Synthesis, Structure, and Reactivity of Group 4 Metallacarboranes Bearing the Ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$

Dongmei Liu,[†] Yaorong Wang,[†] Hoi-Shan Chan,[†] Yong Tang,[‡] and Zuowei Xie*[,†]

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories,
Hong Kong, People's Republic of China, and State Key Laboratory of Organometallic Chemistry,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032,
People's Republic of China

Received May 17, 2008

The new inorganic/organic hybrid ligand $[NMe_3H][Me_2C(C_9H_7)(C_2B_9H_{11})]$ was prepared via a selective deboration of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ with piperidine in ethanol. Reaction of the ligand with $Zr(NMe_2)_4$ provided the neutral group 4 metal amide complex *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**3**) through an amine elimination reaction. Treatment of the trianionic salt of the ligand with $MCl_4(THF)_2$ gave the mixed sandwich complexes *trans*-$[\{\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}MCl_2][Na(DME)_3]$ (M = Zr (**4**), Hf (**5**)). Complex **4** reacted with KCH_2Ph, C_5H_5Na, or $NaNH(C_6H_3\text{-}2,6\text{-}Me_2)$ to afford *trans*-$[\{\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**6**), *trans*-$\{[\eta^1:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]ZrCl(\eta^5\text{-}C_5H_5)\}\{Na(DME)_3\}$ (**7**), or *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NHC_6H_3Me_2)(THF)$ (**8**), respectively. Both **6** and **7** were thermally stable, and no NaCl elimination was observed upon heating their DME solutions. Complex **4** also reacted with excess NaH in THF to generate the ring-opening product *trans*-$[\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(OCH_2CH_2CH_2CH_3)(THF)$ (**9**). In the presence of excess MAO (methylalumoxane), complexes **3**, **4**, and **6** were 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

The 14-electron bent metallocene alkyl complexes $(C_5R_5)_2Ln(R^1)$,[1] $(C_5R_5)_2M(R^1)^+$,[2] and $(C_5R_5)(C_2B_9H_{11})M(R^1)$[3] (Ln = lanthanides, M = group 4 metals) share common features of ligand exchange, insertion, olefin polymerization, and C−H bond activation. These characteristics of electrophilic metal alkyls are highly sensitive to the structural and electronic properties of the $(C_5R_5)_2M$ fragment.[1−3] Therefore, extensive work on the modification of cyclopentadienyl ligands has been done in order to control the properties of metallocenes. In sharp contrast, modifications of the dicarbollyl ligand in $(C_5R_5)(C_2B_9H_{11})M(R^1)$ have been much less explored,[3] although many examples of group 4 metallacarboranes bearing tethered Lewis base functionalities have been documented.[4] We have very recently reported the ansa ligand $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$.[5] It can largely increase the "bite angle"[2h] of the resulting group 4 metallocenes, in comparison with the angles for the corresponding unbridged species.[5] On the other hand, the high electrophilicity of the metal center and a more open coordination sphere make the synthesis of neutral metal alkyls very difficult. To overcome this problem, we extended our work to indenyl systems, in the hope that the sterically demanding yet planar indenyl ring and the known diverse bonding modes ($\eta^5-\eta^3-\eta^1$) between the central metal and the five-membered ring of the

---

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

[†] The Chinese University of Hong Kong.

[‡] Shanghai Institute of Organic Chemistry.

(1) 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. (c) Li, X.; Hou, Z. *Coord. Chem. Rev.* **2008**, *252*, 1842.

(2) 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. (f) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (g) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457. (h) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (i) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85. (j) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (k) Wang, B. *Coord. Chem. Rev.* **2006**, *250*, 242. (l) Hoveyda, A. H.; Morken, J. P. In *Metallocenes-Synthesis, Reactivity, Applications*; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, p 625. (m) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. (n) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691.

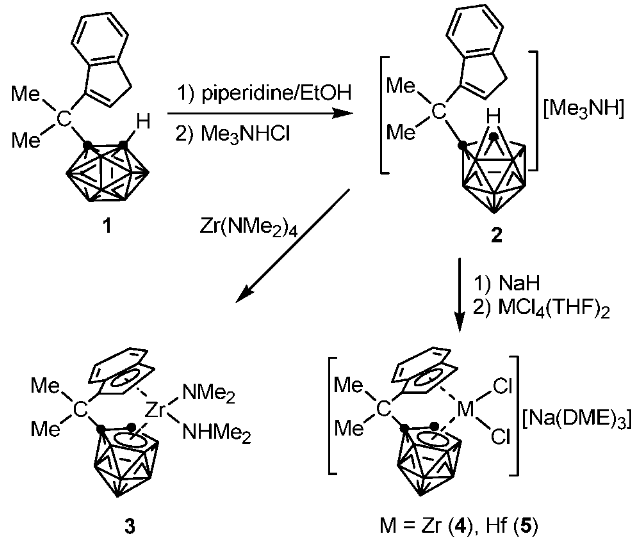
(3) (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (c) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (d) Yoshida, M.; Crowther, 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. (h) Bowen, D. E.; Rogers, R. D.; Jordan, R. F. *Organometallics* **1995**, *14*, 3630.

(4) (a) Kim, D.-H.; Won, J. H.; Kim, S.-J.; Ko, J.; Kim, S.-H.; Cho, S.; Kang, S. O. *Organometallics* **2001**, *20*, 4298. (b) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. *Chem. Commun.* **2003**, 1364. (c) Lee, Y.-J.; Lee, J.-D.; Jeong, H.-J.; Son, K.-C.; Ko, J.; Cheong, M.; Kang, S. O *Organometallics* **2005**, *24*, 3008. (d) Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 3037. (e) Cheung, M.-S.; Chan, H.-S.; Bi, S.; Lin, Z.; Xie, Z. *Organometallics* **2005**, *24*, 4333. (f) Cheung, M.-S.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 5217. (g) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* **2006**, *25*, 2578. (h) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2007**, *26*, 2694. (i) Shen, H.; Chan, H.-S.; Xie, Z *Organometallics* **2006**, *25*, 5515. (j) Zhu, Y.; Vyakaranam, K.; Maguire, J. A.; Quintana, W.; Teixidor, F.; Viñas, C.; Hosmane, N. S. *Inorg. Chem. Commun.* **2001**, *4*, 486. (k) Wang, J.; Zhu, Y.; Li, S.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.* **2003**, *680*, 173. (l) Zhu, Y.; Zhong, Y.; Carpenter, K.; Maguire, J. A.; Hosmane, N. S. *J. Organomet. Chem.* **2005**, *690*, 2802. (m) Zhu, Y.; Sia, S. L. P.; Kooli, F.; Carpenter, K.; Kemp, R. A. *J. Organomet. Chem.* **2005**, *690*, 6284.

(5) Wang, Y.; Liu, D.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 2825.

10.1021/om800452f CCC: $40.75

Scheme 1



indenyl ligand could facilitate the formation of neutral metal alkyls.[6] In this contribution, we report the new Me_2C-linked indenyl−dicarbollyl ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ and its group 4 metal chloride, amide, oxide, and alkyl complexes. Similarities and differences between $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$ and $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ with regard to their coordination chemistry are also discussed.

