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Group 4 complexes derived from *o*-carborane: synthesis, structures and ethylene polymerization properties

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Abstract

Nine thermally stable complexes (η^5-Cp*)[η^5-$(C_5H_4)CMe_2CB_{10}H_{10}CR$]$MCl_2$ (R = H and Me) and (η^5-Cp*)[η^5; η^1-$(C_5H_4)CMe_2(CB_{10}H_{10}C)$]MCl have been prepared via metathesis reactions of Cp*MCl_3 (M = Ti, Zr and Hf, Cp* = pentamethylcyclopentadienyl) with monolithium salts of $(C_5H_5)CMe_2(CB_{10}H_{10}CR)$ (R = H and Me) and with dilithium salt of $(C_5H_5)CMe_2(CB_{10}H_{10}CH)$, respectively. These compounds have been fully characterized by various spectroscopic methods and elemental analyses. All of the compounds except (η^5-Cp*)[η^5-$(C_5H_4)CMe_2CB_{10}H_{10}CMe$]$HfCl_2$ were additionally characterized by a single crystal X-ray diffraction study, establishing their monomeric bent metallocene structural feature with carborane acting as a substituent or an ancillary ligand. The titanium and zirconium complexes produce high-density polyethylenes with the activity range of about 10^3–10^4 g PE per mol of M bar h in the presence of modified methylaluminoxane cocatalyst.

Keywords: Metallocene; MMAO; *o*-Carborane; Ethylene; Polymerization

1. Introduction

In the olefin polymerization, metallocene catalysts based on Group 4 metals have attracted much interest due to their high catalytic performance and research efforts have been focused to delve into their polymerization behavior [1]. Among these studies, there have been growing interests in introducing carboranes, known to be capable of forming diverse bond patterns [2], to metallocene-based catalytic systems as a weakly coordinating anion [3–6], as an alternative to cyclopentadienyl ligand (Cp) [7–14], or as a Cp-linked σ-donor ancillary ligand [15]. Carborane was first introduced as a weakly coordinating anion into the homogeneous catalyst systems $Cp'_2ZrMe(C_2B_9H_{12})$ (Cp′ = Cp*, C_5Me_4Et) where the carborane exists as nido-type [4b]. And it was 1991 when dicarbollide form of carborane was employed as an alternative to Cp ligand in preparing Group 4 metal catalyst to explore ethylene polymerization [11d]. The use of carborane as a σ-donor ancillary ligand in preparing Group 4 metallocene olefin catalysts has been demonstrated only in recent years [15]. Nonetheless, the example of effective carborane based Group 4 catalytic systems amenable to ethylene polymerization is very scarce.

The catalytic behavior of metallocene catalysts is very sensitive to the change in factors such as polymerization temperature, cocatalyst, solvent, monomer concentration and substituent at Cp ring. Especially, the steric and electronic environments around the metal center are most important and can be controlled directly by changing the ancillary Cp ring. From this point of view, a new *ansa*-ligand $[(C_5H_4)CMe_2(CB_{10}H_{10}C)]^{2-}$ was developed and the catalytic property of its homoleptic complex *rac*-Zr(η^5:η^1-$CpCMe_2CB_{10}H_{10}C$)$_2$ was pursued, revealing that the attachment of carborane cage resulted in excellent thermal stability and unusual polymerization behavior of the complex [15b]. In order to further use this ligand, the effect of carborane cage as

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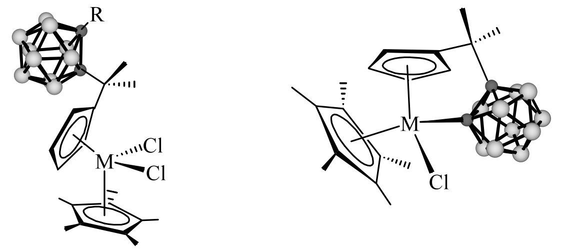
a substituent at Cp ring and as a σ-donor ligand in Group 4 metallocene catalysts on ethylene polymerization has been explored. In this paper, we describe the synthesis, structures and ethylene polymerization properties of Group 4 metallocene-based homogeneous catalysts, **1**–**3** and **4**–**6**, containing orthocarboranyl or 1-methylorthocarboranyl group as a substituent or an ancillary ligand (Chart 1).



