ |
| | 6.43 (m, 1 H) | 4,5-Cp″H | (*o*-C$_4$H$_4$B carbons not observed due to poor solubility and broadening of B nucleus) | |
| | 6.53 (m, 1 H) | *m*-C$_4$H$_4$B | | |
| Cp″Zr(C$_6$F$_5$)(NC*t*Bu) | -0.07, 0.12 (s, 9 H each) | SiMe$_3$ | −0.59, 0.01 | both SiMe$_3$ |
| {$\eta^5$-C$_4$H$_4$BC$_6$F$_5$}, **3H** | 0.67 (s, 9 H) | NC*t*Bu | 26.24 | NC*t*Bu |
| (C$_6$D$_6$, 20 °C) | 5.90 (m, 1 H) | *m*-C$_4$H$_4$B | 114.73 | 4,5-Cp″ |
| | 6.18 (m, 1 H) | *o*-C$_4$H$_4$B | 115.4 (v br) | *o*-C$_4$H$_4$B |
| | 6.29 (m, 1 H) | *m*-C$_4$H$_4$B | 119.01 | *m*-C$_4$H$_4$B |
| | 6.31 (m, 2 H) | 4,5-Cp″H | 119.81 | 2-Cp″ |
| | 6.38 (m, 1 H) | 2-Cp″H | 119.9 (v br) | *o*-C$_4$H$_4$B |
| | 6.51 (m, 1 H) | *o*-C$_4$H$_4$B | 121.94 | *m*-C$_4$H$_4$B |
| | | | 129.61 | 4,5-Cp″ |
| Cp″Zr(C$_6$F$_5$)(NC*t*Bu) | 0.26, 0.41 (s, 9 H each) | SiMe$_3$ | −0.49, −0.08 | both SiMe$_3$ |
| {$\eta^5$-(3-MeC$_4$H$_3$BC$_6$F$_5$)}, **3Me** | 1.74 (s, 9 H) | NC*t*Bu | 20.00 | NC*t*Bu |
| (CD$_2$Cl$_2$, 20 °C) | 2.38 (s, 3 H) | C$_4$H$_3$*Me*B | 27.40 | C$_4$H$_3$*Me*B |
| (major isomer) | 5.45, 5.88 (m, 1 H each) | *o*-C$_4$*H*$_3$MeB | 110.19 | *m*-C$_4$H$_3$MeB |
| | 6.33 (m, 1 H) | *m*-C$_4$*H*$_3$MeB | 120.28, 121.18 | 4,5-Cp″ |
| | 6.49 (m, 1 H) | 2-Cp″H | 131.98 | 2-Cp″ |
| | 6.83, 6.87 (m, 1 H) | 4,5-Cp″H | | |
| (minor isomer) | 0.16, 0.47 (s, 9 H each) | SiMe$_3$ | −0.68, 0.13 | both SiMe$_3$ |
| | 1.59 (s, 9 H) | NC*t*Bu | 19.33 | NC*t*Bu |
| | 2.38 (s, 3 H) | C$_4$H$_3$*Me*B | 27.08 | C$_4$H$_3$*Me*B |
| | 5.40, 6.00 (m, 1 H each) | *o*-C$_4$*H*$_3$MeB | 112.90 | 2-Cp″ |
| | 6.31 (s, 1 H) | *m*-C$_4$*H*$_3$MeB | 120.75 | *m*-C$_4$H$_3$MeB |
| | 6.51 (m, 1 H) | 2-Cp″H | 120.67, 130.26 | 4,5-Cp″ |
| | 6.54, 6.96 (m, 1 H each) | 4,5-Cp″H | | |
| Cp″Zr(C$_6$F$_5$)(CN*t*Bu)$_2$ | 0.18 (s, 18 H) | SiMe$_3$ | 0.74 | SiMe$_3$ |
| {$\eta^5$-C$_4$H$_4$BC$_6$F$_5$}, **4H** | 0.79 (s, 18 H) | NC*t*Bu | 28.31 | NC*t*Bu |
| (toluene-*d*$_8$, −20 °C) | 5.20 (m, 2 H) | *o*-C$_4$H$_4$B | 100.21 (br) | *o*-C$_4$H$_4$B |
| | 6.03 (m, 2 H) | *m*-C$_4$H$_4$B | 108.45 | *m*-C$_4$H$_4$B |
| | 6.06 (m, 2 H) | 4,5-Cp″H | 114.97 | 4,5-Cp″ |
| | 6.23 (m, 1 H) | 2-Cp″H | 123.44 | 2-Cp″ |
| Cp″Zr(C$_6$F$_5$)(CN*t*Bu)$_2$- | 0.13, 0.23 (s, 9 H each) | SiMe$_3$ | 0.81, 0.90 | both SiMe$_3$ |
| {$\eta^5$-(3-MeC$_4$H$_3$BC$_6$F$_5$)}, **4Me** | 0.83, 0.84 (s, 9 H each) | NC*t*Bu | 20.00 | C$_4$H$_3$B*Me* |
| (toluene-*d*$_8$, −10 °C) | 2.24 (s, 3 H) | C$_4$H$_3$*Me*B | 28.47, 28.54 | both NC*t*Bu |
| | 4.96, 5.24 (m, 1H each) | *o*-C$_4$H$_3$MeB | 98.4 (v br), 105.6 (v br) | both *o*-C$_4$H$_3$MeB |
| | 5.72 (m, 1 H) | 4,5-Cp″H | 112.56 | 4,5-Cp″ |
| | 5.74 (m, 1 H) | *m*-C$_4$H$_3$MeB | 114.24 | *m*-C$_4$H$_3$MeB |
| | 5.98 (m, 1 H) | 2-Cp″H | 117.10 | 2-Cp″ |
| | 6.40 (m, 1 H) | 4,5-Cp″H | 124.89 | 4,5-Cp″ |
| Cp″Zr{$\eta^2$-(C$_6$F$_5$CN*t*Bu)}(CN*t*Bu)- | 0.16, 0.20 (s, 9 H each) | SiMe$_3$ | 0.68, 0.96 | both SiMe$_3$ |
| {$\eta^5$-C$_4$H$_4$BC$_6$F$_5$}, **5H** | 0.84 (s, 9 H) | CN*t*Bu | 28.94 | CN*tBu* |
| (C$_6$D$_6$, 20 °C) | 0.96 (s, 9 H) | C(C$_6$F$_5$)N*t*Bu | 29.01 | C(C$_6$F$_5$)N*t*Bu |
| | 4.49 (m, 1 H) | *m*-C$_4$H$_4$B | 96.3 (v br) | *o*-C$_4$H$_4$B |
| | 4.74 (m, 1 H) | *o*-C$_4$H$_4$B | 104.4 (v br) | *o*-C$_4$H$_4$B |
| | 5.71, 5.81 (m, 1 H each) | 4,5-Cp″H | 106.43 | *m*-C$_4$H$_4$B |
| | 5.90 (m, 1 H) | 2-Cp″H | 111.35 | *m*-C$_4$H$_4$B |
| | 6.04 (m, 1 H) | *o*-C$_4$H$_4$B | 111.79, 118.10 | both 4,5-Cp″ |
| | 6.29 (m, 1 H) | *m*-C$_4$H$_4$B | 124.90 | 2-Cp″ |
| | | | 160.18 | *C*N$^t$Bu |
| | | | 223.78 | *C*(C$_6$F$_5$)N*t*Bu |
| Cp″Zr{$\eta^2$-(C$_6$F$_5$CN*t*Bu)}(CN*t*Bu)- | 0.17, 0.25 (s, 9 H each) | SiMe$_3$ | 1.10, 1.20 | both SiMe$_3$ |
| {$\eta^5$-(3-MeC$_4$H$_3$BC$_6$F$_5$}, **5Me** | 0.98 (s, 9 H) | CN*t*Bu | 20.98 | C$_4$H$_3$*Me*B |
| (major isomer, toluene-*d*$_8$, 20 °C) | 1.00 (s, 9 H) | (C$_6$F$_5$)CN($^t$Bu) | 28.68 | CN*t*Bu |
| | 2.29 (s, 3 H) | C$_4$H$_3$*Me*B | 28.97 | C(C$_6$F$_5$)N*t*Bu |
| | 4.18, 4.63 (m, 1 H each) | *o*-C$_4$H$_3$MeB | 102.9 (v br) | *o*-C$_4$H$_3$MeB |
| | 5.66 (m, 1 H) | 4,5-Cp″H | 104.7 (v br) | *o*-C$_4$H$_3$MeB |
| | 5.84 (m, 1 H) | 2-Cp″H | 106.98 | *m*-C$_4$H$_3$MeB |
| | 5.95 (m, 1 H) | *m*-C$_4$H$_3$MeB | 113.33, 119.59 | both 4,5-Cp″ |
| | 5.98 (m, 1 H) | 4,5-Cp″H | 127.39 | 2-Cp″ |
| | | | 162.05 | *C*N$^t$Bu |
| | | | 221.95 | (C$_6$F$_5$)*C*N($^t$Bu) |

