

# Reactions of $L_2Zr(NMe_2)_2$ with $Me_3Al$ and $PhC\equiv CH$ : synthesis and structural characterization of new zirconium carborane complexes [ $L_2 = Me_2Si(C_9H_6)(C_2B_{10}H_{10})$ and $Me_2C(C_5H_4)(C_2B_{10}H_{10})$ ]

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## Abstract

Reaction of  $[\eta^5\text{-}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$  with excess  $Me_3Al$  in toluene gave  $[\eta^5\text{-}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(\mu\text{-}Me)_2AlMe_2(NMe_2)$  (**2**). **2** is inactive toward ethylene, but shows a very high activity in ethylene polymerization upon activation with modified methylalumoxane. Recrystallization of **2** from THF/toluene afforded  $\{[\eta^5\text{-}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr\}_2(\mu\text{-}O)\{\mu\text{-}N[AlMe_2(THF)]\}$  (**3**). Treatment of  $[\eta^5\text{-}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$  with two equivalents of  $PhC\equiv CH$  produced, after recrystallization from THF/toluene,  $\{[\eta^5\text{-}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)\}_2\{\eta^2\text{-}\eta^2\text{-}(PhC=C=C=CPh)\}$  (**5**). They were characterized by various spectroscopic data and elemental analyses. Compounds **3** and **5** were further confirmed by single-crystal X-ray analyses.

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**Keywords:** Carborane; Cumulene; Metal alkyl; Metallacycle; Metal amide

## 1. Introduction

It has been documented that a ligand containing bifunctional groups often offers complexes with some additional advantage [1]. Recently developed constrained-geometry ligands containing both monocyclopentadienyl and  $\sigma$ -heteroatom components have attracted considerable attention [2]. Group 4 metallocenes derived from these ligands are very active catalysts for the copolymerization of ethylene with  $\alpha$ -olefins due to the increased electron-deficiency and more open coordination environment of the central metal ions [2]. Given the impact of the cyclopentadienyl-appended heteroatom donor groups on the catalytic performance of the Group 4 metal complexes, we have recently designed several silicon-, carbon- and boron-bridged

versatile ligands,  $Me_2A(C_5H_5)(C_2B_{10}H_{11})$  ( $A = C$  [3], Si [4]),  $Me_2A(C_9H_7)(C_2B_{10}H_{11})$  ( $A = C$  [5], Si [6]),  $Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})$  [7], and  $iPr_2NB(C_9H_7)(C_2B_{10}H_{11})$  [8], which can be conveniently converted into a novel class of constrained-geometry ligands bearing a carboanion as  $\sigma$ -donor. These ligands contain a highly electron-deficient carborane moiety, which can enhance the Lewis acidity of the central metal ion, leading to a class of extremely reactive catalysts for ethylene polymerization [9,10].

It is suggested that treatment of  $L_2Zr(NMe_2)_2$  or  $L_2ZrCl_2$  [ $L_2 = Me_2Si(C_9H_6)(C_2B_{10}H_{10})$  and  $Me_2C(C_5H_4)(C_2B_{10}H_{10})$ ] with excess methylalumoxane gives the active species  $[L_2ZrMe]^+$  that catalyze the polymerization of olefins [9,10]. These proposed species contain three types of Zr–C bondings: Zr–C  $\pi$ -bond, Zr–cage C  $\sigma$ -bond and Zr–Me  $\sigma$ -bond, respectively. We are interested in this system and attempt to prepare this type of compounds. This paper reports our studies on the reactions of  $L_2Zr(NMe_2)_2$  with  $Me_3Al$  and  $PhC\equiv CH$ .

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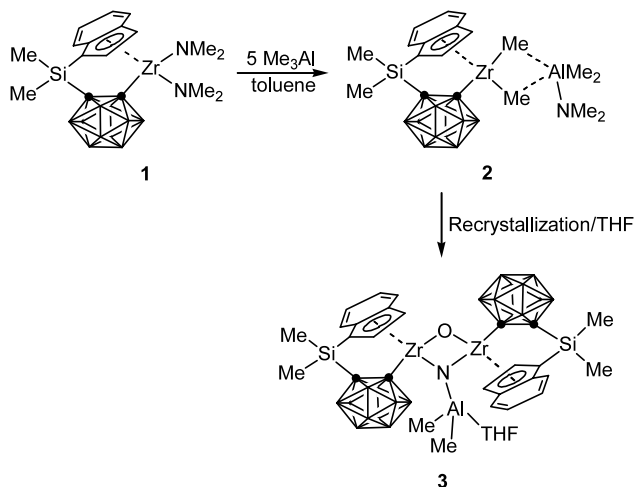
E-mail address: [zxie@cuhk.edu.hk](mailto:zxie@cuhk.edu.hk) (Z. Xie).