M = Ti, **1**; Zr, **2**; Hf, **3**
R = H, **a**; Me, **b**

M = Ti, **4**; Zr, **5**; Hf, **6**

(Chart1)

2. Experimental

2.1. General procedures

All operations were performed under pure dry nitrogen atmosphere using a Vacuum Atmosphere drybox equipped with a Model HE 493 Dri-Train gas purifier or standard Schlenk techniques [16]. Dinitrogen was deoxygenated with activated Cu catalyst and dried with drierite. *n*-Hexane, benzene, and toluene were distilled under dinitrogen from sodium–potassium alloy and stored over the activated molecular sieves 3A [17]. Dichloromethane was distilled under dinitrogen from CaH_2. $CDCl_3$ was dried over activated molecular sieves (4A) and vacuum-transferred to a Schlenk tube equipped with J. Young valve for further use. (η^5-Cp*)MCl_3 (M = Ti, Zr and Hf) were prepared according to the reported procedure [18]. *o*-$C_2B_{10}H_{12}$ and 1-Methyl-*o*-$C_2B_{10}H_{11}$ were purchased from Bchem(Czeco republick). Modified methylaluminoxane (MMAO) (3A type) was supplied by Akzo Co. Other chemicals were purchased from Aldrich. Capillaries for X-ray experiment were purchased from AKZO (Japan). ^{1}H and ^{13}C-{^{1}H}-FT-NMR spectra were recorded on a Bruker AC200 or AM300 spectrometer. Tow-dimensional NMR studies were performed using a Bruker ARX500. Unless otherwise stated, the spectra were recorded in $CDCl_3$ and referenced internally to residual solvent peaks or to Me_4Si. ^{11}B-NMR spectra were recorded at 96.259 MHz on a Bruker AM300 instrument and referenced to external BF_3OEt_2 at 298 K. Melting points of polymer were determined using an Electrothermal Model 1307 digital analyzer. Elemental analyses were performed by Korea Basic Science Institute, Seoul.

2.2. X-ray structural determination

Crystals suitable for X-ray crystallography were obtained by slow cooling of dichloromethane/hexane solution at $-15\,^{\circ}C$. Total independent reflections were measured on an Enraf-Nonius CAD4TSB diffractometer at 293 K with λ (Mo–K_{α} radiation) = 0.71073 Å. The structures were solved by Semi-invariant direct method (SIR 92 in MolEN) and refined by full-matrix least-squares calculation (SHELXL 93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were placed at their geometrically calculated positions ($d_{C-H} = 0.96$ for methyl hydrogens, $d_{C-H} = 0.97$ for methylene hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters (1.5 U for methyl hydrogens, 1.2 U for methylene hydrogens). All calculation was performed on a Silicon Graphics Indigo2XZ Workstation. The detailed crystallographic data are listed in Tables 1 and 2.

2.3. Ethylene polymerization

Ethylene polymerizations were carried out in 250-ml Schlenk flask for 1 bar ethylene pressure with stirring. Toluene, the polymerization solvent, was distilled from sodium–potassium alloy under argon atmosphere just before use. Polymerizations were carried out as following: toluene, MMAO were injected into a reactor with magnetic stirring in that order at the desired temperatures of 30, 50 and 75 °C. Then, the reactor was degassed with ethylene several times, and was saturated with ethylene with vigorous stirring. The polymerization was initiated by the injection of catalyst. After the desired reaction time was reached, the reaction was terminated by the addition of 100 ml of methanol and the addition of 50 ml of 10% HCl in methanol was followed. The resulting precipitated polymer was washed three times each with 500 ml of methanol and dried in vacuo at 70 °C for 12 h. The thermal properties of the polymers were investigated by Thermal Analyst 200 DSC system under nitrogen atmosphere at a heating rate of 10 $^{\circ}C\ min^{-1}$. For each given polymerization run, two or three serial experiments were carried out to confirm the reproducibility of the formation of the polymer and the average values of these serial experimental results are given.