Results and Discussion

Ligand Synthesis. Treatment of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (**1**)[7] with a large excess amount of piperidine in refluxing ethanol for 2 days gave, after addition of Me_3NHCl, the selective deboration product $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**2**) in 91% isolated yield (Scheme 1). The reaction was closely monitored by ^{11}B NMR spectra. It was noted that piperidine/EtOH is the best reagent for this reaction after screening many reagents such as MOH/MeOH (M = Na, K),[8] the fluoride ion,[9] and various amines,[10] which led to either a mixture of products or the cleavage of the $C_{bridge}-C_{cage}$ bond.

The composition of **2** was fully characterized by various spectroscopic techniques and elemental analyses. Its ^{11}B NMR spectrum showed a 2:2:1:1:1:1:1 pattern, which differs significantly from that of its parent compound **1**. Both ^1H and ^{13}C NMR data showed that the bridging carbon atom in **2** is bonded only to the sp^2 carbon of the indenyl unit, which is confirmed by single-crystal X-ray analyses (Figure 1). The C(24)−C(25)/C(24)−C(32)/C(25)−C(30)/C(30)−C(31)/C(31)−C(32) distances of 1.481(4)/1.330(4)/1.394(4)/1.498(5)/1.494(4) Å and the planar geometry of the C(24) atom clearly indicate the sp^2 hybridization of C(24).

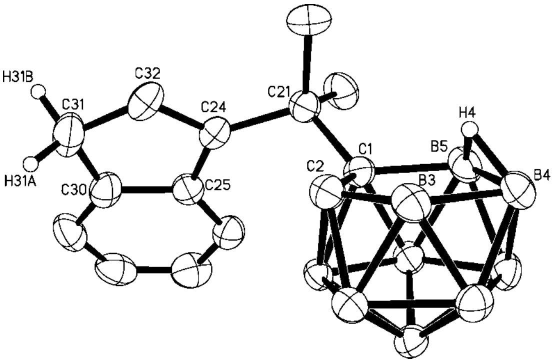
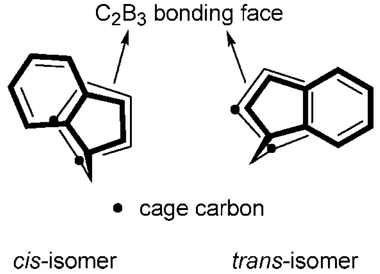


Figure 1. Molecular structure of the anion in $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**2**) (thermal ellipsoids drawn at the 30% probability level).

Chart 1



Group 4 Metal Complexes. Compound **2** contains three types of acidic protons, namely B−H−B, sp^3 CH_2 of the indenyl group, and NH, which may be deprotonated by metal amides.[2d,11] Treatment of **2** with 1 equiv of $Zr(NMe_2)_4$ in DME (1,2-dimethoxyethane) at room temperature overnight afforded the neutral metal amide complex *trans*-$[\eta^5:\eta^5$-$Me_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (**3**) in 54% isolated yield (Scheme 1). Only the trans isomer was isolated, in which the six-membered ring of indenyl is trans to the unbridged cage carbon atom (Chart 1).[12] This complex has a very low solubility in toluene and benzene, decomposes in $CDCl_3$ and CD_2Cl_2, and

---

[6] (a) O′Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (b) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233−234*, 157. (c) Calhorda, M. J.; Veiros, L. F. *Coord. Chem. Rev.* **1999**, *185−186*, 37.

[7] (a) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (b) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334. (c) Wang, H.; Wang, Y.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 5110. (d) Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2003**, *22*, 4522. (e) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. *Organometallics* **2004**, *23*, 5864.

[8] For examples, see: (a) Viñas, C.; Laromaine, A.; Teixidor, F.; Horáková, H.; Langauf, A.; Vespalec, R.; Mata, I.; Molins, E. *Dalton Trans.* **2007**, 3369. (b) Fox, M. A.; Goeta, A. E.; Hughes, A. K.; Johnson, A. L. *Dalton Trans.* **2002**, 2132. (c) Park, J.-S.; Kim, D.-H.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C. H.; Kang, S. O. *Organometallics* **2001**, *20*, 4632. (d) Park, J.-S.; Kim, D.-H.; Kim, S.-J.; Ko, J.; Kim, S. H.; Cho, S.; Lee, C.-H.; Kang, S. O. *Organometallics* **2001**, *20*, 4483. (e) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

[9] For examples, see: (a) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K.; Colquhoun, H. M. *Polyhedron* **1996**, *15*, 565. (b) Fox, M. A.; MacBride, J. A. H.; Wade, K. *Polyhedron* **1997**, *16*, 2499. (c) Wei, X.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2006**, *25*, 609. (d) Yoo, J.; Hwang, J.-W.; Do, Y. *Inorg. Chem.* **2001**, *40*, 568. (e) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812. (f) Fox, M. A.; Wade, K. *J. Organomet. Chem.* **1999**, *573*, 279. (g) Fox, M. A.; Wade, K. *Polyhedron* **1997**, *16*, 2517.

[10] For examples, see: (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) Wise, S. D.; Au, W.-S.; Getman, T. D. *Main Group Met. Chem.* **2002**, *25*, 411. (d) Brockman, R.; Challis, K.; Froehner, G.; Getman, T. D. *Main Group Met. Chem.* **2002**, *25*, 629. (e) Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Hughes, A. K.; Malget, J. M. J. *Dalton Trans.* **2001**, 1820. (f) Teixidor, F.; Viñas, C.; Benakki, R.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 1719. (g) Laromaine, A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Benakki, R.; Grüner, B.; Viñas, C. *Dalton Trans.* **2005**, 1785. (h) Teixidor, F.; Gómez, S.; Lamrani, M.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Organometallics* **1997**, *16*, 1278.

[11] (a) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 1157. (b) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. *Organometallics* **2006**, *25*, 2578. (c) Wang, J.; Li, H.; Guo, N.; Li, L.; Stern, C. L.; Marks, T. J. *Organometallics* **2004**, *23*, 5112. (d) Wang, J.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2003**, *22*, 4839.

[12] Selective formation of the *rac* isomer is reported from the reaction of $ZrCl_4(THF)_2$ with *ansa*-indenyl ligands; see: (a) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590. (b) Alonso-Moreno, C.; Antiñolo, A.; Carrillo-Hermosilla, F.; Carrión, P.; López-Solera, I.; Otero, A.; Prashar, S.; Sancho, J. *Eur. J. Inorg. Chem.* **2005**, 2924.

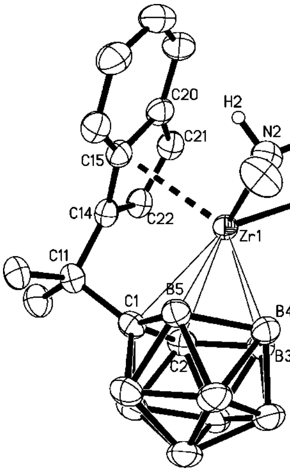


Figure 2. Molecular structure of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($NMe_2$)($NHMe_2$) (**3**) (thermal ellipsoids drawn at the 30% probability level).

reacts slowly with THF. Its ^1H and ^{13}C NMR spectra in pyridine-d_5 showed, in addition to the ligand protons, a free dimethylamine and a dimethylamido group. The amine is dissociated in pyridine-d_5, resulting in the observation of only one set of NMR data. The ^{11}B NMR spectrum exhibited a 1:2:3:2:1 pattern due to the coincidence of resonances.

