Synthesis, Structural Characterization, and Reactivity of Group 4 Metallacarboranes Containing the Ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$

Yaorong Wang, Dongmei Liu, Hoi-Shan Chan, and Zuowei Xie*

Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Received March 13, 2008

The new inorganic/organic hybrid π ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ was prepared via a selective deboration of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ with piperidine in ethanol. Treatment of its sodium salt with $MCl_4(THF)_2$ gave the mixed-sandwich complexes $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**4**), Hf (**5**)). Complex **4** reacted with C_5H_5Na, KCH_2Ph, or $NaNH(C_6H_3\text{-}2,6\text{-}Pr^i_2)$ to afford $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_2\}$ (**7**), $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**8**), or $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**9**), respectively. Both **7** and **8** were stable, and no NaCl elimination was observed upon heating the toluene solution. In the presence of excess MAO (methylalumoxane), complexes **4**, **5**, and **8** were very active catalysts for ethylene polymerization. All complexes were fully characterized by various spectroscopic techniques and elemental analyses. Some were further confirmed by single-crystal X-ray analyses.

Introduction

Fourteen-electron, d^0 bent metallocene alkyl complexes of the general type $(C_5R_5)_2M(R)^{n+}$ (M = lanthanide, $n = 0$; M = group 4 metals, $n = 1$) have received a great deal of attention, as they exhibit a rich insertion, olefin polymerization, and C−H bond activation chemistry, which is highly sensitive to the structural and electronic properties of the $(C_5R_5)_2M$ fragment.[1,2] The Jordan group reported that the replacement of a uninegative $C_5R_5^-$ ligand of the cationic group 4 metal alkyls $(C_5R_5)_2M(R)^+$ by the isolobal, dinegative dicarbollide ligand ($C_2B_9H_{11}^{2-}$) leads to the formation of a class of neutral mixed-sandwich complexes $(C_5R_5)(C_2B_9H_{11})M(R)$, showing a variety of ligand exchange, insertion, and ligand C−H activation characteristics of electrophilic metal alkyls.[3] In view of the differences in chemical and physical properties between $(C_5H_5)_2MCl_2$ and $[Me_2C(C_5H_4)_2]MCl_2$ complexes,[4] we wondered whether an Me_2C linkage could be introduced to the $(C_5R_5)(C_2B_9H_{11})M(R)$ system to link the organic π ligand $C_5R_5^-$ and inorganic π ligand $C_2B_9H_{11}^{2-}$, thus alternating the geometry of the resulting mixed-sandwich complexes so as to change their properties.

It is well-documented that $C_2B_9H_{11}^{2-}$ can be conveniently prepared from deboration of $o\text{-}C_2B_{10}H_{12}$.[5] However, the selective deboration of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$[6] using typical reagents such as MeOH/KOH, MeOH/Na_2CO_3, and MeOH/CsF was unsuccessful. Only $C_2B_9H_{12}^-$ was generated via the cleavage of the $C_{cage}−C_{bridge}$ bond. Such a result may be ascribed to the electron-withdrawing nature of the carboranyl unit, enhancing the electrophilicity of the bridging carbon atom in the ligand which is easily attacked by nucleophiles, resulting in the cleavage of the $C_{cage}−C_{bridge}$ bond. We found, after many attempts, that piperidine/EtOH reagent can selectively remove one BH vertex from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ and leave the $C_{cage}−C_{bridge}$ bond intact. This work reports the synthesis and structural characterization of the new ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ and its group 4 metal complexes.

Results and Discussion

Ligand Synthesis. Treatment of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (**1**) with a large excess amount of piperidine in refluxing ethanol for 2 days gave, after addition of Me_3NHCl, the selective deboration product $[Me_3NH][Me_2C(C_5H_5)(C_2B_9H_{11})]$ (**2**) in 80%

---

* To whom correspondence should be addressed. Fax: (852)26035057. Tel: (852)26096269. E-mail: zxie@cuhk.edu.hk.

(1) For reviews, see: (a) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (b) Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765. (c) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309. (d) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259. (e) Negishi, E.; Montchamp, J.-L. In *Metallocenes-Synthesis, Reactivity, Applications*; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 241.

(2) For reviews, see: (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (b) Arndt, S.; Okuda, J *Chem. Rev.* **2002**, *102*, 1953.

(3) (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (c) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (d) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (e) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508. (f) Bei, X.; Kreuder, C.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17*, 1085. (g) Bei, X.; Young, V. G., Jr.; Jordan, R. F. *Organometallics* **2001**, *20*, 355.

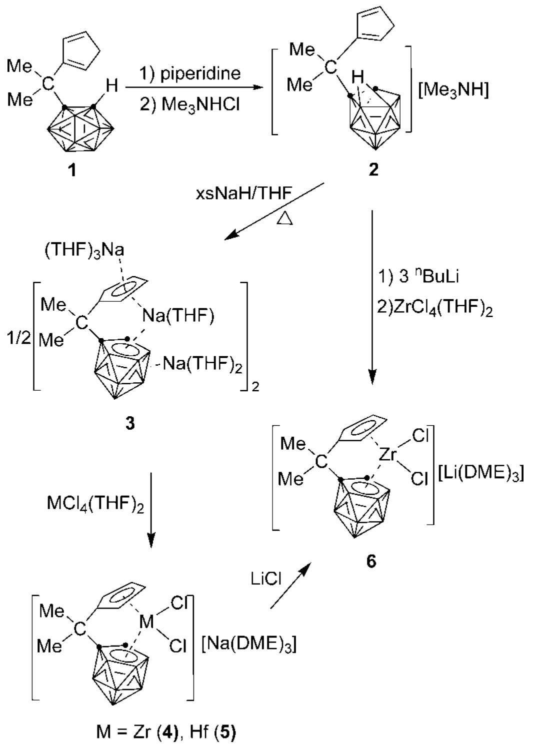
(4) For reviews, see: (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (b) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457. (c) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (d) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85. (e) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (f) Wang, B. *Coord. Chem. Rev.* **2006**, *250*, 242. (g) Hoveyda, A. H.; Morken, J. P. In *Metallocenes-Synthesis, Reactivity, Applications*; Wiley-VCH: Weinheim Germany, 1998,; Vol. 2, p 625. (h) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.

(5) (a) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642. (b) Dunks, G. B.; Hawthorne, M. F. *Acc. Chem. Res.* **1973**, *29*, 124.

(6) (a) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (b) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947. (c) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391. (d) Wang, H.; Wang, Y.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 5110. (e) Wang, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 3772. (f) Wang, Y.; Wang, H.; Wang, H.; Chan, H.-S.; Xie, Z. *J. Organomet. Chem.* **2003**, *683*, 39. (g) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. *Organometallics* **2004**, *23*, 5864. (h) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. *Chem, Commun.* **2004**, 2588. (i) Wang, H.; Wang, Y.; Chan, H.-S.; Xie, Z. *Inorg. Chem.* **2006**, *45*, 5675. (j) Hong, E.; Kim, Y.; Do, Y. *Organometallics* **1998**, *17*, 2933.

10.1021/om800235w CCC: $40.75

Scheme 1



yield (Scheme 1). The reaction was closely monitored by ^{11}B NMR. It is noteworthy that piperidine/EtOH is the best reagent for this reaction after examining many primary, secondary, and tertiary amines in MeOH or EtOH.[7]

The composition of **2** was fully characterized by various spectroscopic techniques and elemental analyses. Its ^{11}B NMR showed a 2:2:1:1:1:1:1 pattern, which differs significantly from that of its parent compound **1**. Both ^{1}H and ^{13}C NMR data suggested that **2** is a mixture of isomers in which the bridging carbon atom bonds to either the sp^3 or sp^2 C of the cyclopentadienyl ring.