2.4. Synthesis

2.4.1. Synthesis of $(C_5H_5)CMe_2(CB_{10}H_{10}CH)$ (*a*)

A solution of *o*-$C_2B_{10}H_{12}$ (7.1 g, 50 mmol) in 150 ml of C_6H_6/Et_2O (2:1) was added by syringe over 10 min to cold ($-78\,^{\circ}C$) solution of *n*-BuLi (2.5 M, 22 ml) in

Table 1
Crystallographic data for compounds **1a**, **1b**, **2a**, **2b**, and **3a**

Compound	**1a**	**1b**	**2a**	**2b**	**3a**
Empirical formula	$C_{20}H_{36}B_{10}Cl_2Ti$	$C_{21}H_{38}B_{10}Cl_2Ti$	$C_{20}H_{36}B_{10}Cl_2Zr$	$C_{21}H_{38}B_{10}Cl_2Zr$	$C_{20}H_{36}B_{10}Cl_2Hf$
Formula weight	503.39	517.41	546.71	560.73	633.98
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	13.5304(15)	13.521(5)	13.657(4)	13.645(4)	13.602(3)
b (Å)	14.7864(15)	14.966(5)	15.033(4)	15.043(2)	14.552(3)
c (Å)	13.783(5)	14.621(10)	14.587(5)	14.590(6)	15.111(2)
α (°)	90	90	90	90	90
β (°)	105.442(12)	113.15(5)	112.08	112.90(3)	113.150(12)
γ (°)	90	90	90	90	90
V (Å^3)	2658.0(10)	2720.4(23)	2760.9(14)	2758.7(14)	2750.3(8)
Z	4	4	4	4	4
D_{calc} (g cm^{-3})	1.258	1.263	1.315	1.350	1.531
F(0 0 0)	1048	1080	1120	1152	1248
Crystal size (mm)	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.1	0.2 × 0.2 × 0.2	0.3 × 0.1 × 0.1
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
μ(Mo–K$_\alpha$) (mm^{-1})	0.71073	0.71073	0.71073	0.71073	0.71073
θ range (°)	$1.87 \leq \theta \leq 25.00$	$2.04 \leq \theta \leq 24.01$	$2.03 \leq \theta \leq 25.79$	$2.03 \leq \theta \leq 23.97$	$2.03 \leq \theta \leq 23.99$
Number of unique reflections	4226	3942	4073	4106	4000
Number of observed reflections [$I > 2\sigma(I)$]	3482	3504	2946	3749	3749
Number of parameters refined	306	315	305	315	315
$R_1[I > 2\sigma(I)]$ [a]	0.0449	0.0618	0.0763	0.0449	0.0449
$wR_2[I > 2\sigma(I)]$ [b]	0.1047	0.1606	0.1786	0.1127	0.1127
Goodness-of-fit [$I > 2\sigma(I)$]	1.154	1.143	1.094	1.173	1.173
Min and max dens (e Å^{-3})	−0.337, +0.389	−0.761, +0.960	−1.354, +1.149	−0.862, +1.112	−0.862, +1.112

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2
Crystallographic data for compounds **4**, **5**, and **6**

Compound	**4**	**5**	**6**
Empirical formula	$C_{20}H_{35}B_{10}ClTi$	$C_{20}H_{35}B_{10}ClZr$	$C_{20}H_{35}B_{10}ClHf$
Formula weight	466.90	510.25	597.52
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pbca$	$Pbca$	$Pbca$
a (Å)	15.288(2)	15.463(2)	15.452(2)
b (Å)	15.657(2)	15.650(2)	15.664(2)
c (Å)	20.671(5)	20.944(5)	20.889(5)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	4947.9(15)	5068.4(15)	5056.0(15)
Z	8	4	4
D_{calc} (g cm^{-3})	1.254	1.337	1.570
F(0 0 0)	1952	2096	2352
Crystal size (mm)	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2
T (K)	293(2)	293(2)	293(2)
μ(Mo–K$_\alpha$) (mm^{-1})	0.71073	0.71073	0.71073
θ range (°)	$2.11 \leq \theta \leq 23.96$	$2.09 \leq \theta \leq 23.94$	$2.35 \leq \theta \leq 23.93$
Number of unique reflections	2965	3287	3368
Number of observed reflections [$I > 2\sigma(I)$]	1763	2355	2694
Number of parameters refined	296	296	296
$R_1[I > 2\sigma(I)]$ [a]	0.0686	0.0508	0.0343
$wR_2[I > 2\sigma(I)]$ [b]	0.1252	0.0969	0.0642
Goodness-of-fit [$I > 2\sigma(I)$]	1.209	1.109	1.088
Min and max dens (e Å^{-3})	−0.286, +0.269	−0.766, +0.464	−0.557, +0.772