## 2. Results and discussion

### 2.1. Reaction of $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ with $\text{Me}_3\text{Al}$

It has been reported that the Zr–NMe<sub>2</sub> bond can be conveniently converted into the Zr–Me one by treatment with excess Me<sub>3</sub>Al [11]. Reaction of  $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$  (**1**) with five equivalents of Me<sub>3</sub>Al in toluene at –30 to 25 °C gave  $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2(\text{NMe}_2)$  (**2**) in 50% isolated yield, shown in Scheme 1. Its composition was confirmed by various spectroscopic data and elemental analyses. Many attempts were made to grow X-ray-quality crystals from toluene or CH<sub>2</sub>Cl<sub>2</sub> or a mixed solvent of toluene/hexane and CH<sub>2</sub>Cl<sub>2</sub>/hexane, but all failed. Suitable single-crystals for X-ray analysis were obtained from a solution of toluene/THF at room temperature over weeks. The <sup>1</sup>H-NMR spectrum indicates the presence of AlMe<sub>2</sub>, THF and the ligand in the ratio of 1:1:2 and absence of both Zr–Me and NMe protons, which is significantly different from that of **2**. Its <sup>11</sup>B-NMR spectrum resembles that of **2** showing a 1:1:2:1 splitting pattern. Its composition was identified as  $\{[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}\}_2(\mu\text{-O})\{(\mu\text{-N}[\text{AlMe}_2(\text{THF})])\} \cdot 0.5(\text{C}_7\text{H}_8)$  (**3**·0.5C<sub>7</sub>H<sub>8</sub>) by a combination of spectroscopic data, elemental analyses and single-crystal X-ray analyses.

The solid-state structure of **3** is shown in Fig. 1. It consists of two  $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}$  units connected by a μ-oxo and a μ-imido group, respectively, and shows half toluene of solvation. Each Zr(IV) ion is η<sup>5</sup>-bound to the five-membered ring of the indenyl group and σ-bound to one cage carbon atom, one doubly bridging oxygen atom and one doubly bridging nitrogen atom in a distorted-tetrahedral geometry. The average Zr–C (C<sub>5</sub> ring) distance of 2.527(6) Å and Zr–C (σ) distance of 2.319(6) are similar to those found in **1**



Scheme 1.

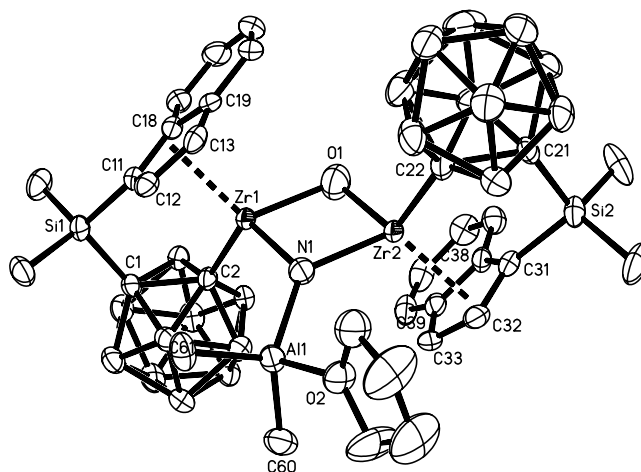


Fig. 1. Perspective view of the molecular structure of **3**.

[9] (Table 1). The average Zr–O distance of 2.201(5) Å and Zr–N distance of 2.163(5) Å compare to the corresponding values of 2.123(6) and 2.084(7) Å in  $\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\}\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\}(\mu\text{-NBu}^t)(\text{OCO})$  [12].