Compound **2** was easily converted to its sodium salt $[\{[(\mu\text{-}\eta^5):\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Na(THF)\}\{Na(THF)_3\}\{Na(THF)_2\}]_2$ (**3**) by reacting with an excess amount of NaH in refluxing THF solution (Scheme 1). The ^{1}H NMR showed two multiplets at 6.58 and 6.37 ppm attributable to the cyclopentadienyl ring protons, two singlets at 1.90 and 1.65 ppm corresponding to the Me_2C linkage, and two multiplets of THF molecules. The ^{13}C NMR data were consistent with the above result. Its ^{11}B NMR exhibited a 6:2:1 pattern. Thus, this deprotonation was closely followed by ^{11}B NMR. The molecular structure of **3** was further confirmed by single-crystal X-ray analyses.

There are two crystallographically independent molecules in the unit cell. One of them is shown in Figure 1. It is a centrosymmetric dimer with the inversion center at the midpoint of the Na(1)···Na(1A) connectivity. The Na(2) atom is η^5-bound to both the cyclopentadienyl ring and dicarbollyl ligand and coordinated to one THF molecule to form the structural motif. Two such units are linked to each other via several B−H···Na(1)/B−H···Na(1A) interactions, leading to the formation of a dimeric structure. The average Na(2)/Na(3)−C_{ring} distances of 2.744(1)/2.766(1) Å compare to those of 2.705(4)/2.775(4) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$[8] and 2.736(9) Å in $[(THF)_3Na(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_5)(\eta^2\text{-}PhNHNPh)Sm]_2(\mu\text{-}\eta^2:\eta^3\text{-}N_2Ph_2)_2$.[9] The average Na(2)−cage atom distance of 2.894(1) Å is much longer than that of 2.743(18) Å in $\{Na_2(THF)_4[2,4\text{-}(SiMe_3)_2C_2B_4H_4]\}_2$.[10] The average Na(1)···B distance of 3.006(1) Å is comparable to those of 2.977(9)/3.029(9)/3.015(9) Å in $[\{[\eta^5:\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$,[6c] 3.010(4)/3.019(4) Å in $[\{(\mu\text{-}\eta^5):\eta^7\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})\}Zr(NEt_2)_2\{Na_3(THF)_4\}]_n$,[8] 3.012(6) Å in $[\eta^5\text{-}(Me_3Si)_2C_2B_4H_5]Na(THF)$,[11] and 2.953(6) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{Na(THF)_3\}$.[12] The Cent($C_5$)−Na(2)−Cent($C_2B_3$) angle is 104.1°.

Group 4 Metal Complexes. Reaction of **3** with 1 equiv of $MCl_4(THF)_2$ in THF at room temperature afforded, after recrystallization from a DME solution, the mixed-sandwich complexes $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**4**), Hf (**5**)) in ~70% isolated yields. The yields were much lower using one-port synthesis from **2**. The ^{1}H and ^{13}C NMR spectra of **4** and **5** were very similar. Their ^{11}B NMR spectra were different: **4** showed a 1:1:3:3:1 pattern, whereas **5** exhibited a 1:1:2:1:2:1:1 pattern. Single-crystal X-ray analyses revealed that **4** has an ionic structure, consisting of well-separated, alternating layers of discrete tetrahedral anions $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2]^-$ and octahedral cations $[Na(DME)_3]^+$. In the anion, the Zr atom is η^5-bound to both the cyclopentadienyl ring and dicarbollyl and σ-bound to two terminal chlorine atoms in a distorted-tetrahedral geometry (Figure 2). The Zr−Cent(C_5 ring) distance of 2.188 Å (Table 1) is shorter than that of 2.196 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$ and 2.234 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$.[3a] The average Zr−cage atom distance of 2.528(4) Å is comparable to that of 2.523(5) Å in $[\eta^1:\eta^5\text{-}(Me_2NCH_2)C_2B_9H_{10}]_2Zr$,[13] 2.538(5) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$,[14] 2.499 Å in $(Cp^*)(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$,[3a] 2.535/2.533 Å in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[3a] 2.568(4) Å in $[\eta^1:\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[15] 2.601(5) Å in $[\eta^1:\eta^5\text{-}({}^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[16] and 2.544(6) Å in $[\eta^1:\sigma:\eta^5\text{-}\{MeN(CH_2)CH_2CH_2\}C_2B_9H_{10}]Zr(CH_2SiMe_3)(THF)$.[17] The average Zr−Cl distance of 2.447(1) Å is similar to that

---

[7] (a) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1966**, *99*, 1049. (b) Fussstetter, H.; Nöth, H.; Wrackmeyer, B.; McFarlane, W. *Chem. Ber.* **1977**, *110*, 3172. (c) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun.* **2003**, 1364. (d) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* **2006**, *25*, 2578. (e) Wise, S. D.; Au, W.-S.; Getman, T. D. *Main Group Met. Chem.* **2002**, *25*, 411. (f) Brockman, R.; Challis, K.; Froehner, G.; Getman, T. D. *Main Group Met. Chem.* **2002**, *25*, 629. (g) Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Malget, J. M. *Dalton Trans.* **2001**, 1820. (h) Teixidor, F.; Viñas, C.; Benakki, R.; Kevekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 1719. (i) Laromaine, A.; Teixidor, F.; Kevekäs, R.; Sillanpää, R.; Benakki, R.; Grüner, B.; Viñas, C. *Dalton Trans.* **2005**, 1785. (j) Teixidor, F.; Gómez, S.; Lamrani, M.; Viñas, C.; Sillanpää, R.; Kevekäs, R. *Organometallics* **1997**, *16*, 1278. (k) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 1157.

[8] Wang, Y.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3311.

[9] Yuan, F.; Qian, H.; Min, X. *Inorg. Chem. Commun.* **2006**, *9*, 391.

[10] Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg. Chem.* **1991**, *30*, 3793.

[11] Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001.

[12] Kwong, W.-C.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2004**, *23*, 4301.

[13] Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

[14] Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Han, W.-S.; Cheong, M.; Ko, J.; Kang, S. O. *J. Organomet. Chem.* **2007**, *692*, 5403.

[15] Lee, Y.-J.; Lee, J.-D.; Jeong, H.-J.; Son, K.-C.; Ko, J.; Cheong, M.; Kang, S. O. *Organometallics* **2005**, *24*, 3008.

[16] Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* **2006**, *25*, 2578.

[17] Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 5217.