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

hexane under N_2 atmosphere. The flask was allowed to warm to room temperature (r.t.). The evolution of C_4H_{10} began, the colorless solution turned white slurry solution. This white slurry was stirred and degassed occasionally over 16 h. This reaction mixture was added by cannular over 30 min to an orange solution of 6,6-dimethylfulvene (5.0 g, 47 mmol) in benzene (50 ml). The resulting pale yellow solution was stirred at room temperature over 16 h. Half of this solution was removed under vacuum, and aqueous NH_4Cl was added. The organic layer was collected by extraction with Et_2O and the removal of the solvent gave pale yellowish solid. The crude product was purified by sublimation at 70 °C, yielding the desired product in a yield of 85% (10 g). Data for a: ^1H-NMR ($CDCl_3$, 300.133 MHz); $\delta = 1.52$ (s, 6H, $C(CH_3)_2$), 3.01 (m, 2H, Cp(*H*)), 3.32 (s, 1H, $CB_{10}C(H)$), 6.21 (m, 1H, Cp(*H*)), 6.47–6.53 (m, 2H, Cp(*H*) from isomer). ^{11}B-$\{^1H\}$-NMR ($CDCl_3$, 96.275 MHz); $\delta = -4.35$(2B), -9.27(2B), -11.78(2B), -14.04(4B).

2.4.2. Synthesis of $(C_5H_5)CMe_2(CB_{10}H_{10}CMe)$ (b)

A colorless solid **b** was prepared in a yield of 61% (7.6 g) by reacting the lithium salt of 1-methyl-*o*-$C_2B_{10}H_{11}$ (7.8 g, 50 mmol) with 6,6-dimethylfulvene (5.0 g, 47 mmol) in a manner analogous to the procedure for **a**. Data for **b**: ^1H-NMR ($CDCl_3$, 300.133 MHz); $\delta = 1.53$ (s, 6H, $C(CH_3)_2$), 2.00 (s, 3H, $CB_{10}C(CH_3)$), 2.96 (m, 2H, Cp(*H*)), 6.11 (m, 1H, Cp(*H*) from isomer), 6.42 (m, 1H, Cp(*H*) from isomer), 6.69 (m, 1H Cp(*H*) from isomer). ^{11}B-$\{^1H\}$-NMR ($CDCl_3$, 96.275 MHz); $\delta = -3.52$(1B), -5.56(1B), -8.93(2B), -9.80(2B), -11.36(2B).

2.4.3. Synthesis of $(\eta^5$-Cp*)[η^5-$(C_5H_4)CMe_2(CB_{10}H_{10}CH)]TiCl_2$ (1a)

A solution of **a** (0.50 g, 2.0 mmol) in 150 ml of benzene/Et_2O (2:1) was added by syringe over 10 min to cold (-78 °C) solution of *n*-BuLi (2.5 M, 0.9 ml) in hexane under N_2 atmosphere. The reaction flask was allowed to warm to room temperature over 12 h. The colorless solution turned yellowish solution and the brownish sticky precipitate was aggregated. The solvent was removed by vacuum from the reaction mixture, giving brownish sticky oil that turned to yellow solid upon stirring in hexane (30 ml) for 1 h. The solid was collected by decantation, dried under the vacuum and weighed into a new flask with the equivalence to Cp*$TiCl_3$ (0. 58 g, 2.0 mmol) in the Glove box. After the reaction flask was cooled to -78 °C, toluene (30 ml) was slowly added to it with stirring. The resulting red solution was stirred for 12 h at room temperature. White solid residue obtained by removal of solvent under vacuum was redissolved in dichloromethane and filtered through a Celite bed. The evaporation of solvent from the dark red filtrate gave the desired product **1a**. The product was recrystallized by cooling to -20 °C overnight from dichloromethane/hexane, affording red crystals in 49% yield. Data for **1a**: ^1H-NMR ($CDCl_3$, 300.133 MHz); $\delta = 6.27$ (t, 2Hs, Cp*H proximal*), 5.92 (t, 2H, Cp*H distal*), 2.96 (s, 1H, $CB_{10}CH$), 2.03 (s, 15H, $Cp(CH_3)_5$), 1.84 (s, 6H, $C(CH_3)_2$). ^{13}C-$\{^1H\}$-NMR ($CDCl_3$, 75.475 MHz); $\delta = 138.82$ (Cp(*C*)H), 130.85 (Cp*(*C*)), 123.84 (Cp(*C*)H), 111.92 (Cp(*C*)H), 87.49 ($CB_{10}C$), 62.41 ($CB_{10}C$), 42.90 ($C(CH_3)_2$), 28.15 ($C(CH_3)_2$), 13.62 (Cp–CH_3). ^{11}B-$\{^1H\}$-NMR ($CDCl_3$, 96.275 MHz); $\delta = -14.12$(4B), -11.60(2B), -9.23(2B), -4.15(2B). Anal. Calc. for $C_{20}H_{36}B_{10}Cl_2Ti$: C, 47.72; H, 7.21%. Found: C, 47.34; H, 7.15.