The unusual small Zr–O–Zr angle of 94.2(2)° in **3** represents a very rare example of a zirconium complex

Table 1  
Selected bond lengths (Å) and angles (°)

For compound <b>3</b>			
<i>Bond lengths</i>			
Zr1–N1	2.177(5)	Zr2–N1	2.149(5)
Zr1–O1	2.177(5)	Zr2–O1	2.225(5)
Zr1–C2	2.322(5)	Zr2–C22	2.315(6)
Zr1–C11	2.513(5)	Zr2–C31	2.510(5)
Zr1–C12	2.486(5)	Zr2–C32	2.450(6)
Zr1–C13	2.493(6)	Zr2–C33	2.481(5)
Zr1–C18	2.569(5)	Zr2–C38	2.588(6)
Zr1–C19	2.578(5)	Zr2–C39	2.579(5)
Al1–O2	1.933(4)	Al1–C60	1.988(7)
Al1–C61	1.981(6)	Al1–N1	2.008(5)
<i>Bond angles</i>			
N1–Zr1–O1	84.9(2)	N1–Zr2–O1	84.4(2)
Zr1–O1–Zr2	94.2(2)	Zr2–N1–Zr1	96.4(2)
For compound <b>5</b>			
<i>Bond lengths</i>			
Zr1–N1	1.988(12)	Zr2–N2	1.990(12)
Zr1–C2	2.332(14)	Zr2–C32	2.331(15)
Zr1–C21	2.439(13)	Zr2–C51	2.444(13)
Zr1–C22	2.308(13)	Zr2–C52	2.311(14)
Zr1–C11	2.510(13)	Zr2–C41	2.512(13)
Zr1–C12	2.502(14)	Zr2–C42	2.522(16)
Zr1–C13	2.495(17)	Zr2–C43	2.511(16)
Zr1–C14	2.518(16)	Zr2–C44	2.502(16)
Zr1–C15	2.510(15)	Zr2–C45	2.520(13)
C21–C22	1.268(17)	C51–C52	1.298(18)
C21–C21a	1.38(3)	C51–C51b	1.35(3)
<i>Bond angles</i>			
C21–C22–C23	128.9(13)	C51–C52–C53	128.1(13)
C22–C21–C21a	150.3(18)	C52–C51–C51b	150.2(18)

Symmetry transformation: a:  $-x+1, -y+1, -z+1$ ; b:  $-x+2, -y, -z+1$ .

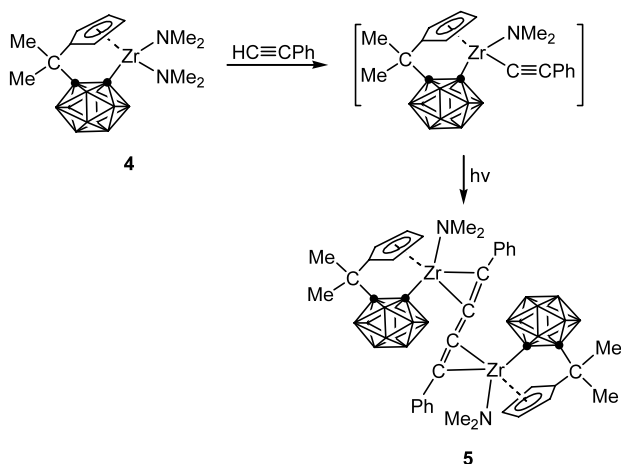
bearing a  $Zr_2NO$  four-membered unit. The closest example reported in the literature is  $[(\eta^5-C_5H_5)_2Zr]_2(\mu-O)(\mu-NBu^t)$  with no structural data [13]. The formation of **3** is not yet clear. But it might involve the elimination of ethane followed by partial hydrolysis.

Compound **2** is inactive toward ethylene. It, however, can catalyze the polymerization of ethylene upon activation with modified methylalumoxane (MMAO). The activity is about  $3.0 \times 10^6$  g (mol atm h) $^{-1}$  at 60 °C in toluene, which is in the same range as its chloride analogues [9].