Single-crystal X-ray analyses confirm the formation of the trans isomer of **3**. The Zr atom is η^5-bound to both the five-membered ring of the indenyl group and the dicarbollyl ligand, σ-bound to one NMe_2 moiety, and coordinated to one $NHMe_2$ molecule in a distorted-tetrahedral geometry (Figure 2; bond distances and angles are given in Table 1). The average Zr−C(C_5 ring) distance of 2.599(3) Å is comparable to that of 2.610(2) Å in *rac*-[$Me_2Si(C_9H_6)_2$]Zr(NMe_2)$_2$,[13] 2.515(4)/2.514(4) Å in *meso*-[$Me_2C(C_9H_6)_2$]$ZrCl_2$,[14] 2.513(3) Å in *rac*-[$Me_2C(C_9H_6)_2$]$ZrCl_2$,[14] 2.521(8) Å in [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$,[7c] and 2.541(5) Å in [η^5:σ-$Me_2Si(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$.[7c] The average Zr−cage atom distance of 2.597(3) Å is similar to that of 2.601(5) Å in [η^1:η^5-(^{i}$Pr_2C_6H_3N$=CH)$C_2B_9H_{10}$]Zr(NMe_2)$_2$($NHMe_2$)[11b] and 2.585(3) Å in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($NHC_6H_3^{i}Pr_2$)(THF)[5] but is longer than that of 2.469(8) Å in [σ:η^5-$(C_9H_6)(C_2B_9H_{10})$]Zr(NMe_2)(DME),[11a] 2.523(5) Å in [η^1:η^5-(Me_2NCH_2)$C_2B_9H_{10}$]$_2$Zr,[15] 2.538(5) Å in [η^1:η^5-($C_5H_4NCH_2$)-$C_2B_9H_{10}$]Zr(NMe_2)$_2$,[16] 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]$_2$(μ-CH_2),[3a]2.568(4) Å in [η^1:η^5-($BzNCH_2$)(CH_3)$C_2B_9H_{10}$]$ZrCl_2$(THF),[4c] and 2.544(6) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF).[4f] The Zr−N(1) distance of 2.057(2) Å is very similar to that of 2.078(2) Å in *rac*-[$Me_2Si(C_9H_6)_2$]Zr(NMe_2)$_2$,[13] 2.016(8) Å in [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Zr($NMe_2$)$_2$,[7c] 2.036(4)/2.043(4) Å in [η^1:η^5-(^{i}$Pr_2C_6H_3N$=CH)$C_2B_9H_{10}$]Zr(NMe_2)$_2$($NHMe_2$),[11b] 2.029(4)/2.020(4) Å in [η^5-($C_2B_9H_{10}$)(CH_2)$_2$$NBz_2$)]Zr($NMe_2$)$_2$($NHMe_2$),[4c] and 2.015(3)/2.018(3) Å in [η^1:η^5-($C_5H_4NCH_2$)$C_2B_9H_{10}$]Zr(NMe_2)$_2$.[16] The Cent(C_5 ring)−Zr−Cent(C_2B_3) angle of 115.9° is smaller than that of 119.2° in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]Zr($NHC_6H_3^{i}Pr_2$)(THF)[5] and is significantly smaller than the 122.9° in *rac*-[$Me_2Si(C_9H_6)_2$]Zr(NMe_2)$_2$[13] and 134.9° in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2).[3a] These data suggest that the open coordination sphere around the Zr atom in **3** is larger than that observed in the corresponding cyclopentadienyl analogue and is significantly larger than that found in the unbridged species.

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

	3	**6**	**7**	**8**	**9**
Zr−C(C_5 ring)	2.468(3)	2.480(5)	2.452(6)	2.431(4)	2.422(6)
	2.515(3)	2.491(5)	2.490(7)	2.482(5)	2.517(6)
	2.599(3)	2.640(6)	2.517(7)	2.595(5)	2.558(6)
	2.677(3)	2.692(5)	2.537(7)	2.630(6)	2.671(7)
	2.738(3)	2.792(6)	2.541(7)	2.747(6)	2.734(6)
av Zr−C_{ring}	2.599(3)	2.619(6)	2.507(7)	2.577(6)	2.580(7)
av Zr−cage atom	2.597(3)	2.591(7)	2.536(8)	2.583(6)	2.554(8)
av Zr−Cl		2.442(2)	2.511(2)		
Zr−N	2.057(2)			2.035(4)	
Zr−O					1.930(5)
Zr−C		2.312(6)	2.420(6)		
Zr−Cent(C_5)[a]	2.300	2.327	2.213	2.275	2.282
Zr−Cent(C_2B_3)[a]	2.164	2.154	2.090	2.147	2.105
Cent(C_5)−Zr−Cent(C_2B_3)	115.9	117.3		119.4	120.6
C_{ring}−C_{bridge}−C_{cage}	103.1(2)	103.8(4)	108.0(5)	104.4(4)	103.8(5)

[a] Cent(C_5) and Cent(C_2B_3) denote the centroids of the five-membered rings of the indenyl and the C_2B_3 bonding face, respectively.

The above amine elimination method serves a convenient way to prepare neutral metal amide complexes. We then attempted the alkane elimination for the synthesis of neutral metal alkyls. Unfortunately, reaction of **2** with 1 equiv of Zr(CH_2Ph)$_4$ or Zr(CH_2SiMe_3)$_4$ was complicated under various reaction conditions, as indicated by ^1H NMR spectra, and no pure product was isolated from the above reactions. Since organotransition-metal halides are useful precursors for a variety of organometallics, their syntheses have therefore been explored.

Treatment of **2** with excess NaH in refluxing THF gave presumably the trianionic salt [$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Na_3(THF)_x$, followed by reaction with MCl_4(THF)$_2$ to afford, after recrystallization from DME, the mixed sandwich complexes *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$MCl_2$][Na(DME)$_3$] (M = Zr (**4**), Hf (**5**)) as the single isomer[12] in ~60% isolated yields (Scheme 1). Their ^1H NMR spectra showed multiplets in the range 7.96−6.66 ppm attributable to the indenyl protons, two singlets at 1.85 and 1.74 ppm corresponding to the Me_2C linkage, and two singlets at 3.48 and 3.25 ppm assignable to the DME molecules. The ^{13}C NMR data were consistent with the above results. Their ^{11}B NMR spectra exhibited a 1:1:3:3:1 pattern. The compositions of both **4** and **5** were confirmed by elemental analyses.

Reaction of **4** with 1 equiv of KCH_2Ph in THF at room temperature produced, after recrystallization from DME, *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}ZrCl($CH_2C_6H_5$)][Na(DME)$_3$] (**6**) in 29% isolated yield (Scheme 2). In addition to the peaks derived from the bridging ligand, one broad resonance at 2.60 ppm attributable to the CH_2 protons of the benzyl group[17] and two singlets at 3.48 and 3.25 ppm corresponding to the DME molecule were observed in the ^1H NMR spectrum. Its ^{11}B NMR spectrum showed a 1:1:1:1:2:1:1:1 pattern. A single-crystal X-ray diffraction study confirms that **6** is a trans isomer and is ionic in nature. The Zr atom is η^5-bound to both the five-membered ring of the indenyl group and the dicarbollyl unit and σ-bound to one benzyl and one chlorine atom in a distorted-

---

(13) Vogel, A.; Priermeier, T.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *527*, 297.