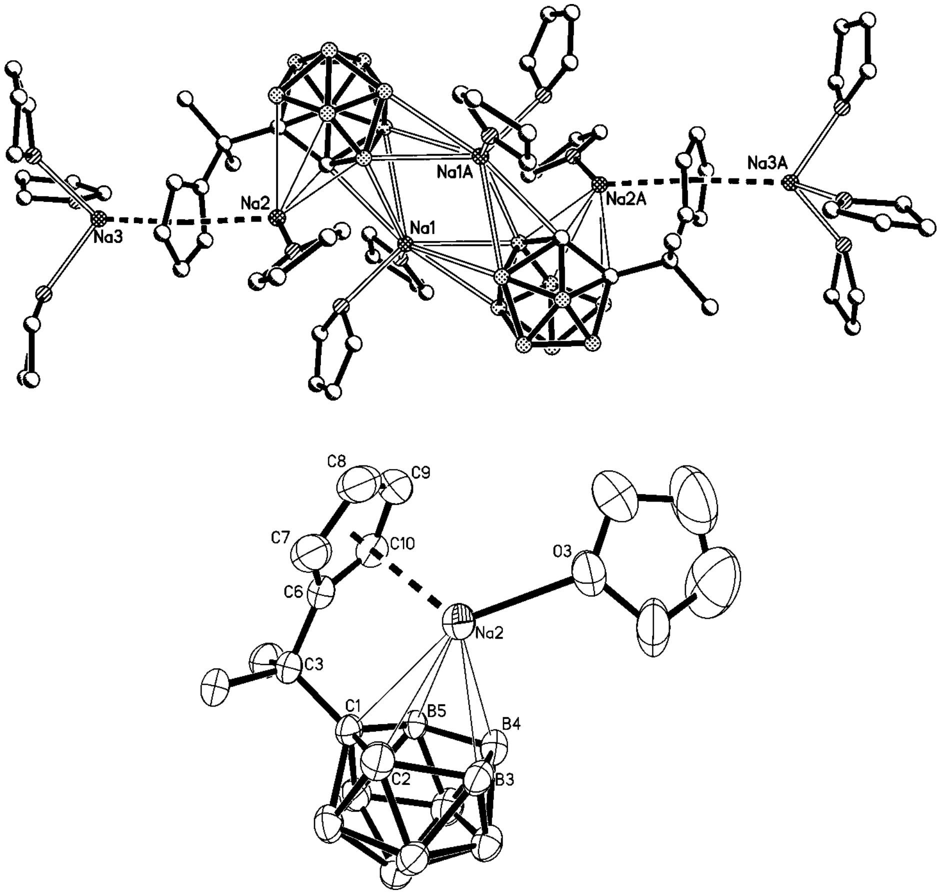


Figure 1. (Top) Molecular structure of $[\{[(\mu\text{-}\eta^5):\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Na(THF)\}\{Na(THF)_3\}\{Na(THF)_2\}]_2$ (**3**). (Bottom) Closer view of the coordination around the Na(2) (thermal ellipsoids drawn at the 30% probability level).

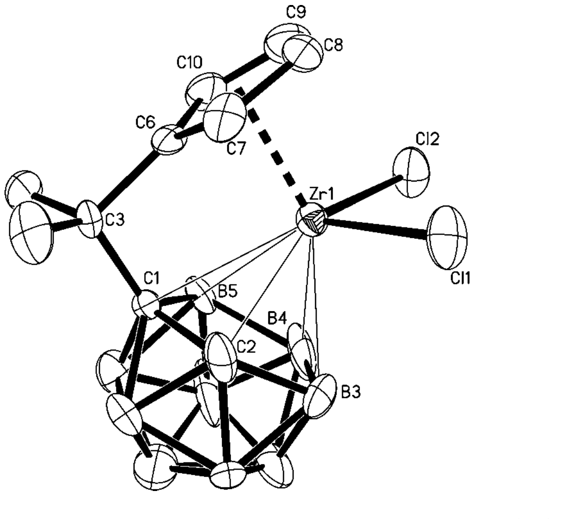


Figure 2. Molecular structure of the anion in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (**4**) (thermal ellipsoids drawn at the 30% probability level).

of 2.414(1) Å in $[\eta^1:\eta^5\text{-}(BzNCH_2)(CH_3)C_2B_9H_{10}]ZrCl_2(THF)$,[15] 2.395(2)/2.388(1) Å in $\{\eta^4:\eta^2\text{-}[(C_6H_5CH_2)_2C_2B_9H_9]_2ZrCl(THF)\}\{M(THF)_x\}$ (M = Na, x = 3; M = Li, x = 4),[12] 2.403(2) Å in $[[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(THF)_4]]$,[18] and 2.436(1) Å in $[Me_2C(C_5H_4)_2]ZrCl_2$.[19] As expected, the Cent(C_5)−Zr−Cent(C_2B_3) angle of 120.5° is significantly smaller than that of 141.3° in $(Cp^*)(C_2B_9H_{11})Zr[C(Me)=CMe_2]$[3a] and 134.9° in $[(Cp^*)(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$,[3a] due to the presence of a short Me_2C linkage, but it is larger than that of 116.7° observed in $[Me_2C(C_5H_4)_2]ZrCl_2$.[19] These data suggest that the open coordination sphere of the Zr atom in **4** is much larger than that of the corresponding unbridged ones. This is probably why the chloride ion can approach the electrophilic Zr center to form the complex anion.

The cation in **4** is exchangeable. Reaction of **4** with 1 equiv of LiCl at room temperature produced, after recrystallization from DME, $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl_2][Li(DME)_3]$ (**6**) in 24% yield. This complex was also prepared in 41% yield from the reaction of $[Me_2C(C_5H_4)(C_2B_9H_{10})]Li_3(THF)_x$ with 1 equiv of $ZrCl_4(THF)_2$ at room temperature. Its spectroscopic data were very similar to those of **4**. X-ray analyses revealed that **6** and **4** are isostructural. The structural parameters of both **6** and **4** are given in Table 1.

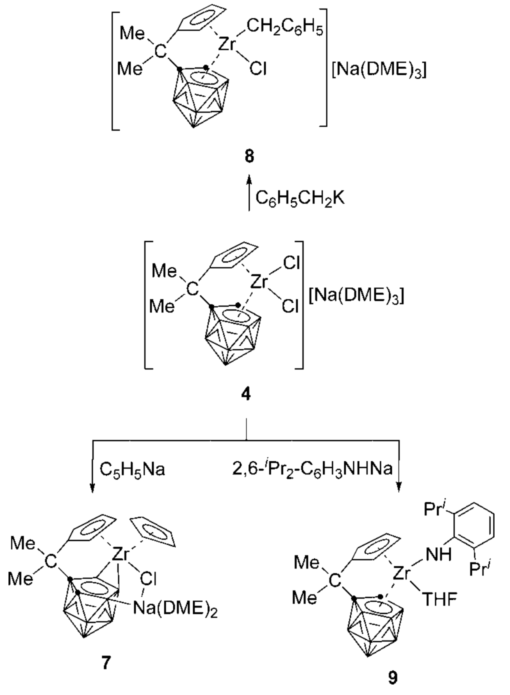
In general, Cp_2ZrCl_2 is an excellent precursor for the preparation of organozirconium alkyls and amides.[20] The chloro group in **4** can also be replaced by other groups. Treatment of **4** with 1 equiv of C_5H_5Na in THF at room temperature afforded, after recrystallization from DME, $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_2\}$ (**7**) in 47% isolated yield (Scheme 2). It is noted that **7** is stable even in refluxing DME, and no elimination of NaCl was observed, suggesting a strong bonding interaction between the Zr center and Cl atom. In addition to the resonances of the bridged ligand, the ^1H NMR spectrum showed a singlet at 6.39 ppm attributable to the Cp protons and two singlets at 3.48 and 3.25 ppm corresponding to DME protons. A pattern of 1:1:1:1:1:2:1:1 was observed in its ^{11}B NMR spectrum. An X-ray diffraction study revealed that the Zr atom in **7** adopts a distorted-tetrahedral geometry by two η^5-cyclopentadienyl rings, one unsymmetrical η^2-dicarbollyl ligand, and one doubly bridging chlorine atom (Figure 3). The