**Table 1 (Continued)**

| | $^1H$ NMR | | $^{13}C$ NMR | |
|---|---|---|---|---|
| complex | $\delta$ | assgnt | $\delta$ | assgnt |
| $Cp'Zr(C_4H_7)(C_4H_6)$, **6a** ($C_6D_6$, 20 °C) | -0.74 (dd, 1H, $J = 7.2, 10.9$) | $=CH_2$ anti | 0.21 | $SiMe_3$ |
| | -0.45 (dd, 1H, $J = 7.2, 10.9$) | $=CH_2$ anti | 18.51 | $CH_3$ of $C_4H_7$ |
| | 0.22 (s, 9H) | $SiMe_3$ | 46.30 | $=CH_2$ |
| | 0.94 (dd, 1H, $J = 3.2, 13.4$) | $CH_2$ of $C_4H_7$ | 49.88 | $=CH_2$ |
| | 1.29 (dd, 1H, $J = 3.5, 9.3$) | $CH_2$ of $C_4H_7$ | 50.19 | $CH_2$ of $C_4H_7$ |
| | 1.38 (d, 3H, $J = 5.7$) | $CH_3$ of $C_4H_7$ | 74.16 | CHMe of $C_4H_7$ |
| | 1.79 (t, 1H, $J = 8.0$) | $=CH_2$ syn | 111.65 | Cp′ |
| | 1.98 (m, 1H) | CHMe | 112.14 | =CH |
| | 2.14 (t, 1H, $J = 8.1$) | $=CH_2$ syn | 112.23, 115.62, 116.59 | Cp′ |
| | 5.41 (m, 1H) | =CH | 126.59 | CH of $C_4H_7$ |
| | 5.60 (m, 1H) | =CH | | |
| | 5.92, 5.99 (m, 1H each) | Cp′ | | |
| | 6.43 (m, 2H) | Cp′ | | |
| $Cp^{Me}Zr(C_4H_7)(C_4H_6)$, **6b** ($C_6D_6$, 20 °C) | -0.63 (dd, 1H, $J = 7.5, 11.2$) | $=CH_2$ anti | 15.71 | Me of $Cp^{Me}$ |
| | -0.36 (dd, 1H, $J = 7.7, 11.0$) | $=CH_2$ anti | 18.72 | $CH_3$ of $C_4H_7$ |
| | 0.94 (dd, 1H, $J = 3.2, 13.2$) | $CH_2$ of $C_4H_7$ | 46.51 | $=CH_2$ |
| | 1.37 (d, 3H, $J = 5.9$) | $CH_3$ of $C_4H_7$ | 49.76 | $=CH_2$ |
| | 1.41 (dd, 1H, $J = 3.4, 9.4$) | $CH_2$ of $C_4H_7$ | 50.61 | $CH_2$ of $C_4H_7$ |
| | 1.73 (t, 1H, $J = 8.0$) | $=CH_2$ syn | 74.90 | CHMe |
| | 1.99 (s, 3H) | Me of $Cp^{Me}$ | 108.09, 108.30, 110.07, 110.70 | $Cp^{Me}$ |
| | 2.00 (m obscured by other peaks, 1H) | CHMe | 112.76, 112.97 | =CH |
| | 2.13 (t, 1H, $J = 8.9$) | $=CH_2$ syn | 122.25 | ipso $Cp^{Me}$ |
| | 5.44 (m, 1H) | =CH | 126.87 | CH of $C_4H_7$ |
| | 5.64 (m, 1H) | =CH | | |
| | 5.88 (m obscured by other peaks, 1H) | CH of $C_4H_7$ | | |
| | 5.92 (m, 2H) | $Cp^{Me}$ | | |
| | 6.11 (m, 2H) | $Cp^{Me}$ | | |
| $Cp'Zr(C_6F_5)\{\eta^4\text{-}CH_2CHCHCH\text{-}B(C_6F_5)_2\}$**7a** (toluene-$d_8$, 20 °C) | -0.10 (s, 9H) | $SiMe_3$ | −1.19 | $SiMe_3$ |
| | 0.19 (t, 1H, $J = 9.8$) | $=CH_2$ | 70.45 | $=CH_2$ |
| | 2.45 (t, 1H, $J = 9.2$) | $=CH_2$ | 95.0 (v br) | =CHB |
| | 2.89 (d, 1H, $J = 12.8$) | CHB | 114.86 | Cp′ |
| | 5.91 (t obscured by Cp′ peak, 1H) | =CH | 118.43 | Cp′ |
| | | | 119.52 | Cp′ |
| | 5.94 (m, 1H) | Cp′H | 121.58 | Cp′ |
| | 6.11 (m, 1H) | Cp′H | 126.89 | =CH |
| | 6.39 (q, 1H, $J = 9.6$) | =CH | 134.54 | =CH |
| | 6.48 (m, 1H) | Cp′H | | |
| | 6.64 (m, 1H) | Cp′H | | |
| $Cp^{Me}$ $Zr(C_6F_5)\{\eta^4\text{-}CH_2CHCHCH\text{-}B(C_6F_5)_2\}$, **7b** (toluene-$d_8$, 20 °C) | 0.11 (t, 1H, $J = 10.9$) | $=CH_2$ | 1.59 | Me of $Cp^{Me}$ |
| | 1.61 (s, 3H) | Me of $Cp^{Me}$ | 71.46 | $=CH_2$ |
| | 2.44 (t, 1H, $J = 9.4$) | $=CH_2$ | 95.2 (v br) | =CHB |
| | 2.93 (d, 1H, $J = 12.8$) | =CHB | 112.70 | $Cp^{Me}$ |
| | 5.82 (m, 1H) | H of $Cp^{Me}$ | 113.93 | $Cp^{Me}$ |
| | 5.84 (m, 1H) | H of $Cp^{Me}$ | 114.17 | $Cp^{Me}$ |
| | 5.91 (t obscured by $Cp^{Me}$, 1H) | =CH | 114.53 | $Cp^{Me}$ |
| | 5.95 (m, 1H) | H of $Cp^{Me}$ | 126.50 | =CH |
| | 6.28 (m, 1H) | H of $Cp^{Me}$ | 135.08 | =CH |
| | 6.39 (q, 1H, $J = 9.6$) | =CH | | |
| $CpZr(C_6F_5)\{\eta^4\text{-}CH_2CHCHCH\text{-}B(C_6F_5)_2\}$, **7c** ($C_6D_6$, 20 °C) | -0.01 (t, 1H, $J = 10.8$) | $=CH_2$ | 71.00 | $=CH_2$ |
| | 2.39 (t, 1H, $J = 9.7$) | $=CH_2$ | 95.8 (v br) | =CHB |
| | 2.85 (d, 1H, $J = 12.8$) | =CHB | 114.09 | Cp |
| | 5.94 (t obscured by Cp) | =CH | 127.09 | =CH |
| | 6.00 (s, 5H) | H of Cp | 135.06 | =CH |
| | 6.31 (q, 1H, $J = 9.7$) | =CH | | |
| $Zr_2Cp'_2(C_6F_5)_2\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4B\text{-}CH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$, **8a** ($C_6D_6$, 20 °C) | -0.16 (s, 9H) | $SiMe_3$ | −1.46, −1.02 | both $SiMe_3$ |
| | -0.10 (s, 9H) | $SiMe_3$ | 14.48 | $\mathrm{B}\mathit{C}\mathrm{H_2CHCHCHB}$ |
| | 1.48 (m, 1H) | $\mathrm{BC}\mathit{H}_2\mathrm{CHCHCHB}$ | 77.65 | $\mathrm{BCH_2}\mathit{C}\mathrm{HCHCHB}$ |
| | 1.86 (m, 1H) | $\mathrm{BC}\mathit{H}_2\mathrm{CHCHCHB}$ | 107.88 | $\mathrm{BCH_2CHCH}\mathit{C}\mathrm{HB}$ |
| | 2.90 (m, 1H) | $\mathrm{BCH_2C}\mathit{H}\mathrm{CHCHB}$ | 131.69 | $\mathrm{BCH_2CH}\mathit{C}\mathrm{HCHB}$ |
| | 3.33 (m, 1H) | $m\text{-}C_4H_4B$ | 98.64, 126.19 | $m\text{-}C_4H_4B$ |
| | 4.83 (d obscured by borole and Cp′ peaks, 1H) | $\mathrm{BCH_2CHCHC}\mathit{HB}$ | 114.80, 118.20 | $o\text{-}C_4H_4B$ |
| | 4.88 (m, 1H) | $o\text{-}C_4H_4B$ | 113.55, 113.67, 116.60, 117.70, 118.67, 120.88, 126.42 | all Cp′ |
| | 4.93 (m, 1H) | Cp′H | | |
| | 5.33 (m, 2H) | Cp′H | | |
| | 5.60 (m, 1H) | Cp′H | | |
| | 5.72 (m, 1H) | $\mathrm{BCH_2CHC}\mathit{H}\mathrm{CHB}$ | | |
| | 6.09 (m, 1H) | Cp′H | | |
| | 6.40 (m, 1H) | Cp′H | | |
| | 6.52 (m, 1H) | Cp′H | | |
| | 6.88 (m, 1H) | Cp′H | | |
| | 7.12 (m, 1H) | $o\text{-}C_4H_4B$ | | |
| | 7.36 (m, 1H) | $m\text{-}C_4H_4B$ | | |

**Table 1 (Continued)**

| | $^1$H NMR | | $^{13}$C NMR | |
|---|---|---|---|---|
| complex | $\delta$ | assgnt | $\delta$ | assgnt |
| $Zr_2Cp^{Me}{}_2(C_6F_5)_2\{\mu$-$\eta^5$:$\eta^5$-$C_4H_4B$-$CH_2$-$\eta^3$,$\kappa F$-$CHCHCHB(C_6F_5)_3\}$, **8b** ($C_6D_6$/1,2-difluorobenzene, 25 °C) | 1.49 (dd, 1 H, $J = 5.19, 12.58$) | $\mathrm{BC}H_2\mathrm{CHCHCHB}$ | 13.97, 15.03 | both Me of $Cp^{Me}$ |
| | 1.68, 1.76 (s, 3 H each) | Me of $Cp^{Me}$ | 14.40 | $\mathrm{B}C\mathrm{H_2CHCHCHB}$ |
| | 1.91 (dd, 1 H, $J = 10.45, 12.64$) | $\mathrm{BC}H_2\mathrm{CHCHCHB}$ | 79.52 | $\mathrm{BCH_2}C\mathrm{HCHCHB}$ |
| | 2.97 (m, 1 H) | $\mathrm{BCH_2C}H\mathrm{CHCHB}$ | 101.07, 109.04 | both $C_4H_4B$ |
| | 3.90 (s, 1 H) | $C_4H_4B$ | 109.59, 111.17, | |
| | 4.89 (d, 1 H, $J = 18.64$) | $\mathrm{BCH_2CHCHC}H\mathrm{B}$ | 111.63, 112.55, | |
| | 5.05 (s, 1 H) | $C_4H_4B$ | 113.54, 114.85, | |
| | 5.18 (tr, 2 H, $J = 2.95$) | H of $Cp^{Me}$ | 114.98, 117.89 | all $Cp^{Me}$ |
| | 5.44 (q, 1 H, $J = 2.57$) | H of $Cp^{Me}$ | 132.78 | $\mathrm{BCH_2CH}C\mathrm{HCHB}$ |
| | 5.64 (q, 1 H, $J = 2.33$) | H of $Cp^{Me}$ | (other peak obscured by solvent) | |
| | 5.68 (dd, 1 H, $J = 8.22, 18.63$) | $\mathrm{BCH_2CHC}H\mathrm{CHB}$ | | |
| | 6.00 (q, 1 H, $J = 2.39$) | H of $Cp^{Me}$ | | |
| | 6.09 (q, 1 H, $J = 2.24$) | H of $Cp^{Me}$ | | |
| | 6.30 (q, 1 H, $J = 2.33$) | H of $Cp^{Me}$ | | |
| | 6.45 (q, 1 H, $J = 2.39$) | H of $Cp^{Me}$ | | |
| | 7.58 (m, 1 H) | $C_4H_4B$ | | |
| | (1 $C_4H_4B$ obscured by 1,2-difluorobenzene) | | | |
| $Zr_2Cp_2(C_6F_5)_2\{\mu$-$\eta^5$:$\eta^5$-$C_4H_4B$-$CH_2$-$\eta^3$,$\kappa F$-$CHCHCHB(C_6F_5)_3\}$ **8c** ($C_6D_6$/1,2-difluorobenzene, 25 °C) | 1.47 (dd, 1 H, $J = 5.43, 12.47$) | $\mathrm{BC}H_2\mathrm{CHCHCHB}$ | 14.41 (br) | $\mathrm{B}C\mathrm{H_2CHCHCHB}$ |
| | 1.85 (dd, 1 H, $J = 10.71, 12.76$) | $\mathrm{BC}H_2\mathrm{CHCHCHB}$ | 78.03 | $\mathrm{BCH_2}C\mathrm{HCHCHB}$ |
| | 3.11 (m, 1 H) | $\mathrm{BCH_2C}H\mathrm{CHCHB}$ | 99.84 (br) | $C_4H_4B$ |
| | 3.78 (s, 1 H) | $C_4H_4B$ | 109.16 (br) | $C_4H_4B$ |
| | 4.83 (d, 1 H, $J = 18.93$) | $\mathrm{BCH_2CHCHC}H\mathrm{B}$ | 110.56 | Cp |
| | 5.08 (s, 1 H) | $C_4H_4B$ | 115.61 | Cp |
| | 5.48 (s, 5 H) | Cp | 124.62 | $\mathrm{BCH_2CHCH}C\mathrm{HB}$ |
| | 5.69 (dd, 1 H, $J = 8.51, 18.93$) | $\mathrm{BCH_2CHC}H\mathrm{CHB}$ | 128.12 | $C_4H_4B$ |
| | 6.26 (s, 5 H) | Cp | 132.51 | $\mathrm{BCH_2CH}C\mathrm{HCHB}$ |
| | 7.51 (m, 1 H) | $C_4H_4B$ | | |
| | (1 $C_4H_4B$ obscured by 1,2-difluorobenzene) | | | |
| $Zr_2Cp''_2(C_6F_5)_2\{\mu$-$\eta^5$:$\eta^5$-$C_4H_4B$-$CH_2$-$\eta^3$,$\kappa F$-$CHCHCHB(C_6F_5)_3\}$ **8d** ($C_6D_6$, 20 °C) | -0.38, −0.01, −0.08, 0.20 (s, 9H each) | $SiMe_3$ | −1.20, −0.84, | |
| | 1.51 (d, 2 H, $J = 8.04$) | $\mathrm{BC}H_2\mathrm{CHCHCHB}$ | −0.69, −0.21 | all $SiMe_3$ |
| | 3.36 (q, 1 H, $J = 8.27$) | $\mathrm{BCH_2C}H\mathrm{CHCHB}$ | 14.95 | $\mathrm{B}C\mathrm{H_2CHCHCHB}$ |
| | 3.91 (m, 1 H) | *m*-$C_4H_4B$ | 81.40 | $\mathrm{BCH_2}C\mathrm{HCHCHB}$ |
| | 4.81 (d, 1 H, $J = 19.44$) | $\mathrm{BCH_2CHCHC}H\mathrm{B}$ | 98.71 | *m*-$C_4H_4B$ |
| | 4.98 (m, 1 H) | *o*-$C_4H_4B$ | 105.72, 111.34 | both *o*-$C_4H_4B$ |
| | 5.51 (m, 1 H) | 4,5-Cp″H | 119.73 | 4,5-Cp″H |
| | 5.81 (d, 1 H, $J = 6.46$) | $\mathrm{BCH_2CHC}H\mathrm{CHB}$ | 121.54 | $\mathrm{BCH_2CHCH}C\mathrm{HB}$ |
| | 5.89 (m, 1 H) | 2-Cp″H | 123.87 | $\mathrm{BCH_2CH}C\mathrm{HCHB}$ |
| | 6.03, 6.66 (m, 1 H each) | 4,5-Cp″H | 124.01, 124.78 | 4,5-Cp″H |
| | 6.74 (m, 1 H) | 2-Cp″H | 126.64 | *m*-$C_4H_4B$ |
| | 6.81 (m, 1 H) | *o*-$C_4H_4B$ | 127.69, 129.50 | both 2-Cp″H |
| | 7.08 (m, 1 H) | 4,5-Cp″H | 129.95 | 4,5-Cp″H |
| | 7.87 (m, 1 H) | *o*-$C_4H_4B$ | | |