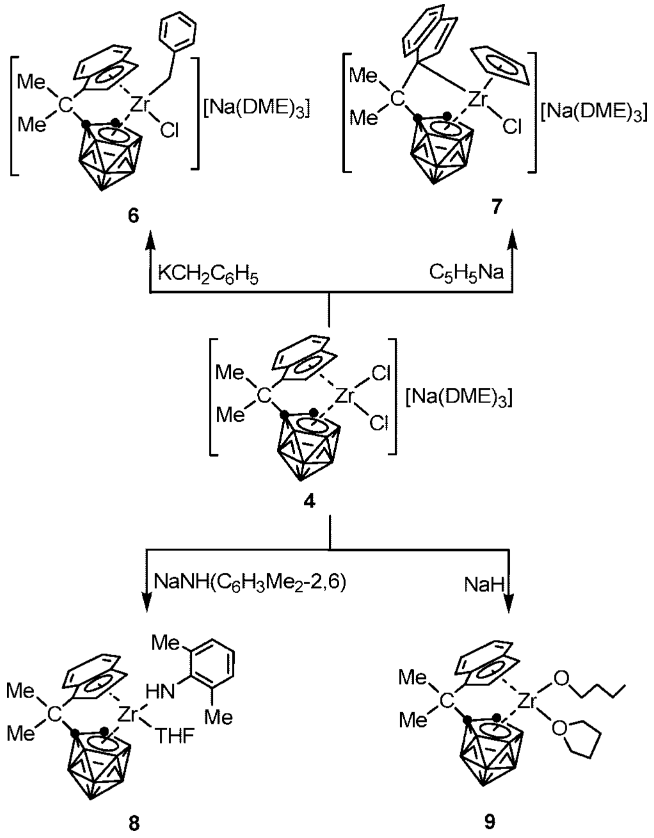
(14) Voskoboynikov, A. Z.; Agarkov, A. Y.; Chernyshev, E. A.; Beletskaya, I. P.; Churakov, A. V.; Kuz′mina, L. G. *J. Organomet. Chem.* **1997**, *530*, 75.

(15) Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

(16) 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.

(17) One broad resonance of the ZrCH_2 protons is likely due to rapid exchange of η^2- and η^1-benzyl groups; see: (a) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235. (b) Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303. (c) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

Scheme 2



tetrahedral geometry (Figure 3; bond distances and angles are given in Table 1). The average Zr−C(C_5 ring) and Zr−cage atom distances of 2.619(6) and 2.591(7) Å are similar to the corresponding values of 2.599(3) and 2.597(3) Å observed in **3**. The Cent(C_5 ring)−Zr−Cent(C_2B_3) angle of 117.3° is quite comparable to that of 115.9° in **3** and 119.3° in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$.[5] The Zr−Cl distance of 2.442(2) Å is very close to that of 2.466(1) Å in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$,[5] 2.421(1)/2.413(1) Å in *meso*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[14] 2.417(1) Å in *rac*-$[Me_2C(C_9H_6)_2]ZrCl_2$,[14] and 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] The Zr−C distance of 2.312(6) Å is comparable to that of 2.316(1) Å in $[\{\eta^5:\eta^5\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$,[5] 2.301(1) Å in $[\eta^5\text{-}C_9H_5\text{-}1,3\text{-}(SiMe_3)_2]_2Zr(OCH_2CH_2CH_2CH_2)$,[19] 2.256(3) Å in $[\eta^5\text{-}C_9H_6\text{-}2\text{-}(5\text{-}Me\text{-}C_4H_3O)]_2Zr(CH_2CMe_3)_2$,[20] 2.298(2)/2.289(2) Å in $(\eta^5\text{-}4,7\text{-}F_2C_9H_6)_2Zr(CH_2C_6H_5)_2$,[17c] and 2.269(2)/2.242(2) Å in [*meso*-$CH_2CH_2\text{-}(4,7\text{-}Me_2\text{-}C_9H_4)_2]ZrMe_2$.[21]

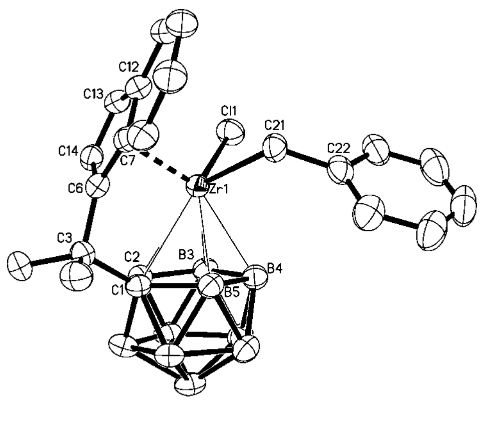


Figure 3. Molecular structure of the anion in *trans*-$[\{\eta^5:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl(CH_2C_6H_5)][Na(DME)_3]$ (**6**) (thermal ellipsoids drawn at the 30% probability level).

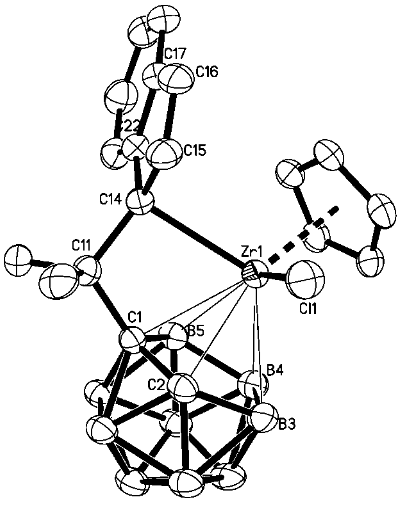


Figure 4. Molecular structure of the anion in *trans*-$[\{\eta^1:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl(\eta^5\text{-}C_5H_5)][Na(DME)_3]$ (**7**) (thermal ellipsoids drawn at the 30% probability level).

Treatment of **4** with 1 equiv of C_5H_5Na in THF at room temperature afforded, after recrystallization from DME, *trans*-$\{[\eta^1:\eta^5\text{-}Me_2C(C_9H_6)(C_2B_9H_{10})]ZrCl(\eta^5\text{-}C_5H_5)\}\{Na(DME)_3\}$ (**7**) in 53% isolated yield (Scheme 2). It was noted that **7** is stable even in refluxing DME, and no elimination of NaCl was observed.[22] Addition of chloride abstracting reagents such as $AgClO_4$ and $AgBPh_4$ led to an inseparable mixture of products, as indicated by NMR spectra. An X-ray diffraction study revealed that the Zr atom in **7** adopts a distorted-tetrahedral geometry by η^5 bonding to both the cyclopentadienyl ring and dicarbollyl ligand and η^1 bonding to the indenyl group and chlorine atom, respectively (Figure 4; bond distances and angles are given in Table 1). The average Zr−cage atom distance of 2.536(8) Å is shorter than that of 2.597(3) in **3** and 2.591(7) Å in **6** but is longer than that of 2.469(8) Å in $[\sigma:\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$.[11a] The average Zr−C(Cp ring) distance of 2.507(7) Å is similar to that of 2.534(3)/2.518(3) Å in $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_3\}$.[5] The Zr−C($\eta^1$) distance of 2.420(6) Å is comparable to that of 2.477(6) Å in $[\sigma:\eta^5\text{-}(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(DME)$[11a] but is much shorter than that of 2.603(8) Å in $(Ph_2C_9H_6P{=}NPh)Zr(CH_2C_6H_5)_3$.[23] The Zr−Cl distance of 2.511(2) Å is longer than that of 2.442(2) Å in **6** but is slightly shorter than that of 2.547(1) Å in $\{[\eta^5:\eta^2\text{-}Me_2C(C_5H_4)(C_2B_9H_{10})]Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}\{Na(DME)_3\}$.[5]

---

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

(19) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 16600.