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3, 4, and 6−9

	3^b (M = Na)	**4**^{b} (M = Zr)	**6** (M = Zr)	**7** (M = Zr)	**8** (M = Zr)	**9** (M = Zr)
av M−C_{ring}	2.755(1)	2.531(3)	2.526(6)	2.534(3)2.518(3)	2.523(1)	2.516(3)
av. M−cage atom	2.899(1)	2.528(4)	2.558(7)	2.545(3)	2.573(1)	2.585(3)
av Zr−Cl		2.458(1)	2.596(2)	2.547(1)	2.466(1)	
Zr−N						2.055(2)
Zr−C					2.316(1)	
M−Cent(C_5)^a	2.513	2.219	2.225	2.234	2.221	2.214
M−Cent(C_2B_3)^a	2.540	2.090	2.112		2.132	2.148
Cent(C_5)−M−Cent(C_2B_3)	104.1	120.3	119.3		119.5	119.2
C_{ring}−C_{bridge}−C_{cage}	108.7(1)	102.2(1)	103.0(4)	103.5(2)	103.3(1)	103.3(2)

^{a} Cent(C_5) and Cent(C_2B_9) are the centroids of the cyclopentadienyl ring and the C_2B_3 bonding face, respectively. ^{b} Average values of the two crystallographically independent molecules in the unit cell.

Scheme 2



two average Zr−C(C_5 ring) distances (2.534(3) and 2.518(3) Å) are similar. These measured values are also close to that of 2.531(3) Å in **4**. The average Zr−B distance of 2.545(3) Å is longer than that of 2.485(6) Å in {η^4:η^2-[$(C_6H_5CH_2)_2$-$C_2B_9H_9$]$_2$ZrCl(THF)}{Na$(THF)_3$}.[12] The Zr−Cl distance of 2.547(1) Å is much longer than that of 2.447(1) Å in **4**, 2.394(2) Å in {η^4:η^2-[$(C_6H_5CH_2)_2C_2B_9H_9$]$_2$ZrCl(THF)}{Na$(THF)_3$},[12] 2.461(1) Å in {[η^5-$(Me_3Si)_2C_2B_4H_4$]$_2$ZrCl(THF)}{Li-$(THF)_2$},[21] and 2.469(2) Å in $Cp_2Zr(\mu$-Cl)(μ-$C_2B_{10}H_{10}$)-Li$(OEt_2)_2$.[22] This result clearly indicates that the coordination mode of the dicarbollyl is changed from η^5 in **4** to η^2 in **7**, probably due to steric reasons. It is unexpected that the second chloro atom still bonds to the Zr atom in **7**, suggesting the high Lewis acidity of the metal center.

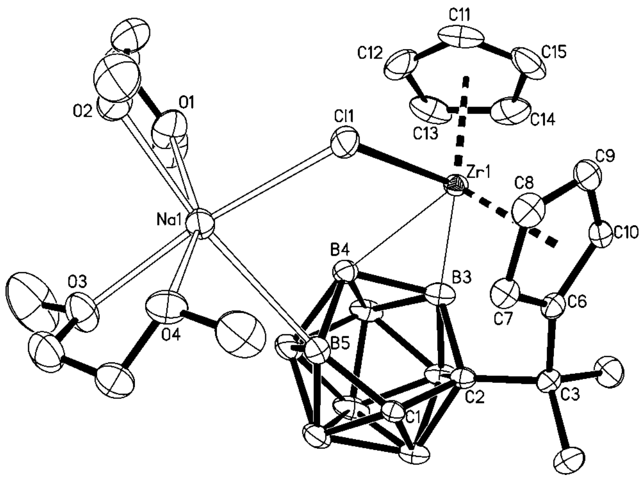


Figure 3. Molecular structure of {[η^5:η^2-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($\eta^5$-$C_5H_4$)($\mu$-Cl){Na$(DME)_2$} (**7**) (thermal ellipsoids drawn at the 30% probability level).

Reaction of **4** with 1 equiv of KCH_2Ph in THF at room temperature produced, after recrystallization from DME, [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}ZrCl$(CH_2C_6H_5)$][Na$(DME)_3$] (**8**) in 36% isolated yield. In addition to the peaks derived from the bridged ligand, three multiplets in the range 7.48−6.92 ppm corresponding to the aromatic protons of the benzyl group, one broad resonance at 2.60 ppm attributable to the CH_2 protons of the benzyl, and two singlets of the DME molecule were observed in the ^{1}H NMR spectrum. Its ^{11}B NMR spectrum showed a 1:1:1:2:1:1:1 pattern. The ionic nature of **8** was confirmed by a single-crystal X-ray diffraction study. The geometry of the anion [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}-ZrCl$(CH_2C_6H_5)$]$^-$ is similar to that found in **4**, with one Cl atom being replaced by a benzyl group (Figure 4). The average Zr−C(C_5 ring)/Zr−Cl distances (2.523(1)/2.466(1) Å) and the Cent(C_5)−Zr−Cent(C_2B_3) angle (119.3°) are similar to the corresponding values (2.531(3)/2.447(1) Å and 120.3°) observed in **4**, whereas the average Zr−cage atom distance of 2.573(1) Å in **8** is longer than that of 2.528(4) Å in **4**. The Zr−C σ bond distance of 2.316(1) Å is much longer than that of 2.233(6) Å in [η^1:σ:η^5-{MeN$(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF),-[17] 2.209(6) Å in [{η^1:σ:η^5-[MeN$(CH_2)CH_2CH_2$]$C_2B_9H_{10}$]}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$,[17] 2.198(4) Å in (Cp*)($C_2B_9H_{11}$)-Zr[C(Me)=CMe_2],[3a] and 2.187(6)/2.176(7) Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2),[3a] but it is comparable to that of 2.294(4) Å in [η^1:σ-^{t}Bu$C_6H_3(PPh_2)O$]Zr$(CH_2Ph)_2$[23] and 2.308(5) Å in [Bu^n(H)C(η^5-C_5Me_4)(η^5-C_5H_4)]Zr$(CH_2Ph)_2$.[24]

The aforementioned results showed that the chloro group always bonds to the Zr atom to stabilize the electron-deficient

---

(18) Wang, H.; Li, H.-W.; Huang, X.; Lin, Z.; Xie, Z. *Angew. Chem, Int. Ed.* **2003**, *42*, 4347.

(19) Koch, T.; Blaurock, S.; Somoza, F. B., Jr.; Voigt, A.; Kirmse, R.; Hey-Hawkins, E. *Organometallics* **2000**, *19*, 2556.

(20) (a) Sassmannshausen, J.; Track, A.; Stelzer, F. *Organometallics* **2006**, *25*, 4427. (b) Cornelissen, C.; Erker, G.; Kehr, G.; Froehlich, R. Z. *Naturforsch.* **2004**, *59*, 1246. (c) Wiecko, M.; Girnt, D.; Rastaetter, M.; Panda, T. K.; Roesky, P. W. *Dalton Trans.* **2005**, 2147. (d) Mason, M. R.; Ogrin, D.; Fneich, B.; Barnard, T. S.; Kirschbaum, K. *J. Organomet. Chem.* **2005**, *690*, 157.

(21) Thomas, C. J.; Jia, L.; Zhang, H.; Siriwardance, U.; Maguire, J. A.; Wang, Y.; Brooks, K. A.; Weiss, V. P.; Hosmane, N. S. *Organometallics* **1995**, *14*, 1365.