[a] All shifts are in ppm and $J$ values are in Hz. $^{13}$C NMR signals for the $C_6F_5$ groups are not reported.

complexes and thus may exhibit different bonding arrangements.[6]

Treatment of solutions of **1H** and **1Me** in toluene-$d_8$ at −20 °C with 4 equiv of *tert*-butyl isocyanide leads to a rapid color change from red to yellow. The products in both cases are the bis-isocyanide adducts Cp″Zr($C_6F_5$)(CN*t*Bu)$_2$\{$\eta^5$-(3-R$C_4H_3BC_6F_5$)\} (**4H**, **4Me**). The complexation of two isocyanide ligands is revealed by the $^1$H NMR spectrum. For **4H** a sharp singlet is observed at $\delta$ 0.79 representing 18 protons, while for **4Me** there are two singlets at $\delta$ 0.83 and 0.84 (ratio 1:1), since the two isocyanide ligands are rendered inequivalent by the presence of the borole-methyl substituent. The *o*-F signals of the zirconium-$C_6F_5$ group in the $^{19}$F NMR spectra are at very low field ($\delta$ −98.7 and −99.3 for **4H** and $\delta$ −97.7 and −99.5 for **4Me**) and clearly show hindered rotation.

Complexes **4H** and **4Me** are not thermally stable. After 1 h at room temperature the signals associated with these complexes are quantitatively replaced by a new set of signals, corresponding to Cp″Zr\{C(N*t*Bu)-$C_6F_5$\}(CN*t*Bu)\{$\eta^5$-(3-R$C_4H_3BC_6F_5$)\} (**5H**, **5Me**), as the products of the migratory insertion of one molecule of isocyanide into the zirconium−$C_6F_5$ bond. The compounds are isolated as bright yellow crystals. The iminoacyl ligand is $\eta^2$-bonded, as confirmed by a crystallographic study of **5H** (see below). Such migratory insertion reactions are common for organometallic zirconium complexes;[7] however we believe that this represents the first crystallographically characterized example involving an insertion into the rather stable Zr−$C_6F_5$ bond. As with **1Me** and **3Me**, compound **5Me** exists as a pair of diastereomers, although in this case the ratio is closer to 1:0.15. Because of the small amount of the second isomer, only the major isomer was fully characterized. There is no evidence for further insertions, even in the presence of excess isocyanide and over extended periods of time. As would be expected, the $C_6F_5$ group of the iminoacyl ligand shows no sign of hindered

---

(8) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198.

(9) Brackemeyer, T.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 531.

(10) Schubart, M.; Mitchell, G.; Gade, L. H.; Kottke, T.; Scowen, I. J.; McPartlin, M. *Chem Commun.* **1999**, 233.