## 2.2. Reaction of $[\eta^5:\sigma-Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with $PhC\equiv CH$

It has been documented that reaction of  $Cp_2Zr(NMe_2)_2$  with  $PhC\equiv CH$  gives  $Cp_2Zr(C\equiv CPh)_2$  in good yield [14]. Treatment of  $[\eta^5:\sigma-Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$  (**4**) with two equivalents of  $PhC\equiv CH$  in toluene afforded, after recrystallization from THF/toluene,  $\{[\eta^5:\sigma-Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2\}_2\{\eta^2:\eta^2-(PhC=C=C=CPh)\} \cdot THF$  (**5**·THF) in 38% yield, shown in Scheme 2. The  $^1H$ -NMR spectrum shows the presence of phenyl,  $NMe_2$ , THF and the ligand in the ratio of 2:2:1:2. Its  $^{11}B$ -NMR spectrum is similar to that of **4**, displaying a 1:1:2:1 splitting pattern [9]. It is unexpected that only one of the two  $NMe_2$  groups is converted into  $PhCC$  unit, the other one remains intact since two equivalents of  $PhC\equiv CH$  presents in the reaction system. Species  $[\eta^5:\sigma-Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)(C\equiv CPh)$  may serve as an intermediate, which then leads to the formation of **5** in the presence of daylight over the period of recrystallization. Light is necessary for this conversion [15,16].

The molecular structure of **5** was confirmed by single-crystal X-ray analyses. There are two crystallographically independent molecules in the unit cell, and one of them is shown in Fig. 2. It is a centrosymmetric molecule



Scheme 2.

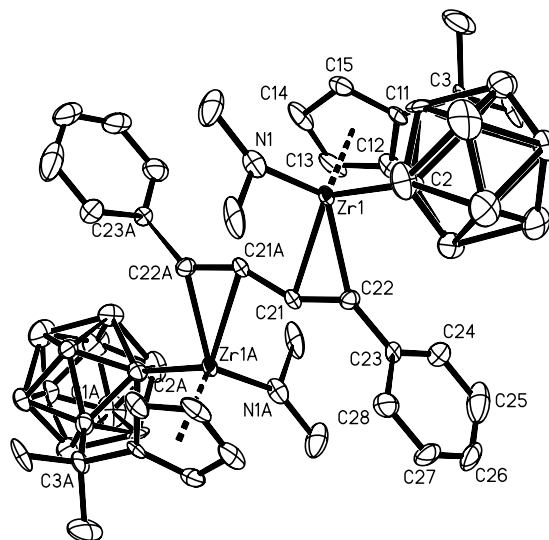


Fig. 2. Perspective view of the molecular structure of **5**.

consisting of two  $[\eta^5:\sigma-Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)$  fragments and one  $\eta^2:\eta^2-(PhC=C=C=CPh)$  cumulene unit. The average Zr–C ( $C_5$  ring) distance of 2.507(16) Å [2.513(16) Å], Zr–C ( $\sigma$ ) distance of 2.332(14) Å [2.331(15) Å] and Zr–N distance of 1.998(12) Å [1.990(12) Å] are very close to the corresponding values found in its parent compound **4** [9] (distances in the brackets are those of the second molecule). The Zr–C ( $\eta^2$ ) (2.308(13), 2.439(13), 2.311(14), 2.444(13) Å), C(21)–C(22) (1.27(2) Å) and C(21)–C(21A) (1.38(3) Å) distances are comparable to the corresponding values found in  $(\eta^5-C_5Me_5)_2Zr[\eta^4-(PhC=C=C=CPh)]$  [15]. The geometry of the  $\eta^2:\eta^2-(PhC=C=C=CPh)$  fragment is very close to that observed in  $\{(\eta^5-C_5Me_5)_2Sm\}_2\{\eta^2:\eta^2-(PhC=C=C=CPh)\}$  [17].

In summary, the reactivity patterns of  $L_2Zr(NMe_2)_2$  are different from those of  $Cp_2Zr(NMe_2)_2$ , probably due to electronic/steric effects of the carboranyl moiety.

## 3. Experimental

### 3.1. General procedure

All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. Solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compounds **1** and **4** were prepared according to the literature methods [9]. 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 spectro-

meter.  $^1\text{H-NMR}$  spectra were recorded on a Bruker DPX 300 spectrometer at 300.13 MHz.  $^{11}\text{B-NMR}$  spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts are reported in  $\delta$  units with references to the residual protons of the deuterated solvents for proton chemical shifts, and to external  $\text{BF}_3 \cdot \text{OEt}_2$  (0.0 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, UK.