(20) Dreier, T.; Bergander, K.; Wegelius, E.; Fröhlich, R.; Erker, G. *Organometallics* **2001**, *20*, 5067.

(21) Balboni, D.; Camurati, I.; Prini, G.; Resconi, L.; Galli, S.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2001**, *40*, 6588.

(22) A similar phenomenon is observed; see: (a) Thomas, C. J.; Jia, L.; Zhang, H.; Siriwardane, U.; Maguire, J. A.; Wang, Y.; Brooks, K. A.; Weiss, V. P.; Hosmane, N. S. *Organometallics* **1995**, *14*, 1365. (b) Mao, S. S. H.; Tilley, T. D.; Rheingold, A. L.; Hosmane, N. S. *J. Organomet. Chem.* **1997**, *533*, 257. (c) Hosmane, N. S.; Zhang, H.; Jia, L.; Colacot, T. J.; Maguire, J. A.; Wang, X.; Hosmane, S. N.; Brooks, K. A. *Organometallics* **1999**, *18*, 516. (d) Kwong, W.-C.; Chan, H.-S.; Tang, Y.; Xie, Z. *Organometallics* **2004**, *23*, 4301.

(23) Oulié, P.; Freund, C.; Saffon, N.; Martin-Vaca, B.; Maron, L.; Bourissou, D. *Organometallics* **2007**, *26*, 6793.

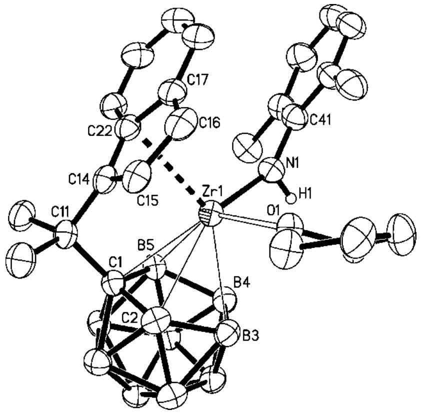


Figure 5. Molecular structure of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NHC_6H_3Me_2$-2,6)(THF) (**8**) (thermal ellipsoids drawn at the 30% probability level).

The aforementioned results show that the chloro group always bonds to the Zr atom to stabilize the electron-deficient metal species, preventing the formation of neutral metal alkyls.[3a] On the other hand, the isolation of **3** suggests that the $p_\pi(N)-d_\pi(Zr)$ interaction can lower the Lewis acidity of the Zr center, resulting in the formation of neutral metal amides. This is supported by the following experiments. Treatment of **4** with 1 equiv of $NaNHC_6H_3Me_2$ in THF at room temperature gave, after recrystallization from toluene, the neutral species *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(NHC_6H_3Me_2)$(THF) (**8**) in 54% isolated yield (Scheme 2). Complex **8** was fully characterized by various spectroscopic techniques and elemental analyses. Its structure was confirmed by a single-crystal X-ray diffraction study. The Zr atom is η^5-bound to both indenyl and dicarbollyl ligands, σ-bound to the amido nitrogen atom, and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 5; bond distances and angles are given in Table 1). The average Zr−C(C_5 ring)/Zr−cage atom distances of 2.577(6)/2.583(6) Å are similar to those of 2.599(3)/2.597(3) Å in **3**. The Cent(C_5 ring)−Zr−-Cent(C_2B_3) angle of 119.4° is larger than that of 115.9° in **3** but is very similar to that of 119.2° in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Zr(NHC_6H_3Pr^i{}_2)$(THF),[5] probably due to steric reasons. The Zr−N distance of 2.035(4) Å is close to that of 2.055(2) Å in [η^5:η^5-$Me_2C(C_5H_4)(C_2B_9H_{10})$]$Zr(NHC_6H_3Pr^i{}_2)$(THF)[5] and 2.057(2) Å in **3**. The relatively large Zr−N−C angle of 150.1(3)° implies the presence of $p_\pi(N)-d_\pi(Zr)$ interactions.

Another example of neutral metal complexes is the metal alkoxide *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(OCH_2CH_2CH_2CH_3)$(THF) (**9**). It was isolated in 33% yield from the reaction of **4** with excess NaH in refluxing THF (Scheme 2). Single-crystal X-ray analyses confirm that **9** is a trans isomer and show a half-molecule of benzene of solvation in the crystal lattice. The Zr atom is η^5-bound to both indenyl and dicarbollyl ligands, σ-bound to the oxygen atom of the alkoxy group, and coordinated to one THF molecule in a distorted-tetrahedral geometry (Figure 6; bond distances and angles are given in Table 1). The average Zr−C(C_5 ring) distance of 2.580(7) Å is similar to that of 2.599(7) Å in **3** and 2.577(6) Å in **8**. The average Zr−cage atom distance of 2.554(8) Å can be compared to that of 2.597(3) Å in **3**, 2.583(6) Å in **8**, and 2.552(6) Å in [{η^1:σ:η^5-[$MeN(CH_2)CH_2CH_2$]$C_2B_9H_{10}$}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$.[4f] The Zr−O distance of 1.930(5) Å is comparable to that of 2.167(3) Å in [{η^1:σ:η^5-[$MeN(CH_2)CH_2CH_2$]$C_2B_9H_{10}$}Zr(μ:η^1-$OCH_2CH_2OCH_3$)]$_2$,[4f] 1.897(3) Å in [*rac*-η^5:η^5-CH_2CH_2-1,2-$(C_9H_6)_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)$][$MeB(C_6F_5)_3$],[24] 2.015(2) Å in [4,6-^{t}Bu$_2$-2-(η^5-C_9H_6)-C_6H_2O]$_2$Zr,[25] 1.979(3)/2.022(3) Å in [*meso*-CH_2CH_2-(4,7-Me_2-$C_9H_4)_2$]$Zr(OC_6F_5)_2$,[21] and 1.918(1) Å in [η^5-C_9H_5-1,3-$(SiMe_3)_2$]$_2$$Zr(OCH_2CH_2CH_2CH_2)$.[19] The Cent($C_5$ ring)−Zr−Cent(C_2B_3) angle of 120.6° in **9** is larger than that of 115.9° in **3** but is close to that of 119.4° in **8**. The C−O−Zr angle of 156.4(6)° is significantly larger than that of 142.4° in [η^5-C_9H_5-1,3-$(SiMe_3)_2$]$_2$$Zr(OCH_2CH_2CH_2CH_2)$[19] and is comparable to that of 152.2(3)° in [*meso*-CH_2CH_2-(4,7-Me_2-$C_9H_4)_2$]$Zr(OC_6F_5)_2$[21] and 159.7(3)° in [*rac*-η^5:η^5-CH_2CH_2-1,2-$(C_9H_6)_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)$][$MeB(C_6F_5)_3$],[24] suggestive of the presence of $p_\pi(O)-d_\pi(Zr)$ interactions. It is assumed that the formation of **9** may involve the organozirconium hydride intermediate,[26] followed by nucleophilic ring opening of THF.[27]

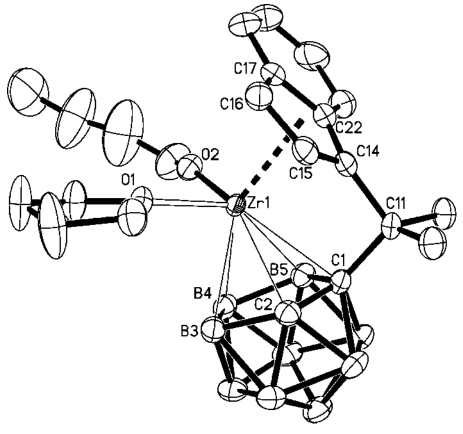


Figure 6. Molecular structure of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]$Zr(OCH_2CH_2CH_2CH_3)$(THF) (**9**) (thermal ellipsoids drawn at the 30% probability level).