**Table 2. $^{19}$F NMR Data for Boryldiene and Borole Compounds**

| complex | $\delta$ | assgnt |
|---|---|---|
| Cp″Zr($C_6F_5$)(NCMe){$\eta^5$-$C_4H_4BC_6F_5$}, **2H** ($C_6D_6$, 25 °C) | −113.3 (br s, 1 F), −121.1 (br s, 1 F), −131.5 (m, 2 F) | *o*-F |
| | −157.2 (t, 1 F, $J_{FF}$ = 19.8), −159.5 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −162.9 (br d, 2 F), −165.2 (m, 2 F) | *m*-F |
| Cp″Zr($C_6F_5$)(NC*t*Bu){$\eta^5$-$C_4H_4BC_6F_5$}, **3H** ($C_6D_6$, 25 °C) | −115.5 (br s, 1 F), −120.19 (br s, 1 F), −131.2 (d, 2 F, $J_{FF}$ = 19.8) | *o*-F |
| | −157.3 (t, 1 F, $J_{FF}$ = 19.8), −159.8 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −163.4 (br s, 1 F), −163.8 (br s, 1 F) overlapping, −165.4 (m, 2 F) | *m*-F |
| Cp″Zr($C_6F_5$)(NC*t*Bu) {$\eta^5$-(3-Me$C_4H_3BC_6F_5$)}, **3Me** ($C_6D_6$, 25 °C, major isomer) | −113.0 (d, 1 F, $J_{FF}$ = 33.9), −119.1 (d, 1 F, $J_{FF}$ = 31.1), −131.4 (m, 2F) | *o*-F |
| | −157.06 (t, 1 F, $J_{FF}$ = 19.8), −159.6 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −162.63 (br m, 2 F), −165.1 (m, 2 F) | *m*-F |
| (minor isomer) | −110.7 (s, 1 F), −120.0 (s, 1 F), −131.5 (m, 2 F) | *o*-F |
| | −157.4 (t, 1 F, $J_{FF}$ = 19.8), −159.9 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −163.2 (br m, 2 F), −165.8 (m, 2 F) | *m*-F |
| Cp″Zr($C_6F_5$)(CN*t*Bu)$_2${$\eta^5$-$C_4H_4BC_6F_5$}, **4H** (toluene-$d_8$, −20 °C) | −98.7 (d, 1 F, $J_{FF}$ = 31.1), −99.3 (d, 1 F, $J_{FF}$ = 33.9), −128.7 (m, 2 F) | *o*-F |
| | −160.1 (t, 1 F, $J_{FF}$ = 19.8), −160.8 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −162.8 (m, 1 F), −164.2 (m, 1 F), −165.5 (m, 2 F) | *m*-F |
| Cp″Zr($C_6F_5$)(CN*t*Bu)$_2${$\eta^5$-(3-Me$C_4H_3BC_6F_5$)}, **4Me** (toluene-$d_8$, −20 °C) | −97.7 (br s, 1 F), −99.5 (br s, 1 F), −128.7 (d, 2 F, $J_{FF}$ = 19.8) | *o*-F |
| | −160.2 (t, 1 F, $J_{FF}$ = 19.8), −161.23 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −162.9 (m, 1 F), −164.5 (m, 1 F), −165.57 (m, 2 F) | *m*-F |
| Cp″Zr{$\eta^2$-($C_6F_5$CN*t*Bu)}(CN*t*Bu){$\eta^5$-$C_4H_4BC_6F_5$}, **5Me** (toluene-$d_8$, −20 °C) | −128.4 (d, 2 F, $J_{FF}$ = 19.8), −138.86 (br s, 2 F) | *o*-F |
| | −157.3 (t, 1 F, $J_{FF}$ = 24.0), −161.1 (t, 1 F, $J_{FF}$ = 24.0) | *p*-F |
| | −161.4 (v br, 2 F), −165.7 (m, 2 F) | *m*-F |
| Cp″Zr{$\eta^2$-($C_6F_5$CN*t*Bu)}(CN*t*Bu) {$\eta^5$-(3-Me$C_4H_3BC_6F_5$)}, **5Me** (major isomer, toluene-$d_8$, 25 °C) | −128.6 (m, 2 F), −138.4 (m, 2 F) | *o*-F |
| | −157.8 (t, 1 F, $J_{FF}$ = 19.8), −162.6 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −162.0 (v br, 2 F), −165.9 (m, 2 F) | *m*-F |
| Cp′Zr($C_6F_5$){$\eta^4$-$CH_2CHCHCHB(C_6F_5)_2$}, **7a** (toluene-$d_8$, 25 °C) | −116.5 (m, 2 F), −130.4 (m, 2 F), −159.3 (s, 2 F) | *o*-F |
| | −150.8 (t, 1 F, $J_{FF}$ = 19.8), −152.1 (t, 1 F, $J_{FF}$ = 19.8), | *p*-F |
| | −154.3 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −160.6 (m, 2 F), −161.7 (m, 4 F) | *m*-F |
| (toluene-$d_8$, −60 °C) | −109.2 (br s, 1 F), −121.1 (br s, 1 F), −130.3 (s, 2 F), | *o*-F |
| | −131.1 (s, 1 F), −172.4 (s, 1 F) | |
| | −149.3 (m, 1 F), −150.7 (m, 1 F), −153.9 (m, 1 F) | *p*−*F* |
| | −156.5 (m, 1 F), −161.6 (br m, 5 F) | *m*-F |
| Cp$^{Me}$Zr($C_6F_5$){$\eta^4$-$CH_2CHCHCHB(C_6F_5)_2$}, **7b** (toluene-$d_8$, 25 °C) | −118.0 (m, 2 F), −130.5 (m, 2 F), −159.6 (s, 2 F) | *o*-F |
| | −151.1 (t, 1 F, $J_{FF}$ = 19.8), −152.6 (t, 1 F, $J_{FF}$ = 19.8), | *p*-F |
| | −154.4 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −162.0 (m, 6 F) | *m*-F |
| (toluene-$d_8$, −60 °C) | −115.7 (vbr s, 2 F), −130.8 (s, 2 F), −131.2 (d, 1 F, $J_{FF}$ = 19.8), | *o*-F |
| | −172.4 (d, 1 F, $J_{FF}$ = 19.8) | |
| | −149.1 (t, 1 F, $J_{FF}$ = 19.8), −150.9 (t, 1 F, $J_{FF}$ = 19.8), | |
| | −153.8 (t, 1 F, $J_{FF}$ = 19.8) | *p*-F |
| | −159.4 (m, 1 F), −160.0 (m, 1 F), −161.0 (m, 4 F) | *m*-F |
| CpZr($C_6F_5$){$\eta^4$-$CH_2CHCHCHB(C_6F_5)_2$}, **7c** (toluene-$d_8$, 25 °C) | −117.1 (m, 2 F), −130.8 (m, 2 F), −159.3 (s, 2 F) | *o*-F |
| | −150.8 (t, 1 F, $J_{FF}$ = 19.8), −151.8 (t, 1 F, $J_{FF}$ = 19.8), | *p*-F |
| | −154.1 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −161.6 (m, 2 F), −162.1 (m, 4 F) | *m*-F |
| (toluene-$d_8$, −60 °C) | −115.6 (br s, 2 F), −130.9 (d, 2 F, $J_{FF}$ = 16.9), | *o*-F |
| | −131.4 (d, 1 F, $J_{FF}$ = 16.9), −173.3 (d, 1 F, $J_{FF}$ = 28.2) | |
| | −149.6 (t, 1 F, $J_{FF}$ = 22.6), −151.1 (t, 1 F, $J_{FF}$ = 22.6), | *p*-F |
| | −153.6 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −156.5 (t, 1 F, $J_{FF}$ = 22.6), −160.4 (br t, 1 F), −160.9 (m, 2 F) | *m*-F |
| | −161.7 (m, 2 F) | |
| $Zr_2Cp'_2(C_6F_5)_2${$\mu$-$\eta^5$:$\eta^5$-$C_4H_4$B-$CH_2$-$\eta^3$,$\kappa F$-CHCHCHB$(C_6F_5)_3$}, **8a** ($C_6D_6$, 20 °C) | −113.2 (br s, 1 F), −115.2 (vbr s, 1 F), −119.8 (br s, 1 F), | *o*-F |
| | −120.7 (vbr s, 1 F), −126.5 (s, 1 F), −130.1 (br s, 2 F), −132.6 (br s, 2 F), | |
| | −222.9 (d, 1 F, $J_{FF}$ = 33.9) | |
| | −151.8 (t, 1 F, $J_{FF}$ = 19.8), −152.9 (t, 1 F, $J_{FF}$ = 19.8), | *p*-F |
| | −156.2 (t, 1 F, $J_{FF}$ = 19.8), −157.9 (t, 1 F, $J_{FF}$ = 19.8), | |
| | −158.4 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −161.5 (br m, 6 F), −164.2 (br s, 3 F), −164.5 (br m, 1 F) | *m*-F |
| $Zr_2Cp^{Me}_2(C_6F_5)_2${$\mu$-$\eta^5$:$\eta^5$-$C_4H_4$B-$CH_2$-$\eta^3$,$\kappa F$-CHCHCHB$(C_6F_5)_3$}, **8b** ($C_6D_6$/1,2-difluorobenzene, 25 °C) | −127.6 (br s, 2 F), −130.6 (vbr s, 3 F), −133.8 (br s, 4 F), | *o*-F |
| | −218.3 (br s, 1 F) | |
| | −153.9 (m, 2 F), −158.2 (m, 1 F), 159.8 (m, 1 F) | |
| | −160.0 (m, 1 F) | *p*-F |
| | −161.6 (br m, 5 F), −167.5 (br m, 5 F) | *m*-F |
| $Zr_2Cp_2(C_6F_5)_2${$\mu$-$\eta^5$:$\eta^5$-$C_4H_4$B-$CH_2$-$\eta^3$,$\kappa F$-CHCHCHB$(C_6F_5)_3$}, **8c** ($C_6D_6$/1,2-difluorobenzene, 25 °C) | −120.2 (vbr s, 4 F), −127.46 (br s, 1 F), −130.6 (br s, 2 F), | *o*-F |
| | −133.8 (br s, 2 F) | |
| | −153.8 (m, 2 F), −157.8 (br s, 1 F), −159.5 (br s, 1 F), | |
| | −159.8 (br s, 1 F) | *p*-F |
| | −161.4 (br s, 1 F), −161.8 (m, 4 F), −164.7 (br m, 5 F) | *m*-F |
| $Zr_2Cp''_2(C_6F_5)_2${$\mu$-$\eta^5$:$\eta^5$-$C_4H_4$B-$CH_2$-$\eta^3$,$\kappa F$-CHCHCHB$(C_6F_5)_3$}, **8d** ($C_6D_6$, 25 °C) | −108.2 (br s, 1 F), −112.8 (vbr s, 1 F), −119.9 (vbr s, 1 F), | *o*-F |
| | −120.2 (br s, 1 F), −126.2 (s, 1 F), −130.0 (vbr s, 2 F), | |
| | −132.9 (br s, 2 F), −217.2 (m, 1 F) | |
| | −152.1 (t, 1 F, $J_{FF}$ = 19.8), −152.5 (t, 1 F, $J_{FF}$ = 19.8), | *p*-F |
| | −157.1 (t, 1 F, $J_{FF}$ = 19.8), −157.6 (t, 1 F, $J_{FF}$ = 19.8), | |
| | −159.0 (t, 1 F, $J_{FF}$ = 19.8) | |
| | −160.2 (t, 1 F, $J_{FF}$ = 19.8), −160.5 (m, 3 F), −161.5 (br s, 1 F) | *m*-F |
| | −162.6 (m, 1 F), −164.2 (m, 2 F), −164.4 (m, 2 F) | |

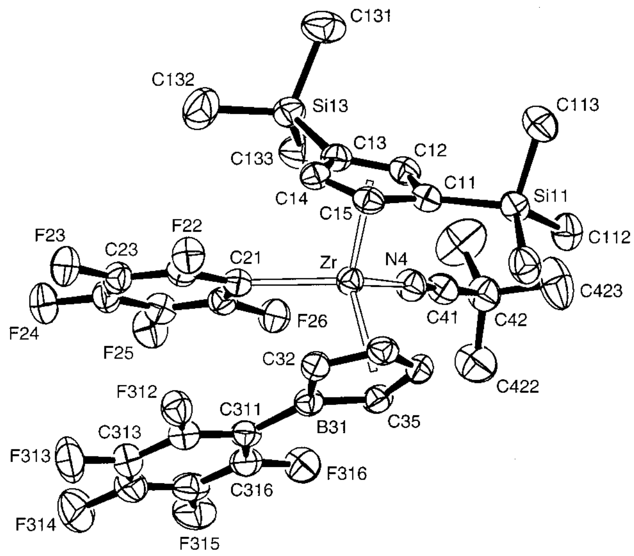


**Figure 1.** Molecular structure of Cp″Zr($C_6F_5$)(CN*t*Bu){$\eta^5$-$C_4H_4BC_6F_5$}, **3H**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

**Table 3. Selected Distances (Å) and Angles (deg) for 3H**

| | | | |
|---|---|---|---|
| Zr−C(11) | 2.523(3) | Zr−C(12) | 2.521(3) |
| Zr−C(13) | 2.550(3) | Zr−C(14) | 2.521(3) |
| Zr−C(15) | 2.500(3) | Zr−C(21) | 2.350(3) |
| Zr−B(31) | 2.626(3) | Zr−C(32) | 2.501(3) |
| Zr−C(33) | 2.433(3) | Zr−C(34) | 2.405(3) |
| Zr−C(35) | 2.485(3) | Zr−N(4) | 2.301(2) |
| N(4)−C(41) | 1.140(4) | C(41)−C(42) | 1.481(4) |
| C(41)−Zr−N(4) | 177.7(2) | N(4)−C(41)−C(42) | 179.5(3) |
| N(4)−Zr−C(21) | 109.73(9) | C(32)−B(31)−C(311) | 129.6(3) |
| C(35)−B(31)−C(311) | 127.4(3) | C(35)−B(31)−C(32) | 103.0(2) |

rotation at room temperature, with a single *o*-F signal in the $^{19}$F NMR spectrum at ca. $\delta$ −138. The $^{13}$C NMR resonances of the iminoacyl carbon atoms are found at $\delta$ 223.78 and 221.95 for **5H** and **5Me**, repectively.[7]

Crystals of **3H** suitable for single-crystal X-ray diffraction were obtained from benzene-$d_6$ at room temperature. The molecular structure of **3H** is depicted in Figure 1. Important bond lengths and angles are collected in Table 3. The structural details are closely similar to those found in **1H**; for example the Zr−C distances to the $C_4H_4BC_6F_5$ ligand (average 2.456 Å) are almost identical to those in **1H** (average 2.455 Å).[4] As in the structure of **1H**,[4] the B−C(aryl) bond distance (1.590(4) Å) in the $C_4H_4BC_6F_5$ ligand of **3H** is typical of a single bond and indicates little $\pi$-bonding contribution.

Single crystals of **5H** suitable for X-ray diffraction were obtained from light petroleum at −20 °C. The asymmetric unit comprises two independent molecules, one of which is depicted in Figure 2. The two independent molecules differ principally in the relative orientation of the *tert*-butyl group of the coordinated isonitrile ligands. Important bond lengths and angles are collected in Table 4. The structure confirms the $\eta^2$-bonding of the iminoacyl ligand, with an "N-inside" orientation and Zr−N distances for the two molecules of 2.279(4) and 2.266(4) Å and Zr−C distances of 2.252(4) and 2.264(4) Å. These are slightly longer than the corresponding parameters in, for example, the $\eta^2$-iminoacyl complex {*p*-*t*Bu-calix[4](OMe)$O_3$}Zr(*t*BuN=CPh) [Zr−N = 2.180(3) Å; Zr−C = 2.260(3) Å].[8] The Zr−C(isocyanide) bond lengths of 2.362 (4) and 2.364(4) Å are longer than the corresponding bond distance in [$Cp_3Zr(C{\equiv}NCMe_3)$][$MeB(C_6F_5)_3$][9] of 2.313(3) Å, but shorter than those observed in [MeSi{$SiMe_2N$(*p*-tol)}$_3$Zr($CNCMe_3$)$_3$][Co(CO)$_4$] at 2.431(7), 2.448(7), and 2.440(7) Å.[10] As expected, the Zr−C≡N− unit is linear (173.63(16)° and 175.8(4)°). The C≡N bond lengths are 1.150(5) and 1.140(5) Å, showing essentially no difference from the C≡N distance in the free isonitrile.[11] Bonding to the borole-carbon atoms is tighter than to Cp″, with an average Zr−C(borole) distance of 2.480 Å as compared with 2.547 Å for Zr−Cp″, while the Zr−B(1) distance is significantly longer, 2.664(5) Å (molecule 1).