(22) Deng, L.; Chan, H.-S.; Xie, Z. *J. Am. Chem. Soc.* **2005**, *127*, 13774.

(23) Long, R. J.; Gibson, V. C.; White, A. J. P. *Organometallics* **2008**, *27*, 235.

(24) Antiñolo, A.; Fernández-Galán, R.; Otero, A.; Prashar, S.; Rivilla, I.; Rodríguez, A. M. *J. Organomet. Chem.* **2006**, *691*, 2924.

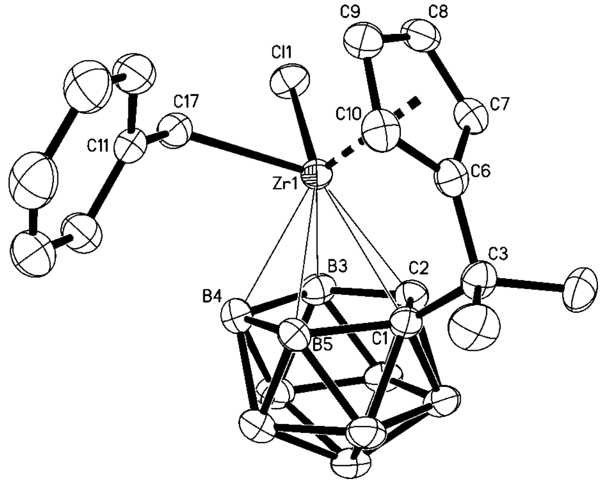


Figure 4. Molecular structure of the anion in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**8**) (thermal ellipsoids drawn at the 30% probability level).

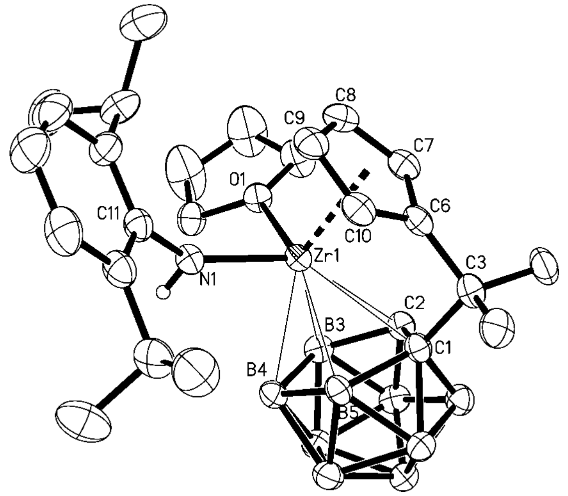


Figure 5. Molecular structure of $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**9**) (thermal ellipsoids drawn at the 30% probability level).

metal species, preventing the formation of neutral metal complexes. We then turned our attention to amido groups, since the additional lone pair can engage in $p_\pi-d_\pi$ back-bonding with the d^0 metal center, facilitating the elimination of NaCl. Treatment of **4** with 1 equiv of $NaNHC_6H_3Pr^i_2$ in THF at room temperature gave, after recrystallization from toluene, the neutral species $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(NHC_6H_3Pr^i_2)(THF)$ (**9**) in 62% isolated yield (Scheme 2). Complex **9** was fully characterized by various spectroscopic techniques and elemental analyses. Single-crystal X-ray analyses revealed that **9** is a neutral species and has one toluene of solvation. The Zr atom is η^5-bound to both cyclopentadienyl and dicarbollyl ligands, σ-bound to the amido nitrogen atom, and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 5). The average Zr−C(C_5 ring) distance of 2.516(3) Å is comparable to that of 2.531(3) Å in **4**, but the average Zr−cage atom distance of 2.585(3) Å is longer than that of 2.528(4) Å in **4**. The Cent(C_5 ring)−Zr−Cent(C_2B_3) angle of 119.2° is very close to that of 120.3° in **4**. The Zr−N distance of 2.055(2) Å is similar to that of 2.036(4)/2.043(4) Å in $[\eta^1:\eta^5\text{-}(^iPr_2C_6H_3N{=}CH)C_2B_9H_{10}]Zr(NMe_2)_2(NHMe_2)$,[16] 2.029(4)/2.020(4) Å in $[\eta^5\text{-}(C_2B_9H_{10})(CH_2)_2NBz_2)]Zr(NMe_2)_2(NHMe_2)$,[15] and 2.015(3)/2.018(3) Å in $[\eta^1:\eta^5\text{-}(C_5H_4NCH_2)C_2B_9H_{10}]Zr(NMe_2)_2$.[14] The relatively shorter Zr−N distance and large Zr−N−C angle of 143.8(1)° imply the presence of $p_\pi(N)-d_\pi(Zr)$ interactions, which reduces the Lewis acidity of the metal center. Such electronic effects plus steric effects imposed by two ^iPr groups lead to the formation of a neutral metal complex.

Table 2. Ethylene Polymerization Results[a]

catalyst	activity (10^6 g/(mol atm h))	$M_w/10^3$	M_w/M_n[b]	T_m (°C)[c]
4(Zr)	4.51	48.6	6.87	131.3
5(Hf)	1.38	26.6	4.38	130.1
8(Zr)	4.32	50.2	6.35	131.0

[a] Condtions: toluene (50 mL), 1 atm of ethylene, T = 25 °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/M = 1500, reaction time = 30 min. [b] Measured by GPC (using polystyrene standards in 1,2,4-trichlorobenzene at 150 °C). [c] Measured by DSC (heating rate 10 °C/min).

Ethylene Polymerization. Complexes **4**, **5**, and **8** underwent preliminary testing for catalytic activity, using methylalumoxane (MAO) as cocatalyst in toluene at room temperature (1 atm of ethylene). The results are compiled in Table 2. All three complexes were very active catalysts for the polymerization of ethylene in the presence of MAO under the reaction conditions specified in Table 2. Their activities were comparable with that of 7.2 × 10^4 g/(mol atm h) for $[(Cp^*)(C_2B_9H_{11})ZrMe]_n$.[3a] However, the catalytic activity of **4** dropped from 4.51 × 10^6 to 1.62 × 10^3 g/(mol atm h) as the Al/Zr molar ratio was decreased from 1500 to 750. When this ratio was 200, only a trace amount of polymer was observed. Complex **8** was inactive in the absence of MAO. These results may indicate that a large excess amount of MAO is necessary to abstract the chloro ligand from the metal complexes, due to the very strong interactions between the electron-deficient metal center and Lewis base Cl^-, as previously discussed. The active species was suggested to be the neutral metal complex $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]M(R)$.

Conclusion

The new inorganic/organic hybrid π ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ was conveniently prepared via a selective deboration of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ by piperidine/EtOH. Its group 1 metal salts were useful synthons for the preparation of group 4 metallocenes. X-ray analyses revealed that the presence of a Me_2C linkage in **4**−**9** increases significantly the open coordination sphere of the central metal center, in comparison with the corresponding unbridged complexes $(Cp^*)(C_2B_9H_{11})MCH_3$, resulting in unsuccessful synthesis of neutral metal alkyls.

Complexes **4**, **5**, and **8** showed a very high activity in ethylene polymerization after activation with a large amount of MAO. The active species were suggested to be the neutral group 4 metal methyl complexes $[\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]MCH_3$.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture, using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[6c] C_5H_5Na,[25] $C_6H_5CH_2K$,[26] $2,6\text{-}^iPr_2C_6H_3$-

---

[25] Hafner, K.; Kaiser, H. *Org. Synth.* **1964**, *44*, 94.