Table 2. Ethylene Polymerization Results[a]

catalyst	activity (10^5 g/(mol atm h))	$M_w/10^3$	M_w/M_n[b]	T_m (°C)[c]
3	1.53	52.2	4.3	133.5
4	6.82	38.5	3.5	133.2
6	2.31	41.1	3.9	132.0

[a] Condtions: toluene (50 mL), 1 atm of ethylene, T = 25 °C, catalyst (3.0 μmol), MAO (4.5 mmol), Al/Zr = 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 **3**, **4**, and **6** 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 active catalysts for the polymerization of ethylene in the presence of MAO under the reaction conditions specified in Table 2. Their activities were higher than that of 7.2×10^4 g/(mol atm h) for [$(Cp^*)(C_2B_9H_{11})ZrMe$]$_n$[3a] but lower than (1.38−4.51) × 10^6 g/(mol atm h) observed in the corresponding cyclopentadienyl analogues [$Me_2C(C_5H_4)(C_2B_9H_{10})$]$ZrX_2$.[5] It was noted that the catalytic activity dropped from 6.82×10^5 to 1.21×10^3 g/(mol atm h) for **4** if the Al/Zr molar ratio was decreased from 1500 to 750. When this ratio was 200, only a trace amount of polymer was observed. These

---

[24] Carpentier, J.-F.; Wu, Z.; Lee, C.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750.

[25] Turner, L. E.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2004**, *23*, 1576.

[26] For reaction of Cp_2ZrHCl with KH, forming Cp_2ZrH_2, see: Chen, X.; Liu, S.; Plečnik, C. E.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Organometallics* **2003**, *22*, 275.

[27] For nucleophilic ring opening of THF by [$(C_5H_4Me)_2ZrH$]$^+$ species, see: Guo, Z.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690.

results may indicate that a large excess amount of MAO is necessary to abstract the chloro ligand from the metal complexes, due to the strong interactions between the electron-deficient metal center and Lewis base Cl^-, as previously discussed. The active species might be the neutral metal alkyl $[\eta^5:\eta^5\text{-Me}_2C(C_9H_6)(C_2B_9H_{10})]Zr(Me)$, in view of the properties of $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})]M(Me)$.[3]

Conclusion

The Me_2C-bridged indenyl–dicarbollyl ligand $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ shows features similar to those observed in the corresponding cyclopentadienyl analogue $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$. In the absence of $p_\pi - d_\pi$ interactions between the central metal ion and the σ ligand, both ansa ligands prefer to form metallocene complex ions, due to the high electron deficiency of the central metal atoms.[3] Neutral metallocenes can be achieved only in the presence of amido or alkoxy coligands, which can be ascribed to the formation of $p_\pi - d_\pi$ interactions between the central metal ion and the heteroatom. Complexes **3**, **4**, and **6** are active catalysts for ethylene polymerization after activation with a large excess amount of MAO, but their activities are lower than for the corresponding cyclopentadienyl analogues.

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. $Me_2C(C_9H_7)(C_2B_{10}H_{11})$,[7b] $C_6H_5CH_2K$,[28] 2,6-$Me_2C_6H_3NHNa$,[29] and $MCl_4(THF)_2$ (M = Zr, Hf)[30] were prepared according to literature methods. $Zr(NMe_2)_4$ and 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. ^1H 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. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed by MEDAC Ltd., Middlesex, U.K.

Preparation of $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (2). To an ethanol (20 mL) solution of $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol) was added piperidine (2.5 mL, 25.0 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 piperidine under vacuum, the residue was dissolved in ethanol (3 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 pale yellow crystals (0.32 g, 91%). X-ray-quality crystals were grown from ethanol solution. ^1H NMR (acetone-d_6): δ 7.90 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 6.19 (t, J = 2.1 Hz, 1H) (C_9H_7), 3.22 (m, 2H) (CH_2), 3.15 (s, 9H) ($(CH_3)_3NH$), 1.84 (s, 1H) (CH of $C_2B_9H_{11}$), 1.47 (s, 3H), 1.34 (s, 3H) ($(CH_3)_2C$), −2.8 (br s, 1H) (B−H−B). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 155.1, 146.7, 146.0, 128.5, 126.2, 124.5, 124.4 (C_9H_7), 46.3 ($(CH_3)_3NH$), 40.3 (CH_2), 37.8, 32.0 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (acetone-d_6): δ −10.6 (2), −15.7 (2), −17.9 (1), −18.8 (1), −22.5 (1), −32.7 (1), −36.0 (1). IR (KBr, cm^{-1}): ν_{BH} 2521 (vs). Anal. Calcd for $C_{17}H_{34}B_9N$ (**2**): C, 58.38; H, 9.80; N, 4.00. Found: C, 58.65; H, 9.55; N, 4.25.

Preparation of *trans*-$[\eta^5:\eta^5\text{-Me}_2C(C_9H_6)(C_2B_9H_{10})]Zr(NMe_2)(NHMe_2)$ (3). To a DME (10 mL) solution of $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**2**; 0.20 g, 0.57 mmol) was slowly added a DME (5 mL) solution of $Zr(NMe_2)_4$ (0.16 g, 0.60 mmol) at room temperature, and the reaction mixture was stirred overnight to give a brown solution. After removal of the solvent under vacuum, the residue was extracted with DME (2 × 5 mL). The combined solutions were concentrated to about 5 mL. Complex **3** was isolated as yellow crystals after this solution stood at room temperature for 5 days (0.14 g, 54%). ^1H NMR (pyridine-d_5): δ 7.71 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 3.3 Hz, 1H), 6.89 (d, J = 3.3 Hz, 1H), 6.56 (t, J = 8.2 Hz, 1H), 6.26 (t, J = 8.2 Hz, 1H) (C_9H_6), 3.22 (s, 6H) ($(CH_3)_2N$), 2.32 (s, 6H) ($(CH_3)_2NH$), 1.98 (s, 3H), 1.76 (s, 3H) ($(CH_3)_2C$), 1.46 (s, 1H) (CH of $C_2B_9H_{10}$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 127.7, 126.2, 125.0, 124.7, 124.6, 122.0, 113.4, 111.8 (C_9H_6), 68.2 ($C_2B_9H_{10}$), 39.8, 38.2 ($(CH_3)_2NH$ + $(CH_3)_2N$), 48.0, 29.5, 28.5 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 0.9 (1), −5.3 (2), −8.6 (3), −12.7 (2), −21.5 (1) (note that the integral 2 or 3 boron resonances are due to coincidence). IR (KBr, cm^{-1}): ν_{BH} 2524 (vs). Anal. Calcd for $C_{18}H_{35}B_9N_2Zr$ (**3**): C, 46.20; H, 7.54; N, 5.99. Found: C, 45.91; H, 7.46; N, 6.01.