### 3.2. Preparation of $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{]Zr}(\mu\text{-Me})_2\text{AlMe}_2(\text{NMe}_2)$ (**2**)

A 2.0 M solution of  $\text{AlMe}_3$  in *n*-hexane (2.50 ml, 5.00 mmol) was slowly added to a toluene (30 ml) solution of  $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{]Zr}(\text{NMe}_2)_2$  (**1**; 0.50 g, 1.01 mmol) with stirring at  $-30^\circ\text{C}$ , resulting in the formation of a yellow suspension. This solution was then stirred at room temperature overnight. After removal of ca. 15 ml of solvent, the resultant precipitate was collected and washed with *n*-hexane (20 ml  $\times$  3) giving **2** as a yellow solid (0.27 g, 50%).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.60 (d,  $J = 7.5$  Hz, 1H, indenyl), 7.08–6.90 (m, 3H, indenyl), 6.10 (d,  $J = 3.6$  Hz, 1H, indenyl), 5.90 (d,  $J = 3.6$  Hz, 1H, indenyl), 2.74 (s, 6H,  $\text{NMe}_2$ ), 0.43 (s, 3H,  $\text{SiMe}_2$ ), 0.29 (s, 3H,  $\text{SiMe}_2$ ),  $-0.40$  (s, 6H,  $\text{ZrMe}_2$ ),  $-0.64$  (s, 6H,  $\text{AlMe}_2$ ).  $^{11}\text{B-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-1.45$  (2B),  $-2.80$  (2B),  $-8.55$  (4B),  $-11.93$  (2B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3066 (w), 2958 (m), 2905 (m), 2870 (m), 2563 (vs), 1412 (m), 1257 (m), 1086 (s), 1047 (m), 808 (s). Anal. Found: C, 42.31; H, 7.72; N, 2.45.  $\text{C}_{19}\text{H}_{40}\text{AlB}_{10}\text{NSiZr}$  Calc.: C, 42.50; H, 7.50; N, 2.61%.

### 3.3. Preparation of $\{[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{]Zr}\}_2(\mu\text{-O})\{\mu\text{-N}[\text{AlMe}_2(\text{THF})]\}_0.5(\text{C}_7\text{H}_8)$ (**3**· $0.5\text{C}_7\text{H}_8$ )

Recrystallization of **2** (0.10 g, 0.18 mmol) from THF/toluene (1:5, 15 ml) at room temperature afforded **3**· $0.5\text{C}_7\text{H}_8$  as pale-yellow crystals over weeks (28 mg, 30%).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.80 (d,  $J = 8.5$  Hz, 2H, indenyl), 7.12–6.80 (m, 8H, indenyl+phenyl), 6.30 (d,  $J = 3.6$  Hz, 2H, indenyl), 6.10 (d,  $J = 3.6$  Hz, 2H, indenyl), 3.65 (m, 4H, THF), 2.04 (s, 1.5H,  $\text{C}_6\text{H}_5\text{CH}_3$ ), 1.61 (m, 4H, THF), 0.55 (s, 6H,  $\text{SiMe}_2$ ), 0.43 (s, 6H,  $\text{SiMe}_2$ ),  $-0.75$  (s, 6H,  $\text{AlMe}_2$ ).  $^{11}\text{B-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-1.48$  (2B),  $-2.93$  (2B),  $-8.72$  (4B),  $-12.03$  (2B). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3071 (w), 2962 (m), 2915 (m), 2865 (m), 2560 (vs), 1417 (m), 1262 (m), 1078 (s), 1056 (m), 821 (s). Anal. Found: C, 42.21; H, 6.30; N, 1.25.  $\text{C}_{35.5}\text{H}_{62}\text{AlB}_{20}\text{NO}_2\text{Si}_2\text{Zr}_2$  Calc.: C, 41.94; H, 6.15; N, 1.38%.