**Triple-Decker Complexes.** The reactions of the diene complexes Cp$^R$Zr($\eta^3$-crotyl)($\eta^4$-butadiene) (**6a**, Cp$^R$ = $C_5H_4SiMe_3$; **6b**, $C_5H_4Me$; **6c**, Cp; **6d**, Cp″) with $B(C_6F_5)_3$ in toluene were studied by NMR spectroscopy. Addition at room temperature generates the boryldiene complexes Cp$^R$Zr($C_6F_5$){$\eta^4$-$\kappa F$-$CH_2CHCHCHB(C_6F_5)_2$} (**7a**−**d**) in quantitative yield (Scheme 2). Presumably the reaction pathway involves a zwitterionic bis(allyl) intermediate, as described for the complexes Cp$^R$Zr($\eta^3$-allyl)($\eta^4$-isoprene) (Cp$^R$ = Cp, Cp$^{Me}$, Cp′, Cp″, and Ind).[12,13] The reaction proceeds with C−H activation and the elimination of butene, with the simultaneous transfer of a $C_6F_5$ group from boron to the metal center. We have previously reported that the Cp″ complex Cp″Zr($C_6F_5$){$\eta^4$-$\kappa F$-$CH_2CHCHCHB(C_6F_5)_2$} (**7d**) exists in solution as a mixture of three isomers, two of which feature the diene ligand in *prone (endo)* and *supine (exo)* orientation with regard to the cyclopentadienyl ring, while in the third the diene is roughly perpendicular to the ring.[13] No such isomerism is detected in **7a**−**c**. However, these complexes do show fluxionality of the $C_6F_5$ ligands, as shown by variable-temperature $^{19}$F NMR spectroscopy. At −60 °C in toluene-$d_8$, the *o*-F atoms of the Zr-$C_6F_5$ ring of **7a** are observed at relatively high frequencies, $\delta$ −109.2 and −120.8, thus indicating hindered rotation, presumably due to a steric interaction with the cyclopentadienyl ring. The *o*-F atoms of one of the boryl-$C_6F_5$ rings are also inequivalent, with resonances at $\delta$ −131.0 and −172.3. The high-field shift of the latter is consistent with coordination to zirconium.[12] By contrast, the second boryl-$C_6F_5$ ring rotates freely at this temperature, as shown by single *o*-F resonance at $\delta$ −130.3. Warming the solution from −60 °C to 20 °C results in the broadening, coalescence, and sharpening of the *o*-F signals. The signals for the Zr-$C_6F_5$ ligand coalesce at −20 °C and eventually form one sharp peak at $\delta$ −115.6. The process is slower for the coordinated B-$C_6F_5$ substituent, where coalescence occurs at 0 °C. Further warming to 20 °C gives a sharp peak at $\delta$ −159.3. This fluxionality could not be studied at higher temperatures due the thermal instability of the complex. **7b** and **7c** exhibit very similar $^{19}$F NMR spectra across the range of temperatures investigated.

Over the course of 48 h the signals associated with the boryl-diene complexes **7** are gradually replaced by those of a new type of product, identified as the triple-

---

(11) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G. A.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1.

(12) Corradi, M. M.; Jiménez Pindado, G. J.; Sarsfield, M. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1150.

(13) Jiménez Pindado, G.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115.

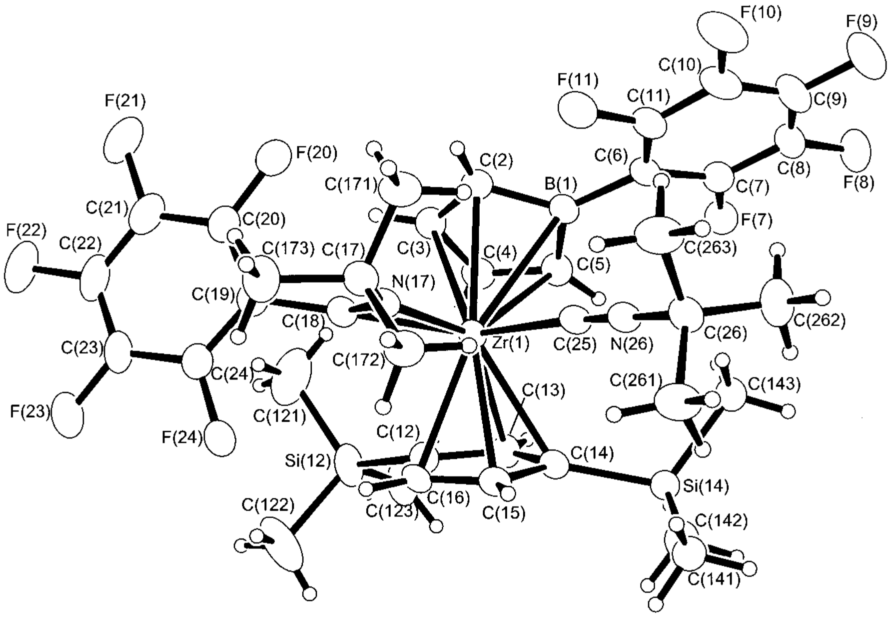


**Figure 2.** Structure of one of the two independent molecules in the unit cell of Cp″Zr($\eta^2$-$C_6F_5CN$*t*Bu)($\eta^5$-$C_4H_4BC_6F_5$), **5H**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

**Table 4. Selected Distances (Å) and Angles (deg) for 5H**

| molecule 1 | | molecule 2 | |
|---|---|---|---|
| Zr(1)−N(17) | 2.279(4) | Zr(2)−N(43) | 2.266(4) |
| Zr(1)−B(1) | 2.664(5) | Zr(2)−B(27) | 2.687(5) |
| Zr(1)−C(18) | 2.252(4) | Zr(2)−C(44) | 2.264(4) |
| N(17)−C(18) | 1.260(6) | N(43)−C(44) | 1.264(6) |
| Zr(1)−C(2) | 2.527(4) | Zr(2)−C(28) | 2.517(4) |
| Zr(1)−C(3) | 2.449(4) | Zr(2)−C(29) | 2.429(5) |
| Zr(1)−C(4) | 2.430(5) | Zr(2)−C(30) | 2.451(4) |
| Zr(1)−C(5) | 2.513(4) | Zr(2)−C(31) | 2.547(4) |
| Zr(1)−C(12) | 2.555(5) | Zr(2)−C(38) | 2.573(4) |
| Zr(1)−C(13) | 2.543(4) | Zr(2)−C(39) | 2.539(4) |
| Zr(1)−C(14) | 2.562(4) | Zr(2)−C(40) | 2.545(4) |
| Zr(1)−C(15) | 2.528(4) | Zr(2)−C(41) | 2.540(4) |
| Zr(1)−C(16) | 2.548(4) | Zr(2)−C(42) | 2.536(4) |
| Zr(1)−C(25) | 2.362(4) | Zr(2)−C(51) | 2.364(4) |
| C(25)−N(26) | 1.150(5) | C(51)−N(52) | 1.140(6) |
| Zr(1)−N(17)−C(18) | 72.7(3) | Zr(2)−N(43)−C(44) | 73.7(3) |
| Zr(1)−C(18)−N(17) | 75.0(3) | Zr(2)−C(44)−N(43) | 73.9(3) |
| Zr(1)−N(17)−C(17) | 154.5(3) | Zr(2)−N(43)−C(43) | 154.0(3) |
| Zr(1)−C(18)−C(19) | 154.2(3) | Zr(2)−C(44)−C(45) | 155.8(3) |
| N(17)−Zr(1)−C(18) | 32.23(14) | N(43)−Zr(2)−C(44) | 32.41(14) |
| N(17)−Zr(1)−C(25) | 81.36(14) | N(43)−Zr(2)−C(51) | 82.24(16) |
| C(18)−Zr(1)−C(25) | 113.63(16) | C(44)−Zr(2)−C(51) | 114.63(17) |
| Zr(1)−C(25)−N(26) | 173.8(3) | Zr(2)−C(51)−N(52) | 175.8(4) |
| C(25)−N(26)−C(26) | 177.5(4) | C(51)−N(52)−C(52) | 178.2(7) |

decker complexes $Zr_2(Cp^R)_2(C_6F_5)_2\{\mu$-$\eta^5$:$\eta^5$-$C_4H_4BCH_2$-$\eta^3$,$\kappa F$-$CHCHCHB(C_6F_5)_3\}$ (**8a**−**d**) (Scheme 3). The conversion is essentially quantitative, with no evidence for any other products, such as the mononuclear borole complex **1H** produced from Cp″Zr($C_6F_5$){$\eta^4$-$CH_2CHCHCHB(C_6F_5)_2$}.[4] Compounds **8a**−**d** were prepared in one-pot reactions from the diene complexes **6a**−**d** and $B(C_6F_5)_3$ in toluene as red to orange solids in good yields.

Compounds **8a** and **8d** show high solubility in most hydrocarbon solvents and ether, while **8b** and **8c** are less soluble. **8b** was obtained pure by recrystallization of the crude reaction product from benzene. A pure sample of **8c** was obtained by stirring an ether solution for 1 h, during which time **8c** precipitated as an orange solid. It seems that the complexes retain toluene to some degree after solvent removal. Once this toluene is removed completely, the complexes become much less soluble, and 1,2-difluorobenzene had to be used to obtain sufficiently concentrated solutions for NMR spectroscopy on **8b** and **8c**.