Preparation of *trans*-$[\{\eta^5:\eta^5\text{-Me}_2C(C_9H_6)(C_2B_9H_{10})\}ZrCl_2][Na(DME)_3]$ (4). To a THF (40 mL) solution of $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**2**; 0.64 g, 1.83 mmol) was added NaH (0.32 g, 13.3 mmol), and the reaction mixture was heated to reflux for 2 days. The excess NaH was filtered off and washed with THF (3 mL). The resulting solution of $[Me_2C(C_9H_6)(C_2B_9H_{10})]Na_3(THF)_x$ was slowly added to a suspension of $ZrCl_4(THF)_2$ (0.69 g, 1.82 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 which was extracted with DME (2 × 10 mL). The DME solutions were combined and concentrated to about 8 mL, to which was added hexane (10 mL). Complex **4** was isolated as a pale yellow crystalline solid after this solution stood at room temperature for 3 days (0.89 g, 60%). ^1H NMR (pyridine-d_5): δ 7.71 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.34 (m, 1H), 6.90 (m, 1H), 6.75 (s, 1H), 6.66 (s, 1H) (C_9H_6), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 1.80 (s, 1H) (CH of $C_2B_9H_{10}$), 1.85 (s, 3H), 1.74 (s, 3H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 130.4, 126.6, 125.6, 125.0, 124.4, 120.2, 113.8, 110.9 107.1 (C_9H_6), 71.4, 57.9 (DME), 66.3, 52.1 ($C_2B_9H_{10}$), 40.5, 30.0, 29.1 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): δ 4.7 (1), −2.1 (1), −5.7 (3), −11.3 (3), −18.8 (1). IR (KBr, cm^{-1}): ν_{BH} 2530 (vs). Anal. Calcd for $C_{26}H_{52}B_9Cl_2NaO_6Zr$ (**4**): C, 42.02; H, 7.05. Found: C, 42.00; H, 7.21.

Preparation of *trans*-$[\{\eta^5:\eta^5\text{-Me}_2C(C_9H_6)(C_2B_9H_{10})\}HfCl_2][Na(DME)_3]$ (5). This compound was prepared as a pale yellow solid from $[Me_3NH][Me_2C(C_9H_7)(C_2B_9H_{11})]$ (**2**; 0.63 g, 1.81 mmol), NaH (0.32 g, 13.3 mmol), and $HfCl_4(THF)_2$ (0.84 g, 1.81 mmol) in THF (50 mL) using the same procedure reported for **4**: yield 0.81 g (54%). ^1H NMR (pyridine-d_5): δ 7.96 (d, J = 8.3 Hz, 1H), 7.69 (m, 1H), 7.37 (m, 1H), 7.07 (m, 1H), 6.83 (d, J = 3.6 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H) (C_9H_6), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 1.80 (s, 1H) (CH of $C_2B_9H_{10}$), 1.83 (s, 3H), 1.71 (s, 3H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 129.4, 125.5, 125.2, 124.8, 124.7, 118.3, 112.2, 109.1, 106.5 (C_9H_6), 71.4, 58.0 (DME), 66.7, 50.2 ($C_2B_9H_{10}$), 40.1, 30.2, 28.5 ($(CH_3)_2C$). $^{11}B\{^1H\}$NMR (pyridine-d_5): δ 3.1 (1), −3.0 (1), −5.8 (3), −13.2 (3), −20.7 (1).

---

(28) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-González, D.; Parkin, A.; Parsons, S *Chem. Eur. J.* **2003**, *9*, 4820.

(29) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652.

(30) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Table 3. Crystal Data and Summary of Data Collection and Refinement for 2, 3, and 6−9

	2	**3**	**6**	**7**	**8**·0.5C_6H_6	**9**·0.5C_6H_6
formula	$C_{17}H_{34}B_9N$	$C_{18}H_{35}B_9N_2Zr$	$C_{33}H_{59}B_9ClNaO_6Zr$	$C_{31}H_{57}B_9ClNaO_6Zr$	$C_{29}H_{43}B_9NOZr$	$C_{25}H_{42}B_9O_2Zr$
cryst size (mm)	0.65 × 0.30 × 0.15	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.20	0.20 × 0.10 × 0.05	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10
fw	349.7	468.0	798.8	772.7	610.2	563.1
cryst syst	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	9.345(1)	14.140(3)	12.265(3)	11.494(2)	27.994(6)	9.879(1)
b, Å	13.462(2)	10.683(2)	13.110(3)	12.777(3)	14.806(3)	11.449(1)
c, Å	34.022(5)	16.648(3)	13.761(3)	14.431(3)	17.521(4)	13.980(1)
α, deg	90	90	78.22(3)	83.71(3)	90	95.84(1)
β, deg	90	111.59(3)	83.36(3)	74.74(3)	93.31(3)	108.74(1)
γ, deg	90	90	84.01(3)	88.56(3)	90	93.90(1)
V, $Å^3$	4280.0(1)	2338.4(8)	2144.1(7)	2032.3(7)	7250.0(3)	1481.0(2)
Z	8	4	2	2	8	2
D_{calcd}, Mg/m^3	1.086	1.329	1.237	1.263	1.118	1.263
radiation (*λ*), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2*θ* range, deg	2.4−50.0	3.1−51.0	3.0−51.7	3.2−50.0	2.9−50.0	3.1−50.0
μ, mm^{-1}	0.055	0.479	0.367	0.385	0.325	0.393
F(000)	1504	968	836	808	2536	586
no. of obsd rflns	3366	4214	5695	5236	5595	5195
no. of params refined	280	271	460	442	372	334
goodness of fit	1.023	1.062	1.050	1.131	1.209	1.019
R1	0.097	0.043	0.063	0.078	0.074	0.068
wR2	0.262	0.121	0.154	0.221	0.237	0.175

IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). Anal. Calcd for $C_{26}H_{52}B_9Cl_2NaO_6Hf$ (**5**): C, 37.61; H, 6.31. Found: C, 37.32; H, 6.16.

Preparation of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}ZrCl($CH_2C_6H_5$)][Na(DME)$_3$] (6). To a THF (15 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**4**; 0.50 g, 0.86 mmol) was added a THF (10 mL) solution of $KCH_2C_6H_5$ (0.11 g, 0.86 mmol) at −78 °C, and the reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was evaporated under vacuum, and the residue was extracted with DME (5 mL × 3). The DME solutions were combined and concentrated to about 5 mL. Complex **6** was isolated as orange crystals after this solution stood at −30 °C for 4 days (0.20 g, 29%). ^1H NMR (pyridine-d_5): *δ* 7.74 (d, *J* = 8.2 Hz, 1H), 7.49 (m, 2H), 7.39 (m, 2H), 7.23−6.80 (m, 4H), 6.71 (d, *J* = 3.6 Hz, 1H), 5.27 (d, *J* = 3.6 Hz, 1H) ($CH_2C_6\mathit{H}_5$ + $C_9\mathit{H}_6$), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 2.60 (s, 2H) ($C\mathit{H}_2C_6H_5$), 2.20 (s, 1H) (C*H* of $C_2B_9H_{10}$), 1.81 (s, 3H), 1.12 (s, 3H) (($C\mathit{H}_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): *δ* 154.8, 130.3, 129.3, 127.0, 126.5, 126.0, 125.6, 124.6, 123.9, 122.1, 121.3, 115.8, 112.4, 104.6 ($CH_2\mathit{C}_6H_5$ + C_9H_6), 71.1, 58.8 (DME), 70.3 ($\mathit{C}H_2C_6H_5$), 65.3, 52.0 ($\mathit{C}_2B_9H_{10}$), 40.7, 29.7, 29.4 (($\mathit{C}H_3)_2\mathit{C}$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): *δ* 0.9 (1), −0.8 (1), −2.7 (1), −5.5 (1), −7.0 (2), −11.3 (1), −13.3 (1), −20.1 (1). IR (KBr, cm^{-1}): ν_{BH} 2533 (vs). Anal. Calcd for $C_{27}H_{44}B_9ClNaO_3Zr$ (**6**–1.5DME): C, 48.87; H, 6.68. Found: C, 48.97; H, 7.06.