[26] Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Lorono-Gonzalez, D.; Parkin, A.; Parsons, S. *Chem. Eur. J.* **2003**, *9*, 4820.

Table 3. Crystal Data and Summary of Data Collection and Refinement for 3·2THF, 4, and 6

	3·2THF	**4**	**6**
formula	$C_{76}H_{152}B_{18}Na_6O_{14}$	$C_{22}H_{50}B_9Cl_2NaO_6Zr$	$C_{22}H_{50}B_9Cl_2LiO_6Zr$
cryst size (mm)	0.60 × 0.45 × 0.35	0.65 × 0.45 × 0.20	0.70 × 0.30 × 0.25
fw	1622.5	693.0	677.0
cryst syst	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a, Å	11.221(2)	30.143(3)	8.824(1)
b, Å	14.459(3)	12.916(2)	13.749(1)
c, Å	33.118(7)	18.608(2)	15.326(1)
α, deg	87.40(1)	90	74.18(1)
β, deg	87.56(1)	90	89.63(1)
γ, deg	67.18(1)	90	82.88(1)
V, Å^3	4945.7(2)	7244.4(2)	1774.3(2)
Z	2	8	2
D_{calcd}, Mg/m^3	1.090	1.271	1.267
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	1.2−50.0	2.7−50.0	3.1−50.0
μ, mm^{-1}	0.091	0.495	0.492
F(000)	1752	2880	704
no. of obsd rflns	14 893	9492	6227
no. of params refnd	1075	735	370
goodness of fit	0.819	1.106	1.071
R1	0.093	0.082	0.066
wR2	0.251	0.199	0.200

Table 4. Crystal Data and Summary of Data Collection and Refinement for 7, 8, and 9·C_7H_8

	7	**8**	**9**·C_7H_8
formula	$C_{23}H_{45}B_9ClNaO_4Zr$	$C_{29}H_{57}B_9ClNaO_6Zr$	$C_{33}H_{54}B_9NOZr$
cryst size (mm)	0.70 × 0.45 × 0.40	0.75 × 0.50 × 0.25	0.60 × 0.35 × 0.25
fw	632.5	748.7	669.3
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a, Å	16.327(1)	10.534(1)	34.270(2)
b, Å	11.679(1)	13.446(1)	12.187(1)
c, Å	19.050(1)	15.148(1)	23.272(1)
α, deg	90	105.49(1)	90
β, deg	114.66(1)	105.52(1)	129.85(1)
γ, deg	90	90.74(1)	90
V, Å^3	3301.1(3)	1984.0(2)	7462.1(6)
Z	4	2	8
D_{calcd}, Mg/m^3	1.273	1.253	1.191
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	2.7−56.0	2.9−52.0	3.1−50.0
μ, mm^{-1}	0.454	0.392	0.321
F(000)	1312	784	2816
no. of obsd rflns	7974	7354	6583
no. of params refnd	352	432	395
goodness of fit	0.990	1.045	1.022
R1	0.037	0.042	0.063
wR2	0.106	0.122	0.190

NHNa,[27] and $MCl_4(THF)_2$ (M = Zr, Hf)[28] were prepared according to literature methods. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300.0 and 75.5 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts; J values are given in Hz. Elemental analyses were performed by MEDAC Ltd., Middlesex, U.K.

Preparation of $[Me_3NH][Me_2C(C_5H_5)(C_2B_9H_{11})]$ (2). To an ethanol (40 mL) solution of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.75 g, 3.0 mmol) was added piperidine (7.5 mL, 75.0 mmol), and the mixture was heated to reflux for 2 days until the ^{11}B NMR spectrum of the solution showed the completion of the reaction. After removal of ethanol and the excess amount of piperidine under vacuum, the residue was dissolved in ethanol (5 mL). Addition of a saturated Me_3NHCl solution gave a sticky solid which was washed with water, reprecipitated from acetone to ether, and dried under vacuum. Compound **2** was then isolated as a pale yellow solid (0.72 g, 80%). ^{1}H NMR (acetone-d_6): δ 6.72 (m), 6.31 (m), 6.24 (m), 6.18 (m), 6.06 (m), 5.88 (m), 2.82 (m) (5H, C_5H_5, a mixture of isomers), 2.99 (s, 9H) ((CH_3)$_3$NH), 1.68 (s, 1H) (cage CH), 1.24 (s, 3H), 1.08 (s, 3H) ((CH_3)$_2$C), −2.70 (br s, 1H) (B−H−B). ^{13}C{^{1}H} NMR (acetone-d_6): δ 161.3, 158.1, 136.0, 132.5, 132.0, 131.0, 124.7, 124.0 (C_5H_5), 45.4 ((CH_3)$_3$NH), 42.9 (C_5H_5), 41.0, 31.3 ((CH_3)$_2C$). ^{11}B{^{1}H} NMR (acetone-d_6): δ −11.1 (2), −16.1 (2), −18.1 (1), −19.4 (1), −22.8 (1), −33.4 (1), −36.8 (1). IR (KBr, cm^{-1}): ν_{BH} 2514 (vs), 2313 (w). Anal. Calcd for $C_{13}H_{32}B_9N$: C, 52.10; H, 10.76; N, 4.67. Found: C, 51.78; H, 10.69; N, 4.88.

---

[27] Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652.

[28] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Preparation of $[\{[(\mu\text{-}\eta^5):\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}]\mathrm{Na(THF)}\}\{\mathrm{Na(THF)_3}\}\{\mathrm{Na(THF)_2}\}]_2\cdot 2\mathrm{THF}$ (3·2THF). To a THF (30 mL) solution of $[\mathrm{Me_2C(C_5H_5)(C_2B_9H_{11})}][\mathrm{Me_3NH}]$ (0.48 g, 1.6 mmol) was added NaH (0.32 g, 13.3 mmol), and the reaction mixture was heated to reflux for 2 days. After removal of the excess amount of NaH by filtration, the resulting clear solution was concentrated to about 10 mL. The compound **3**·2THF was isolated as colorless crystals after this solution stood at room temperature for 3 days (0.62 g, 51%). ^{1}H NMR (pyridine-d_5): δ 6.58 (m, 2H), 6.37 (m, 2H) ($\mathrm{C_5}H_4$), 3.66 (m, 28H) (THF), 2.10 (s, 1H) (cage CH), 1.90 (s, 3H), 1.65 (s, 3H) (($\mathrm{C}H_3)_2$C), 1.63 (m, 28H) (THF). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 101.2, 100.9, 100.8 ($C_5\mathrm{H_4}$), 67.2, 25.2 (THF), 61.4, 36.3 ($C_2\mathrm{B_9H_{10}}$), 31.1, 30.2, 29.9 (($C\mathrm{H_3})_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −21.0 (6), −24.6 (2), −44.9 (1). IR (KBr, cm^{-1}): ν_{BH} 2503 (vs), 2350 (w). Anal. Calcd for $\mathrm{C_{60}H_{120}B_{18}Na_6O_{10}}$ (**3**–2THF): C, 54.02; H, 9.07. Found: C, 54.21; H, 9.01.