The spectra of all four complexes are highly distinctive. The $^{11}B$ NMR spectra of **8a**−**d** show sharp signals at $\delta$ −12 to −13 for the butenyl-$B(C_6F_5)_3$ borate and a broad signal around $\delta$ 0−3 corresponding to the borole ligand. The $^{19}F$ NMR spectra for all three complexes show a signal in the region $\delta$ −215 to −225, which is indicative of the coordination of one of the *ortho*-F atoms of the butenyl-$B(C_6F_5)_3$ moiety to the metal center. Erker and co-workers previously found a similar $^{19}F$ NMR chemical shift in the related complex $Cp_2Zr\{\eta^3$-$CH_2CHCHCH_2B(C_6F_5)_3\}$ ($\delta$ −213.2).[14] However, in that case exchange of *o*-F atoms was slow only at −80 °C, with a coalescence temperature well below 0 °C, indicative of a rather weak Zr···F interaction ($\Delta G^{\ddagger} = 8.1$ kcal $mol^{-1}$), whereas **8a**−**d** show well-resolved *o*-F signals even at room temperature. Variable-temperature $^{19}F$ NMR spectroscopy on **8d** shows that the signals for the *o*-F broaden and eventually coalesce at 68 °C ($\Delta G^{\ddagger} = 13.2$ kcal $mol^{-1}$),[15] although the spectrum is further complicated by the coalescence of the *o*-F signals for the other two $C_6F_5$ groups of the $B(C_6F_5)_3$ unit. Above this temperature all three $C_6F_5$ groups are exchanging fast enough to be indistinguishable on the NMR time scale. Structural characterization of **8d**[5] revealed an unusually short Zr−F distance of 2.355(3) Å when compared to related species with Zr···F coordination, for example, $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu$-$Cl)Cl_2]_2$ [2.430(2) Å],[16] ($C_5Me_5$)Zr($C_6F_5$){$\eta^4$-$C_4H_5B(C_6F_5)_2$} [2.4292(15) Å],[17] and $Cp_2Zr\{\eta^3$-$C_4H_6B(C_6F_5)_3\}$[2.423(3) Å].[14] Since the

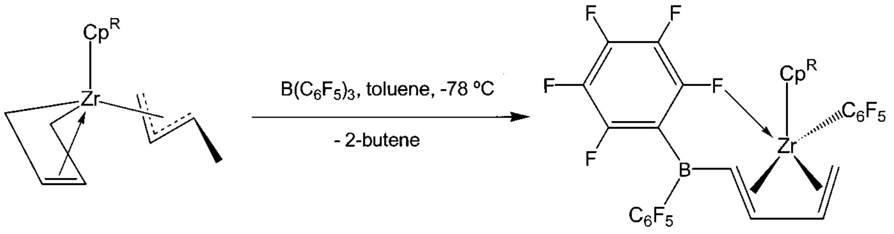
---

(14) (a) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (b) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

(15) $\Delta G^{\ddagger}$ was calculated as follows. $\Delta G^{\ddagger} = 4.57\ T_c(10.32 + \log T_c - \log k_c)$ cal $mol^{-1}$ where $T_c$ = coalescence temperature, $k_c = \pi\Delta\upsilon/\sqrt{2}$, $\Delta\upsilon$ = peak separation in $^{19}F$ NMR at $T_c$.

(16) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829.

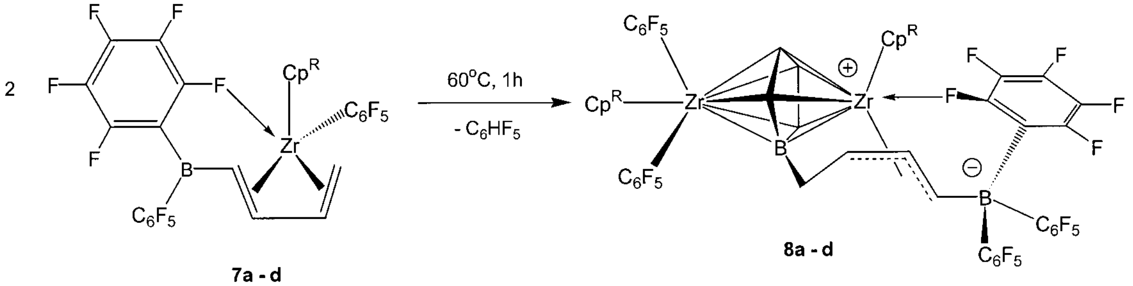
**Scheme 2**



**6a**, $Cp^R = C_5H_4SiMe_3$
**6b**, $Cp^R = C_5H_4Me$
**6c**, $Cp^R = C_5H_5$
**6d**, $Cp^R = 1,3\text{-}C_5H_3(SiMe_3)_2$

**7a - d**

**Scheme 3**



**7a - d**

**8a - d**

NMR spectra for **8a**−**c** are closely similar to those of **8d**, similarly short interactions are probably present in these complexes, but as yet no structural characterization has been possible. Addition of a few drops of pivalonitrile to a solution of **8d** in toluene-$d_8$ results in the disappearance of the *o*-F resonance at $\delta$ −217, and a broad doublet around $\delta$ −128 corresponding to the six *o*-F atoms of the $-B(C_6F_5)_3$ moiety suggests that all three pentafluorophenyl groups are now equivalent.

The $^1H$ NMR spectra of the *ansa*-butenylborole ligand are closely similar in all four complexes. The four protons of the $C_4H_4B$ ring are found over a large chemical shift range, from around $\delta$ 3 to nearly $\delta$ 8. The butenyl protons exhibit a highly characteristic coupling pattern.

The transformation of **6** into **8** is remarkable. Several other triple-decker complexes featuring a central borole ligand are known;[18−21] however, compounds **8** are the first examples for a group 4 metal. Whereas the formation of the mononuclear borole complex $Cp''Zr(C_6F_5)(OEt_2)\{\eta^5\text{-}(3\text{-}RC_4H_3BC_6F_5)\}$ was specific to Cp″, the triple-decker complexes form readily for a variety of Cp ligands. Apparently the sterically highly hindered Cp″ ligand is needed for the formation of **1**, while the triple-decker compounds **8** are formed in high yield even with unsubstituted cyclopentadienyl derivatives. There was no evidence for the formation of mononuclear borole complexes where $Cp^R = C_5H_4SiMe_3$ or $C_5H_4Me$.

The formation of **8** necessarily involves two molecules of **7**, which react with redistribution of the $C_6F_5$ substituents of the $-B(C_6F_5)_2$ units in **7** to give a borole and a borate. Scheme 4 depicts a plausible sequence including an intermediate showing the required rearrangements involved in the formation of **8**. One $C_6F_5$ substituent is lost as pentafluorobenzene following activation of one terminal C−H bond of a boryldiene ligand in the intermediate **7**. During the course of this sequence attack of a dienyl ligand on the B-$C_6F_5$ moiety of a postulated borole intermediate can be envisaged, with the result that one of the original $B(C_6F_5)_3$ molecules loses all of its $C_6F_5$ substituents to form an alkyl-substituted borole ring. Equally unexpected is the transfer of the Zr-$C_6F_5$ ligand on the second zirconium atom, either to the other Zr center or to the boryl-boron. Evidently the zwitterionic structure **8** is favored over its neutral isomer **8′**, possibly because of efficient stabilization of the former by the Zr···*o*-F coordination.

**Ethene Polymerization.** In a previous communication[4] we reported that solutions of the boryldiene complex $Cp''Zr(C_6F_5)\{CH_2C(Me)CHCHB(C_6F_5)_2\}$ in the presence or absence of $AlMe_3$ showed no catalytic activity toward the polymerization of ethene. However, after an induction period of ca. 10 min at 60 °C under 6 bar ethene pressure and in the presence of $AlMe_3$ the onset of polymerization was noted, and it was found that the activity increased slowly with time. This behavior, indicative of the slow buildup of a catalytically active species, was rationalized as the formation of a mononuclear borole-containing species, i.e., **1Me**. Solutions of **1Me** with either $AlMe_3$ or MAO in ratios from 1:15 to 1:40 indeed showed good catalytic activity without an induction period. However, the facile isolation of the triple-decker complexes **8** from the boryldiene complexes **7** led us to question the true identity of the active species in the previous chemistry.

Mixtures of **8d** with $AlMe_3$ (Al:Zr = 30:1) at 25 and 60 °C under 1 bar ethene failed to produce any polymerization. An NMR experiment showed that mixtures of **8d** and $AlMe_3$ in toluene-$d_8$ do not react, in contrast

---

(17) Jiménez Pindado, G.; Thornton-Pett, M.; Bowkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem.* **1997**, *109*, 2457; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358.

(18) Herberich, G. E.; Hessner, B.; Saive, R. *J. Organomet. Chem.* **1987**, *319*, 9.

(19) Herberich, G. E.; Hengesbach, J.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1983**, *116*, 141.

(20) Herberich, G. E.; Hessner, B.; Howard, J. A. K.; Köffer, D. P. J.; Saive, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 165.

(21) Herberich, G. E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 433.

**Scheme 4**

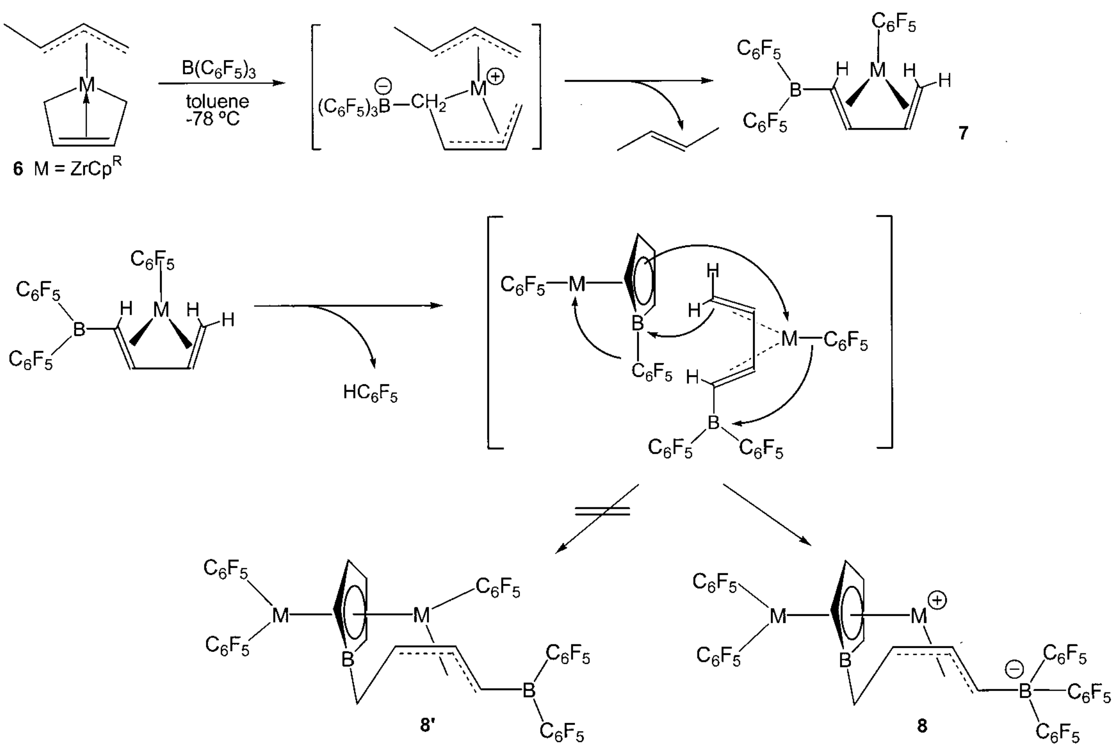


**Table 5. Ethene Polymerizations with Triple-Decker Complexes (8a–d)**[a]

| catalyst precursor | activator | $T$ [°C] | $t$ [min] | Zr [$\mu$mol] | Al/Zr ratio | polymer yield [g] | productivity [$10^3$ g PE (mol M)$^{-1}$ h$^{-1}$ bar$^{-1}$] | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| **8d** | $AlMe_3$ | 25 | 15 | 8.8 | 30 | 0 | | | |
| **8d** | $AlMe_3$ | 60 | 20 | 8.8 | 30 | 0 | | | |
| **8d** | MAO | 60 | 20 | 32.3 | 77.4 | 0.156 | 14.5 | 195 000 | 14 |
| **8d** | MAO | 60 | 20 | 9.7 | 774 | 0.093 | 28.9 | 244 000 | 9.4 |
| **8a** | MAO | 60 | 5 | 25 | 100 | 0.236 | 113 | 101 000 | 8.0 |
| **8a** | MAO | 60 | 5 | 5 | 500 | 0.241 | 577 | 578 000 | 7.4 |
| **8b** | MAO | 60 | 5 | 20 | 100 | 0.308 | 185 | 260 000 | 5.3 |
| **8b** | MAO | 60 | 5 | 20 | 500 | 0.408 | 245 | 198 000 | 3.8 |
| **8b** | MAO | 60 | 5 | 5 | 500 | 0.221 | 531 | 381 000 | 3.5 |
| **8c** | MAO | 60 | 10 | 20 | 500 | 0.425 | 120 | 216 000 | 4.4 |
| **8c** | MAO | 60 | 10 | 5 | 500 | 0.041 | 49.2 | 278 000 | 4.8 |