Preparation of *trans*-[{η^1:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}ZrCl($\eta^5$-$C_5H_5$)][Na(DME)$_3$] (7). To a DME (10 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**4**; 0.25 g, 0.34 mmol) was slowly added a DME (5 mL) solution of C_5H_5Na (0.03 g, 0.34 mmol) at −20 °C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the precipitate, the DME solution was concentrated to about 6 mL under vacuum, to which was added toluene (1 mL). Complex **7** was isolated as red crystals after this solution stood at room temperature for 3 days (0.14 g, 53%). ^1H NMR (pyridine-d_5): *δ* 8.38 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.38 (m, 2H), 6.98 (m, 1H), 6.35 (m, 1H) ($C_9\mathit{H}_6$), 6.08 (s, 5H) ($C_5\mathit{H}_5$), 3.48 (s, 12H), 3.25 (s, 18H) (DME), 2.61 (s, 1H) (C*H* of $C_2B_9H_{10}$), 1.85 (s, 3H), 1.71 (s, 3H) (($C\mathit{H}_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): *δ* 153.8, 144.8, 127.7, 125.3, 123.7, 120.3, 119.9, 119.6, 119.4 (C_9H_6), 115.4 (C_5H_5), 84.2 ($C_2B_9H_{10}$), 71.3, 57.9 (DME), 36.7, 31.1, 28.2 (($\mathit{C}H_3)_2\mathit{C}$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): *δ* 3.8 (1), −3.6 (1), −4.9 (1), −6.4 (2), −10.6 (1), −12.4 (1), −16.2 (2). IR (KBr, cm^{-1}): ν_{BH} 2520 (s). Anal. Calcd for $C_{31}H_{57}B_9ClNaO_6Zr$ (**7**): C, 48.18; H, 7.43. Found: C, 48.01; H, 7.45.

Preparation of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($NHC_6H_3Me_2$-2,6)(THF) (8). To a THF (20 mL) solution of *trans*-[{η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$}$ZrCl_2$][Na(DME)$_3$] (**4**; 0.71 g, 0.96 mmol) was slowly added a THF (5 mL) solution of $NaNHC_6H_3Me_2$-2,6 (0.14 g, 0.96 mmol) at −78 °C, and the reaction mixture was stirred at room temperature for 2 days. After removal of the solvent, the residue was extracted with toluene (15 mL × 3). The toluene solutions were combined and concentrated to about 10 mL. Complex **8** was isolated as yellow crystals after this solution stood at room temperature for 3 days (0.32 g, 54%). X-ray-quality crystals were grown from a benzene solution. ^1H NMR (pyridine-d_5): *δ* 9.38 (s, 1H) (N*H*), 7.86 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.96 (m, 1H), 6.91 (m, 1H), 6.86−6.75 (m, 2H) ($C_9\mathit{H}_6$), 7.04 (d, *J* = 7.5 Hz, 2H), 6.41 (m, 1H) ($NHC_6\mathit{H}_3(CH_3)_2$)), 3.64 (m, 4H), 1.59 (m, 4H) (THF), 2.31 (s, 6H) ($NHC_6H_3(C\mathit{H}_3)_2$), 1.99 (s, 3H), 1.70 (s, 3H) (($C\mathit{H}_3)_2C$). $^{13}C\{^1H\}$ NMR (pyridine-d_5): *δ* 154.0, 129.8, 127.7, 126.5, 125.3, 124.7, 123.8, 121.9, 120.8, 118.9, 114.7, 111.8, 110.3, 108.9 (aromatic *C*), 67.1, 25.1 (THF), 51.1 ($\mathit{C}_2B_9H_{10}$), 40.7, 29.0, 28.9 (($\mathit{C}H_3)_2\mathit{C}$), 20.1, 17.3 ($NHC_6H_3(\mathit{C}H_3)_2$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): *δ* 4.5 (1), −3.3 (1), −4.6 (1), −6.7 (2), −11.5 (3), −18.6 (1). IR (KBr, cm^{-1}): ν_{BH} 2524 (s). Anal. Calcd for $C_{24}H_{36}B_9NO_{0.5}Zr$ (**8**–0.5THF): C, 53.87; H, 6.78; N, 2.62. Found: C, 53.55; H, 6.66; N, 2.36.

Preparation of *trans*-[η^5:η^5-$Me_2C(C_9H_6)(C_2B_9H_{10})$]Zr($OCH_2CH_2CH_2CH_3$)(THF) (9). To a THF solution (15 mL) of **4** (0.37 g, 0.5 mmol) was added NaH (48 mg, 2.0 mmol), and the mixture was refluxed for 2 days. After removal of excess NaH, the clear solution was evaporated to dryness. The residue was extracted with toluene (8 mL × 3). The toluene solutions were combined and concentrated to about 15 mL. Complex **9** was isolated as pale yellow crystals after this solution stood at room temperature for 5 days (0.09 g, 33%). X-ray-quality crystals were grown from a benzene solution. ^1H NMR (pyridine-d_5): *δ* 8.37 (d, *J* = 7.8 Hz, 1H), 7.97 (m, 1H), 6.90 (s, 2H), 6.66 (m, 1H), 6.35 (m, 1H) ($C_9\mathit{H}_6$), 3.64 (m, 4H) (THF), 3.51 (t, *J* = 7.5 Hz, 2H) ($OC\mathit{H}_2$), 2.61 (s, 1H) (C*H* of $C_2B_9H_{10}$), 2.07 (s, 3H), 1.78 (s, 3H) (($C\mathit{H}_3)_2C$), 1.62 (m, 2H), 1.20 (m, 2H), 0.84 (t, *J* = 7.0 Hz, 3H) ($OCH_2CH_2CH_2C\mathit{H}_3$), 1.59 (m, 4H) (THF). $^{13}C\{^1H\}$ NMR (pyridine-d_5): *δ* 130.0, 127.7, 127.1, 125.3, 124.7, 113.7, 111.0, 106.9 (C_9H_6), 84.9, 50.3 ($\mathit{C}_2B_9H_{10}$), 74.1 ($O\mathit{C}H_2CH_2CH_2CH_3$), 37.0, 20.6, 17.0 ($OCH_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_3$), 67.2, 25.1 (THF), 41.1 (($CH_3)_2\mathit{C}$), 30.2, 28.6 (($\mathit{C}H_3)_2C$). $^{11}B\{^1H\}$ NMR (pyridine-d_5): *δ* 2.0 (1), −1.9 (1), −6.7 (3), −10.0 (1), −12.9 (1), −15.0 (1), −20.0 (1). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). Anal. Calcd for $C_{22}H_{39}B_9O_2Zr$ (**9**): C, 50.42; H, 7.50. Found: C, 50.23; H, 7.39.

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.[31] 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.[32] 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 **8** and **9** showed half-molecules of benzene of solvation, respectively. Crystal data and details of data collection and structure refinements are given in Table 3. 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 to Z.X. and 20710011 to Y.T.) and a Direct Grant (Project Code 2060340).

Supporting Information Available: Crystallographic data in CIF format for **2**, **3**, **6**, **7**, **8**·$0.5C_6H_6$, and **9**·$0.5C_6H_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800452F

---

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

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