Preparation of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl_2}][\mathrm{Na(DME)_3}]$ (4). To a THF (40 mL) solution of $[\mathrm{Me_2C(C_5H_5)(C_2B_9H_{11})}][\mathrm{Me_3NH}]$ (0.72 g, 2.4 mmol) was added NaH (0.46 g, 19.0 mmol), and the reaction mixture was heated to reflux for 2 days. The resulting solution of $\{[\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}]\mathrm{Na_3(THF)}_x\}$ was transferred via cannula to a suspension of $\mathrm{ZrCl_4(THF)_2}$ (0.91 g, 2.4 mmol) in THF (10 mL) at −78 °C, and the mixture was slowly warmed to room temperature and stirred for 2 days. After removal of the precipitate, the solvent was evaporated under vacuum, leaving an oily residue that was recrystallized from DME to yield **4** as colorless crystals (0.48 g, 29%). ^{1}H NMR (pyridine-d_5): δ 6.95 (m, 2H), 6.40 (m, 1H), 6.20 (m, 1H) ($\mathrm{C_5}H_4$), 3.48 (s, 12H), 3.26 (s, 18H) (DME), 1.68 (s, 1H) (cage CH), 1.62 (s, 3H), 1.48 (s, 3H) (($\mathrm{C}H_3)_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.6, 124.9, 107.1, 104.7 ($C_5\mathrm{H_4}$), 71.4, 58.0 (DME), 66.5, 51.2 ($C_2\mathrm{B_9H_{10}}$), 37.8, 27.9, 26.8 (($C\mathrm{H_3})_2C$).^{11}B{^{1}H} NMR (pyridine-d_5): δ 4.9 (1), −3.1 (1), −5.9 (3), −12.2 (3), −19.3 (1). IR (KBr, cm^{-1}): ν_{BH} 2547 (vs). Anal. Calcd for $\mathrm{C_{18}H_{40}B_9Cl_2NaO_4Zr}$ (**4**–DME): C, 35.86; H, 6.69. Found: C, 35.93; H, 7.19.

Alternate Method. A THF solution (20 mL) of **3** (1.62 g, 2.0 mmol) was slowly added to a THF suspension (20 mL) of $\mathrm{ZrCl_4(THF)_2}$ (0.75 g, 2.0 mmol) at −78 °C, and the mixture was stirred at room temperature overnight. The resulting solution was treated using the same procedures reported above to give **4** as colorless crystals (1.01 g, 73%).

Preparation of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{HfCl_2}][\mathrm{Na(DME)_3}]$ (5). This complex was prepared as pale yellow crystals from $[\mathrm{Me_2C(C_5H_5)(C_2B_9H_{11})}][\mathrm{Me_3NH}]$ (0.72 g, 2.4 mmol), NaH (0.50 g, 20.8 mmol), and $\mathrm{HfCl_4(THF)_2}$ (1.12 g, 2.4 mmol) in THF (40 mL) using the same procedures reported for **4**: yield 0.68 g (36%). ^{1}H NMR (pyridine-d_5): δ 6.92 (m, 1H), 6.87 (m, 1H), 6.26 (d, J = 2.7, 1H), 6.10 (m, 1H) ($\mathrm{C_5}H_4$), 3.49 (s, 12H), 3.26 (s, 18H) (DME), 1.70 (s, 1H) (cage CH), 1.60 (s, 3H), 1.46 (s, 3H) (($\mathrm{C}H_3)_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.4, 124.7, 120.7, 105.2, 102.3 ($C_5\mathrm{H_4}$), 71.4, 58.0 (DME), 66.3, 49.7 ($C_2\mathrm{B_9H_{10}}$), 37.4, 27.7, 27.1 (($C\mathrm{H_3})_2C$).^{11}B{^{1}H} NMR (pyridine-d_5): δ 3.2 (1), −4.2 (1), −6.3 (2), −7.4 (1), −13.3 (2), −14.3 (1), −21.3 (1). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $\mathrm{C_{18}H_{40}B_9Cl_2HfNaO_4}$ (**5**–DME): C, 31.32; H, 5.84. Found: C, 31.41; H, 5.50.

Alternate Method. Complex **5** was also prepared in 70% yield from **3** (1.62 g, 2.0 mmol) and $\mathrm{HfCl_4(THF)_2}$ (0.93 g, 2.0 mmol) in THF (40 mL) using the same procedures reported above.

Preparation of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl_2}][\mathrm{Li(DME)_3}]$ (6). To a THF (10 mL) solution of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl_2}][\mathrm{Na(DME)_3}]$ (**4**; 0.21 g, 0.30 mmol) was added LiCl (0.01 g, 0.30 mmol) at room temperature, and the mixture was stirred overnight. After removal of the solvent, the residue was extracted with toluene (5 mL × 3). The toluene solutions were evaporated under vacuum, leaving an oily residue that was recrystallized from DME at −30 °C to give **6** as pale yellow crystals (0.05 g, 25%). ^{1}H NMR (pyridine-d_5): δ 6.94 (m, 1H), 6.82 (m, 1 H), 6.40 (m, 1H), 6.20 (m, 1H) ($\mathrm{C_5H_4}$), 3.49 (s, 12H), 3.26 (s, 18H) (DME), 1.70 (s, 1H) (cage CH), 1.59 (s, 3H), 1.47 (s, 3H) (($\mathrm{C}H_3)_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 125.7, 120.0, 108.0, 105.0 ($C_5\mathrm{H_4}$), 71.4, 57.9 (DME), 48.4 ($C_2\mathrm{B_9H_{10}}$), 37.3, 27.9, 26.7 (($C\mathrm{H_3})_2C$).^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.9 (1), −3.4 (1), −5.6 (1), −6.9 (2), −13.1 (1), −15.0 (2), −21.1 (1). IR (KBr, cm^{-1}): ν_{BH} 2520 (vs). Anal. Calcd for $\mathrm{C_{20}H_{45}B_9Cl_2LiO_5Zr}$ (**6** - 0.5DME): C, 38.01; H, 7.18. Found: C, 37.76; H, 7.34.

Alternate Method. To a THF (40 mL) solution of $[\mathrm{Me_2C(C_5H_5)(C_2B_9H_{11})}][\mathrm{Me_3NH}]$ (0.72 g, 2.4 mmol) was slowly added ^{n}BuLi (4.5 mL, 7.2 mmol) at −78 °C, and the mixture was stirred at room temperature for 3 h. The resulting $\{[\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}]\mathrm{Li_3(THF)}_x\}$ solution was transferred via cannula to a suspension of $\mathrm{ZrCl_4(THF)_2}$ (0.91 g, 2.4 mmol) in THF (10 mL) at −78 °C, and the mixture was slowly warmed to room temperature and stirred overnight. After removal of the precipitate, the solvent was evaporated under vacuum, leaving an oily residue that was recrystallized from DME to yield **6** as colorless crystals (0.68 g, 41%).