### 3.4. Preparation of $\{[\eta^5\text{-}\sigma\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{]Zr}(\text{NMe}_2)\}_2\{\eta^2\text{-}\eta^2\text{-}(\text{C}_6\text{H}_5\text{C}=\text{C}=\text{C}=\text{CC}_6\text{H}_5)\}_0.5 \cdot \text{THF}$ (**5**·THF)

To a toluene solution (50 ml) of  $[\eta^5\text{-}\sigma\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{]Zr}(\text{NMe}_2)_2$  (**4**; 0.75 g, 1.76 mmol) was added  $\text{HCCC}_6\text{H}_5$  (0.36 g, 3.52 mmol) at room temperature and the reaction mixture was stirred for 4 days, leading to a suspension. After removal of part of solvent (ca. 20 ml), the pale-yellow precipitate was collected by filtration and washed with hexane (5 ml  $\times$  3) to give **5** as a pale-yellow solid (0.35 g, 38%). Single-crystals suitable for X-ray analyses were obtained by recrystallization from a THF/toluene solution.  $^1\text{H-NMR}$  (pyridine- $d_5$ ):  $\delta$  7.58 (m, 4H), 7.50 (m, 4H), 7.34 (m, 2H) ( $\text{CCC}_6\text{H}_5$ ), 6.31 (m, 4H), 5.62 (m, 4H) ( $\text{C}_5\text{H}_4$ ), 3.63 (m, 4H, THF), 2.95 (s, 12H) ( $\text{N}(\text{CH}_3)_2$ ), 1.58 (m, 4H, THF), 1.65 (s, 12H) ( $(\text{CH}_3)_2\text{C}$ ).  $^{11}\text{B-NMR}$  (pyridine- $d_5$ ):  $\delta$   $-4.28$  (2),  $-6.35$  (2),  $-9.91$  (4),  $-11.82$  (2). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3050 (m), 2973 (m), 2874 (m), 2568 (vs), 1637 (w), 1475 (m), 1259 (m), 1048 (s), 925 (w), 807 (s), 747 (m). Anal. Found: C, 49.31; H, 6.57; N, 2.69.  $\text{C}_{40}\text{H}_{62}\text{B}_{20}\text{N}_2\text{Zr}_2$  (**5**) Calc.: C, 49.55; H, 6.45; N, 2.89%.

### 3.5. 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 **2** (3.0  $\mu\text{mol}$ ) together with MMAO (4.5 mmol) and toluene (50 ml). The mixture was stirred at  $60^\circ\text{C}$  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  $80^\circ\text{C}$  overnight (4.49 g).

### 3.6. X-ray structure determination

All single-crystals were immersed in Paratone-N oil and sealed under  $\text{N}_2$  in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K $\alpha$  radiation. An empirical absorption correction was applied using the SADABS program [18]. Both structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on  $F^2$  using the SHELXTL program package [19]. Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Note that thermal parameters of the solvated THF molecules in **5** are high, indicating disorder problems, which cause the



Table 2  
Crystal data and summary of data collection and refinement details for **3**·0.5C<sub>7</sub>H<sub>8</sub> and **5**·THF

Compound	<b>3</b> ·0.5C <sub>7</sub> H <sub>8</sub>	<b>5</b> ·THF
Formula	C <sub>35.5</sub> H <sub>62</sub> AlB <sub>20</sub> NO <sub>2</sub> Si <sub>2</sub> Zr <sub>2</sub>	C <sub>44</sub> H <sub>70</sub> B <sub>20</sub> N <sub>2</sub> OZr <sub>2</sub>
Crystal size (mm)	0.40 × 0.36 × 0.28	0.35 × 0.30 × 0.28
<i>M</i>	1016.7	1041.7
Crystal system	monoclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	36.756(7)	16.008(3)
<i>b</i> (Å)	15.726(3)	16.165(3)
<i>c</i> (Å)	20.004(4)	17.239(3)
$\alpha$ (°)	90.00	117.96(1)
$\beta$ (°)	118.24(3)	117.66(1)
$\gamma$ (°)	90.00	90.00(1)
<i>U</i> (Å <sup>3</sup> )	10187(4)	3352(1)
<i>Z</i>	8	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.326	1.032
$\theta$ Range (°)	2.02–25.00	1.48–25.00
$\mu$ (mm <sup>-1</sup> )	0.507	0.340
<i>F</i> (0 0 0)	4152	1072
No. of obsd reflns	8948	8700
No. of params refnd	575	617
Goodness of fit	0.965	0.998
<i>R</i> <sub>1</sub>	0.055	0.118
<i>wR</i> <sub>2</sub>	0.160	0.293

relatively high *R* values. Crystal data and details of data collection and structure refinements are given in Table 2. The CCDC reference numbers are 205776 and 205777 for **3**·0.5C<sub>7</sub>H<sub>8</sub> and **5**·THF, respectively.

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