[a] 40 mL of toluene, ethene 1 bar.

to mixtures of **1Me** and $AlMe_3$, where Zr-$C_6F_5$/Me exchange takes place readily.[4] However, when **8d** was activated with MAO in Al:Zr ratios of 77:1: and 770:1, some polymer was produced, although the activities were modest ((1–2) × $10^4$ g PE (mol Zr)$^{-1}$ h$^{-1}$ bar$^{-1}$). Polymerization results are collected in Table 5. Solutions of the sterically less hindered compounds **8a** and **8b**, when activated with MAO, gave significantly higher activities (up to ca. 6 × $10^5$ g PE (mol M)$^{-1}$ h$^{-1}$ bar$^{-1}$), while the activity of **8c** is slightly less. The molecular weight distributions are quite broad, particularly so for **8a** and **8d**. This may be due in part to a lack of premixing of the catalyst and activator and thus failure to achieve uniform activation. It is also noted that the molecular weights tend to increase with decreasing catalyst concentration, a feature suggestive of mass transport limitation under the low-pressure conditions employed.

## Conclusion

The Zr-$C_6F_5$ ligand in borole pentafluorophenyl complexes of type **1** is reactive toward alkylating agents, while nitriles and isocyanides readily form adducts. The latter react further with insertion into the Zr–$C_6F_5$ bond to give $\eta^2$-iminoacyl compounds. A variation of the synthetic route leading to **1** provides surprisingly simple access to borole-bridged triple-decker complexes **8**, either by thermal decomposition of boryldiene complexes **7** or directly by treatment of the diene complexes **6** with $B(C_6F_5)_3$. Whereas the formation of **1** was observed only in the case of bulky cyclopentadienyl ligands such as 1,3-$C_5H_3(SiMe_3)_2$, the formation of **8** proved to be quite general and independent of the steric requirements of the Cp ligands. The complexes are zwitterionic and stabilized by remarkably strong Zr···F interactions (ca. 13.2 kcal mol$^{-1}$). Although $B(C_6F_5)_3$ is a widely used and generally very stable catalyst activator,[22] the formation of **8** underlines the very facile $C_6F_5$ transfer from $B(C_6F_5)_3$ to zirconium that is possible under certain conditions. The chemistry of half-sandwich complexes such as the zirconium diene compounds employed in this study is in stark contrast to the behavior of bis-

---

[22] Reviews: Luo, L.; Marks, T. J. *Top. Catal.* **1999**, *7*, 97. Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(cyclopentadienyl)zirconium complexes, where such facile rearrangements are not observed. Since $C_6F_5$ transfer reactions are usually associated with the deactivation of $B(C_6F_5)_3$-activated catalysts, the observed reaction sequence may shed some light on the varied deactivation pathways that are possible in some catalytic systems and may help to explain the differences in stability and lifetime between half-sandwich and metallocene catalysts.

The triple-decker compounds **8**, when activated with MAO, polymerize ethene but react only slowly with $AlMe_3$. This is in contrast to the behavior of mononuclear borole complexes **1**, which were shown earlier to possess good catalytic activity without an induction period.[4] It is concluded that the triple-decker complexes described here are unlikely to be the source of the polymerization activity seen previously. This conclusion is further supported by the fact that Cp″Zr($C_6F_5$){$CH_2C(Me)CHCHB(C_6F_5)_2$} in toluene-$d_8$ at 60 °C converts exclusively into the mononuclear species **1Me**, with no sign for the formation of triple-deckers or any other products.

## Experimental Section

**General Procedures.** All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether, tetrahydrofuran), and sodium−potassium alloy (light petroleum, bp 40−60 °C). Deuterated solvents were stored over 4 Å molecular sieves and degassed by several freeze−thaw cycles. The compounds CpZr(crotyl)(butadiene),[23] Cp″Zr(crotyl)(butadiene) (**6d**),[13] Cp″Zr($C_3H_5$)(isoprene),[13] Cp″Zr($C_6F_5$)($OEt_2$){$\eta^5$-$C_4H_4BC_6F_5$} (**1H**),[4] and Cp″Zr($C_6F_5$)($OEt_2$){$\eta^5$-(3-$MeC_4H_3BC_6F_5$)} (**1Me**)[4] were prepared according to published procedures. *tert*-Butylisocyanide and pivalonitrile were used as purchased. NMR spectra were recorded on a Bruker DPX300 spectrometer. $^1H$ NMR spectra are referenced to residual solvent protons, $^{19}F$ (282.2 MHz) is relative to $CFCl_3$, and $^{11}B$ (96.2 MHz) is relative to $BF_3{\cdot}OEt_2$.

**Cp″Zr($C_6F_5$)(NCMe){$\eta^5$-$C_4H_4BC_6F_5$} (2H).** A solution of **1H** (0.58 g, 0.75 mmol) in toluene (40 mL) at 0 °C was treated with acetonitrile (0.3 mL, 0.23 g, 5.70 mmol). The initial red solution rapidly became deep purple. The reaction was left to stir at room temperature for 30 min. Removal of the volatiles in vacuo and subsequent washing of the residue with light petroleum (2 × 10 mL) provided the title compound as a deep purple solid, yield 0.42 g (75.8%). Anal. Calcd for $C_{32}H_{34}BF_{10}NSi_2Zr$: C, 47.15; H, 3.82; N, 1.90. Found: C, 47.26; H, 3.81; N, 1.70. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 32.2.

**Cp″Zr($C_6F_5$)(NC*t*Bu){$\eta^5$-$C_4H_4BC_6F_5$} (3H).** Following the procedure given for **2H**, compound **3H** was made from **1H** (1.03 g, 1.33 mmol) and pivalonitrile (0.4 mL, 0.30 g, 3.64 mmol) as a deep purple solid, yield 0.79 g (75.8%). Anal. Calcd for $C_{32}H_{34}BF_{10}NSi_2Zr{\cdot}0.25C_7H_8$: C, 50.43; H, 4.51; N, 1.74. Found: C, 50.20; H, 4.46; N, 1.56. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 32.4. Single crystals were obtained from benzene-$d_6$ solution at room temperature; they contained 1.5 molecules of benzene-$d_6$ per molecule of **3H**.

**Cp″Zr($C_6F_5$)(NC*t*Bu){$\eta^5$-(3-$MeC_4H_3BC_6F_5$)} (3Me).** Following the procedure given for **2H**, the compound was made from **1Me** (0.430 g, 0.55 mmol) and pivalonitrile (0.10 mL, 0.05 g, 0.60 mmol) as a deep blue solid, yield 0.312 g (71.8%). Anal. Calcd for $C_{33}H_{36}BF_{10}NSi_2Zr$: C, 49.87; H, 4.57; N, 1.76. Found: C, 49.48; H, 4.48; N, 1.62. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 31.7.

**Generation of Cp″Zr($C_6F_5$)(CN*t*Bu)$_2${$\eta^5$-$C_4H_4BC_6F_5$} (4H).** This compound was not isolated but characterized spectroscopically. To a solution of **1H** (0.03 g, 0.04 mmol) in $C_7D_8$ (0.5 mL) at −20 °C was added *tert*-butylisocyanide (0.05 mL, 0.37 g, 0.44 mmol). The red solution rapidly became yellow and contained **4H** in essentially 100% yield. After 1 h at room temperature the color had changed to golden, and the solution contained **5H** with only traces of **4H**. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 28.8.

**Generation of Cp″Zr($C_6F_5$)(CN*t*Bu)$_2${$\eta^5$-(3-$MeC_4H_3BC_6F_5$)} (4Me).** This compound was not isolated but characterized spectroscopically. To a solution of **1Me** (0.03 g, 0.04 mmol) in $C_7D_8$ (0.5 mL) at −20 °C was added *tert*-butylisocyanide (0.05 mL, 0.37 g, 0.44 mmol). The red-brown solution rapidly became yellow. The NMR spectrum showed that conversion to **4Me** was essentially complete. After 1 h at room temperature the color had changed to golden, and the solution contained **5Me** with only traces of **4Me**. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 25.5.

**Cp″Zr{$\eta^2$-($C_6F_5$CN*t*Bu)}(CN*t*Bu){$\eta^5$-$C_4H_4BC_6F_5$} (5H).** A solution of **1H** (1.11 g, 1.44 mmol) in toluene (50 mL) at −78 °C was treated with *tert*-butylisocyanide (0.50 mL, 0.37 g, 4.42 mmol). The initial purple-red solution rapidly became yellow-orange. The reaction was allowed to reach room temperature and stirred for 16 h, at which time the color was golden yellow. Removal of volatiles left a yellow solid, which was extracted into light petroleum (60 mL). Concentrating to ca. 15 mL and cooling to −20 °C provided the title compound as a yellow crystalline solid, yield 0.96 g (77.2%). Anal. Calcd for $C_{37}H_{43}BF_{10}N_2Si_2Zr{\cdot}0.5C_6H_{14}$: C, 52.97; H, 5.56; N, 3.09. Found: C, 53.04; H, 5.49; N, 3.06. $^{11}B\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 26.8. Single crystals were obtained from petroleum ether at −20 °C.

**Cp″Zr($\eta^2$-$C_6F_5$CN*t*Bu)(CN*t*Bu){$\eta^5$-(3-$MeC_4H_3BC_6F_5$)} (5Me).** Following the procedure given for **5H**, the compound was made from **1Me** (0.250 g, 0.33 mmol) and *tert*-butylisocyanide (0.5 mL, 0.37 g, 4.42 mmol) as a yellow microcrystalline solid. NMR showed the presence of a major and minor diastereomer; only the major isomer was fully characterized. Yield: 0.138 g (49.2%). Anal. Calcd for $C_{38}H_{45}BF_{10}N_2ZrSi_2$: C, 51.99; H, 5.17; N, 3.19. Found: C, 52.42; H, 5.22; N, 3.11.