Preparation of $\{[\eta^5:\eta^2\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}]\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})(\mu\text{-}\mathrm{Cl})\}\{\mathrm{Na(DME)_2}\}$ (7). To a THF (10 mL) solution of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl_2}][\mathrm{Na(DME)_3}]$ (**4**; 0.20 g, 0.29 mmol) was slowly added a THF solution of $\mathrm{C_5H_5Na}$ (10.0 mL, 0.29 mmol) at −20 °C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the precipitate, the filtrate was evaporated to dryness under vacuum. The residue was dissolved in DME. The DME solution was then concentrated to about 6 mL, to which was added ether (1 mL). Complex **7** was isolated as yellow crystals after this solution stood at −30 °C for 3 days (0.09 g, 47%). ^{1}H NMR (pyridine-d_5): δ 6.85 (d, J = 2.7, 1H), 6.69 (m, 1H), 6.29 (m, 1H), 5.42 (d, J = 2.4, 1H) ($\mathrm{C_5}H_4$), 6.39 (s, 5H) ($\mathrm{C_5}H_5$), 3.48 (s, 8H), 3.25 (s, 12H) (DME), 2.55 (s, 1H) (cage CH), 1.39 (s, 3H), 1.33 (s, 3H) (($\mathrm{C}H_3)_2$C). ^{13}C{^{1}H} NMR (pyridine-d_5): δ 113.9, 113.8, 112.8, 107.5, 104.8 ($C_5\mathrm{H_4}$), 112.6 ($C_5\mathrm{H_5}$), 95.8 ($C_2\mathrm{B_9H_{10}}$), 71.4, 57.9 (DME), 35.4, 26.6, 25.2 (($C\mathrm{H_3})_2C$). ^{11}B{^{1}H} NMR (pyridine-d_5): δ −8.5 (1), −9.3 (1), −12.9 (1), −13.5 (1), −15.1 (1), −18.7 (2), −19.7 (1), −34.5 (1). IR (KBr, cm^{-1}): ν_{BH} 2517 (s). Anal. Calcd for $\mathrm{C_{19}H_{35}B_9ClNaO_2Zr}$ (**7**–DME): C, 42.07; H, 6.50. Found: C, 42.51; H, 6.39.

Preparation of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl(CH_2C_6H_5)}][\mathrm{Na(DME)_3}]$ (8). To a THF (15 mL) solution of $[\{\eta^5:\eta^5\text{-}\mathrm{Me_2C(C_5H_4)(C_2B_9H_{10})}\}\mathrm{ZrCl_2}][\mathrm{Na(DME)_3}]$ (**4**; 0.55 g, 0.79 mmol) was slowly added a THF (10 mL) solution of $\mathrm{KCH_2C_6H_5}$ (0.10 g, 0.79 mmol) at −78 °C, and the reaction mixture was then warmed to room temperature and stirred for 4 h. After removal of the solvent, the residue was extracted with DME (5 mL × 3). The DME solutions were combined and concentrated to about 5 mL. Complex **8** was isolated as orange crystals after this solution stood at −30 °C for 3 days (0.21 g, 36%). ^{1}H NMR (benzene-d_6): δ 7.48 (m, 2H), 7.31 (m, 2H), 6.92 (m, 1H) ($\mathrm{CH_2C_6}H_5$), 6.68 (m, 1H), 6.27 (m, 1H), 6.24 (m, 1H), 4.93 (m, 1H) ($\mathrm{C_5}H_4$), 3.07 (s, 12H), 3.06 (s, 18H) (DME), 2.60 (br s, 2H) ($\mathrm{C}H_2\mathrm{C_6H_5}$), 1.99 (s, 1H) (cage C$H$), 1.41 (s, 3H), 0.84 (s, 3H) (($\mathrm{C}H_3)_2$C). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.0, 129.7, 127.1, 126.5, 122.8 ($\mathrm{CH_2}C_6\mathrm{H_5}$), 122.5, 121.6, 120.2, 108.6, 107.2 ($C_5\mathrm{H_4}$), 71.5, 59.3 (DME), 68.3 ($C\mathrm{H_2C_6H_5}$), 66.3, 51.6

($C_2B_9H_{10}$), 38.2, 29.3, 26.3 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 3.6 (1), −0.2 (1), −2.7 (1), −5.7 (2), −7.7 (1), −11.3 (1), −12.5 (1), −18.3 (1). IR (KBr, cm^{-1}): ν_{BH} 2533 (s). Anal. Calcd for $C_{25}H_{47}B_9ClNaO_4Zr$ (**8**–DME): C, 45.59; H, 7.19. Found: C, 45.87; H, 7.58.

Preparation of [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($NHC_6H_3Pr^i_2$)(THF)·$C_7H_8$ (9·C_7H_8). To a THF (15 mL) solution of [{η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**4**; 0.20 g, 0.29 mmol) was slowly added a THF (5 mL) solution of $NaNHC_6H_3Pr^i_2$ (0.06 g, 0.29 mmol) at −20 °C, and the reaction mixture was stirred at room temperature for 2 days. After removal of solvent, the residue was extracted with toluene (15 mL × 3). The toluene solutions were combined and concentrated to about 10 mL. The complex **9**·C_7H_8 was isolated as yellow crystals after this solution stood at room temperature for 4 days (0.12 g, 62%). ^1H NMR (pyridine-d_5): δ 10.29 (s, 1H) (N*H*), 7.26−7.17 (m, 5H) ($C_6H_5CH_3$), 7.13 (d, J = 6.0, 2H), 6.90 (m, 1H) (aryl H), 6.58 (m, 1H), 6.45 (m, 2H), 6.02 (m, 1H) (C_5H_4), 3.64 (m, 4H), 1.60 (m, 4H) (THF), 3.18 (m, 2H) ($(CH_3)_2CH$), 2.20 (s, 3H) ($C_6H_5CH_3$), 1.78 (s, 1H) (cage C*H*), 1.56 (s, 3H), 1.51 (s, 3H) ($(CH_3)_2C$), 1.25 (s, 6H), 1.23 (s, 6H) ($(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 141.5, 140.6, 131.7, 125.5, 128.7, 128.0, 125.1 (aryl *C*), 119.1, 118.8, 117.3, 108.2, 105.9 (C_5H_4), 67.2, 25.1 (THF), 38.2, 27.3, 26.4 ($(CH_3)_2C$), 27.3, 22.1 ($(CH_3)_2CH$), 20.6 ($C_6H_5CH_3$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 2.4 (1), −3.5 (2), −7.1 (3), −13.2 (2), −20.6 (1). IR (KBr, cm^{-1}): ν_{BH} 2534 (s), 2312 (w). Anal. Calcd for $C_{25.5}H_{42}B_9NZr$ (**9**–THF+0.5C_7H_8): C, 55.57; H, 7.68; N, 2.54. Found: C, 55.33; H, 7.45; N, 2.55.

Ethylene Polymerization. This experiment was carried out in a 150 mL glass reactor equipped with a magnetic stirrer and gas inlets. The reactor was charged with the catalyst together with MAO and toluene (50 mL). The mixture was stirred at room temperature for 0.5 h. Ethylene gas was then introduced to the reactor, and its pressure was maintained continuously at 1 atm by means of bubbling. The polymerization was terminated by addition of acidic ethanol (100 mL). The white precipitate was filtered off and washed with ethanol and acetone. The resulting powder was finally dried in a vacuum oven at 80 °C overnight.

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[29] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on F^2 using the SHELXTL program package.[30] For the noncentrosymmetric structure of **4**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.[31] The cage carbon atoms were located by comparing the bond lengths as the average distance between the carbon and carbon/boron atoms would appear shorter than that between the boron atoms. All hydrogen atoms were geometrically fixed using the riding model. Complexes **3** and **9** showed the solvation of two THF and one toluene molecules, respectively. It was noted that several disordered THF molecules in **3** led to a relatively higher R values. Crystal data and details of data collection and structure refinements were given in Tables 3 and 4. Further details are included in the Supporting Information.

Acknowledgment. This work was supported by grants from the NSFC/RGC Joint Research Scheme (N_CUHK446/06) and a Strategic Investments Scheme administrated by The Chinese University of Hong Kong.

Supporting Information Available: Crystallographic data in CIF format for **3**–2THF, **4**, **6**−**8**, and **9**–C_7H_8. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800235W

---

(29) Sheldrick, G. M. SADABS: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 1996.

(30) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.

(31) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.