**Cp′Zr($\eta^3$-$C_4H_7$)($\eta^4$-butadiene) (6a).** The complex was made following the procedure given for CpZr($C_4H_7$)($C_4H_6$).[20] A solution of Cp′$ZrCl_3$(dme) (4.31 g, 10.14 mmol) dissolved in tetrahydrofuran (100 mL) at 0 °C was treated with a solution of crotylmagnesium chloride (90 mL, 0.35 M in thf, 31.5 mmol). The reaction was allowed to warm to room temperature and stirred for 16 h. The color changed from pale yellow to deep maroon over the course of the reaction, and there was some evolution of gas. After removal of volatiles in vacuo the solid residue was extracted with light petroleum (2 × 50 mL). Concentration and cooling to −20 °C overnight afforded the title compound as a red microcrystalline solid, yield 3.03 g (88.5%). Anal. Calcd for $C_{16}H_{26}SiZr$: C, 56.91; H, 7.76. Found: C, 56.36; H, 7.27.

**Cp$^{Me}$Zr($\eta^3$-$C_4H_7$)($\eta^4$-butadiene) (6b).** Following the method described for **6a**, **6b** was prepared as a maroon solid in 77.6% yield. Anal. Calcd for $C_{14}H_{20}Zr$: C, 60.16; H, 7.21. Found: C, 59.57; H, 7.01.

**Generation of Cp′Zr($C_6F_5$){$CH_2CHCHCHB(C_6F_5)_2$} (7a).** To a solution of **6a** (0.030 g, 0.089 mmol) in $C_7D_8$ (0.3 mL) was added at room temperature a solution of $B(C_6F_5)_3$ (0.045 g, 0.088 mmol) in $C_7D_8$ (0.3 mL). The color immediately became dark red. The mixture contained **7a** and butene. $^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): $\delta$ 44.6 (vbr). After 48 h at room temperature the solution contained mainly **8a**.

**Generation of Cp$^R$Zr($C_6F_5$){$CH_2CHCHCHB(C_6F_5)_2$} (7b, Cp$^R$ = Cp$^{Me}$; 7c, Cp$^R$ = Cp).** Following the procedure for **7a**, **7b** and **7c** were similarly generated and characterized in solution.

$^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): **7b**: $\delta$ 43.6 (vbr). **7c**: $\delta$ 43.5 (vbr).

---

(23) Blenkers, J.; de Liefde Meijer, H. J.; Teuben, H. J. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 216. Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383.

**$Zr_2Cp'_2(C_6F_5)_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$ (8a).** A solution of **6a** (0.98 g, 2.90 mmol) in toluene (100 mL) at −78 °C was treated with a cold (−78 °C) solution of B(C$_6$F$_5$)$_3$ (1.53 g, 2.99 mmol) in toluene (100 mL). The mixture immediately turned orange. Warming to room temperature over 2 h gave a deep red solution. The volatiles were removed in vacuo, and toluene (100 mL) was introduced. The mixture was then stirred at room temperature for 2 days, during which time an orange color developed. After removal of the solvent the orange residue was extracted with light petroleum (2 × 100 mL) and the filtrate concentrated and cooled to −20 °C to afford the title compound as an orange microcrystalline solid, yield 1.63 g (80.1%). Anal. Calcd for $C_{54}H_{35}B_2F_{25}Zr_2Si_2$: C, 45.71; H, 2.49. Found: C, 45.13; H, 3.20. $^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): $\delta$ 1.5 (vbr) ($C_4H_4B$), −13.0 (−CHB(C$_6$F$_5$)$_3$).

**$Zr_2Cp^{Me}{}_2(C_6F_5)_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$ (8b).** A solution of **6b** (0.37 g, 1.33 mmol) in toluene (50 mL) at −78 °C was treated with a solution of B(C$_6$F$_5$)$_3$ (0.72 g, 1.41 mmol) in toluene (100 mL) also at −78 °C. On warming to room temperature under a static vacuum over 2 h the orange mixture turned deep red. The volatiles were removed in vacuo, and toluene (100 mL) was introduced. The reaction was now stirred at room temperature for 2 days, during which time an orange color developed. The volatiles were removed in vacuo, and the residue was extracted with ether (100 mL). Removal of the volatiles in vacuo and washing with light petroleum (2 × 40 mL) provided **8b**, yield 0.67 g (77.3%). Anal. Calcd for $C_{50}H_{23}B_2F_{25}Zr_2$: C, 46.10; H, 1.78. Found: C, 46.51; H, 2.06. $^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): $\delta$ 1.0 (vbr) ($C_4H_4B$), −13.1 (−CHB(C$_6$F$_5$)$_3$).

**$Zr_2Cp_2(C_6F_5)_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$ (8c).** Following the procedure for **8b**, the compound was made from **6c** (1.24 g, 4.67 mmol) and B(C$_6$F$_5$)$_3$ (2.43 g, 4.76 mmol) as an orange microcrystalline precipitate, yield 2.17 g (72.9%). Anal. Calcd for $C_{48}H_{19}B_2F_{25}Zr_2$: C, 45.23; H, 1.50. Found: C, 44.78; H, 1.81. $^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): $\delta$ 1.5 (vbr) ($C_4H_4B$), −13.0 (−CHB(C$_6$F$_5$)$_3$).

**$Zr_2Cp''_2(C_6F_5)_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BCH_2\text{-}\eta^3,\kappa F\text{-}CHCHCHB(C_6F_5)_3\}$ (8d).** A solution of Cp″Zr(C$_4$H$_7$)(C$_4$H$_6$) (1.63 g, 3.98 mmol) in toluene (30 mL) at −78 °C was treated with a solution of B(C$_6$F$_5$)$_3$ (1.98 g, 3.87 mmol) also at −78 °C. The reaction was maintained at this temperature for 30 min and then was allowed to reach room temperature. The volatiles were removed in vacuo, toluene (40 mL) was introduced, and the reaction was stirred at 50 °C for 2 h. Removal of the solvent in vacuo provided a brown foam, which was extracted with diethyl ether (50 mL). Concentration of this red solution to ca. 10 mL and cooling to −20 °C overnight provided **8d** as red crystals, yield 2.56 g (82.3%). Anal. Calcd for $C_{60}H_{51}B_2F_{25}Si_4Zr_2$: C, 46.10; H, 3.29. Found: C, 45.36; H, 3.28. $^{11}B\{^1H\}$ NMR ($C_7D_8$, 20 °C): $\delta$ 3.0 (vbr) ($C_4H_4B$), −12.8 (−CHB(C$_6$F$_5$)$_3$).

**General Procedure for Ethene Polymerization.** A magnetically stirred 50 mL reactor was flame-dried in vacuo prior to being charged with 40 mL of dry and degassed toluene. The solvent was equilibrated at the desired polymerization temperature and saturated with ethene (1 bar). Aliquots of a toluene solution of the aluminum alkyl activator were injected, followed by a solution of the zirconium complex in toluene. The pressure was maintained at 1 bar throughout. The reaction was terminated by the injection of 2 mL of methanol. The polymer was precipitated with acidified methanol, washed with methanol, and dried at 60−80 °C for 24 h.

**X-ray Crystallography. 3H.** A suitable crystal was coated in an Nujol oil and mounted in a nitrogen stream at 140 K on a Rigaku R-Axis II image plate diffractometer equipped with a rotating anode X-ray source (Mo Kα radiation) and graphite monochromator. Using 4° oscillations, 46 exposures of 28 min each were made. Data were processed using the DENZO/SCALEPACK programs.[23] The structure was determined by the direct methods routines in the SHELXS program[24] and refined by full-matrix least-squares methods (on $F^2$) in SHELXL.[25] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were constrained to idealized positions. Crystal data of **3H**: $C_{32}H_{34}BF_{10}NSi_2Zr\cdot 1.5(C_6D_6)$, fw 898.0; monoclinic, $P2_1/c$; $a = 11.853(1)$ Å, $b = 28.977(1)$ Å, $c = 12.983(3)$ Å; $\alpha = 90°$, $\beta = 106.25(1)°$, $\gamma = 90°$; $U = 4281.1(11)$ Å$^3$; $Z = 4$; $D_{calc} = 1.393$ Mg/m$^3$; $\mu = 0.386$ mm$^{-1}$; $F(000) = 1836$; $2.16° \le \theta \le 25.50°$; $-14 \le h \le 14$, $-33 \le k \le 32$, $-15 \le l \le 15$; 14 745 reflections collected, of which 7608 were independent [$R_{int} = 0.0310$] and 5789 observed [$I > 2\sigma(I)$]; data/parameters 7608/505; goodness of fit = 1.039; final $R$ indices [$I > 2\sigma(I)$] $R_1 = 0.037$, $wR_2 = 0.090$; $R$ indices (all data) $R_1 = 0.054$, $wR_2 = 0.097$.

**5H.** A suitable crystal was coated in inert perfluoropolyether oil and mounted in a nitrogen stream at 150 K on a Nonius Kappa CCD area-detector diffractometer. Data collection was performed using Mo Kα radiation ($\lambda = 0.71073$ Å) with the CCD detector placed 30 mm from the sample via a mixture of 1° $\phi$ and $\omega$ scans at different $\theta$ and $\kappa$ settings using the program COLLECT.[26] The raw data were processed to produce conventional data using the program DENZO-SMN.[23] The dataset was corrected for absorption using the program SORTAV.[27] The structure was solved by heavy-atom methods using SHELXS-97[24] and refined by full-matrix least-squares refinement (on $F^2$) using SHELXL-97.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized positions. Crystal data of **5H**: $C_{37}H_{43}BF_{10}N_2Si_2Zr$, fw 863.94; triclinic, $P\bar{1}$; $a = 11.3671(2)$ Å, $b = 15.9864(3)$ Å, $c = 25.3180(5)$ Å; $\alpha = 79.6120(10)°$, $\beta = 86.3340(10)°$, $\gamma = 75.1260(10)°$; $U = 4372.97(14)$ Å$^3$; $Z = 4$; $D_{calc} = 1.312$ Mg/m$^3$; $\mu = 0.375$ mm$^{-1}$; $F(000) = 1768$; $3.43° \le \theta \le 26°$; $-14 \le h \le 14$, $-19 \le k \le 19$, $-27 \le l \le 31$; 42 596 reflections collected, of which 16 775 were independent [$R_{int} = 0.097$] and 11 825 observed [$I > 2\sigma(I)$]; data/parameters 16775/979; goodness of fit = 1.032; final $R$ indices [$I > 2\sigma(I)$] $R_1 = 0.0656$, $wR_2 = 0.1603$; $R$ indices (all data) $R_1 = 0.0962$, $wR_2 = 0.1765$.

**Acknowledgment.** This work was supported by the Engineering and Physical Sciences Research Council.

**Supporting Information Available:** Full listing of crystallographic details for **3H** and **5H**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010348I

---

(24) Otwinowski Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1996; Vol. 276, p 307.

(25) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(26) Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, 1997.

(27) *Collect*, data collection software; Nonius B.V.: Delft, The Netherlands, 1999.

(28) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33