2.4.4. Synthesis of $(\eta^5$-Cp*)[η^5-$(C_5H_4)CMe_2(CB_{10}H_{10}CH)]ZrCl_2$ (2a)

A pale yellow solid **2a** was prepared in a yield of 64% (0.70 g) by reacting the lithium salt of **a** (0.56 g, 2.2 mmol) with Cp*$ZrCl_3$ (0.75 g, 2.0 mmol) in a manner analogous to the procedure for **1a**. Data for **2a**: ^1H-NMR ($CDCl_3$, 300.133 MHz); $\delta = 6.27$ (t, 2Hs, Cp*H proximal*), 5.92 (t, 2Hs, Cp*H distal*), 2.96 (s, 1H, $CB_{10}CH$), 2.03 (s, 15H, $Cp(CH_3)_5$), 1.84 (s, 6H, $C(CH_3)_2$). ^{13}C-$\{^1H\}$-NMR ($CDCl_3$, 75.475 MHz); $\delta =$ 138.83 (Cp(*C*)H), 130.65 (Cp*(*C*)), 128.85 (Cp(*C*)H), 111.91 (Cp(*C*)H), 87.46 ($CB_{10}C$), 62.40 ($CB_{10}C$), 42.90 ($C(CH_3)_2$), 28.16 ($C(CH_3)_2$), 13.62 (Cp–CH_3). ^{11}B-$\{^1H\}$-NMR ($CDCl_3$, 96.275 MHz); $\delta = -14.18$(4B), -11.61(2B), -9.25(2B), -4.22(2B). Anal. Calc. for $C_{20}H_{36}B_{10}Cl_2Zr$: C, 43.93; H, 6.63%. Found: C, 43.66; H, 6.20.

2.4.5. Synthesis of $(\eta^5$-Cp*)[η^5-$(C_5H_4)CMe_2(CB_{10}H_{10}CH)]HfCl_2$ (3a)

A pale yellow solid **3a** was prepared in a yield of 35% (0.45 g) by reacting the lithium salt of **a** (0.56 g, 2.2 mmol) with Cp*$HfCl_3$ (0.84 g, 2.0 mmol) in a manner analogous to the procedure for **1a**. Data for **3a**: ^1H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.21$ (t, 2Hs, Cp*H proximal*), 5.85 (t, 2H, Cp*H distal*), 2.86 (s, 1H, $CB_{10}CH$), 2.05 (s, 15H, $Cp(CH_3)_5$), 1.80 (s, 6H, $C(CH_3)_2$). ^{13}C-$\{^1H\}$-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 135.3$ (Cp(*C*)H), 122.7 (Cp*(*C*)), 117.1 (Cp(*C*)H), 108.6 (Cp(*C*)H), 87.3 ($CB_{10}C$), 62.9 ($CB_{10}C$), 42.3 ($C(CH_3)_2$), 28.6 ($C(CH_3)_2$), 12.2 (Cp–CH_3). ^{11}B-$\{^1H\}$-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -4.2$(2B), -9.2(2B), -11.5(2B), -14.1(4B). Anal. Calc. for $C_{20}H_{36}B_{10}Cl_2Hf$: C, 37.88; H, 5.72%. Found: C, 37.29; H, 5.72.

2.4.6. Synthesis of $(\eta^5$-Cp*)[η^5-$(C_5H_4)CMe_2(CB_{10}H_{10}CMe)]TiCl_2$ (1b)

A solution of **b** (0. 50 g, 2.0 mmol) in 150 ml of benzene/Et_2O (2:1) was added by syringe over 10 min to a cold (-78 °C) solution of *n*-BuLi (2.5 M, 0.9 ml) in hexane under N_2 atmosphere. The reaction flask was allowed to warm to room temperature over 12 h. The colorless solution turned yellowish solution and the brownish sticky precipitate was aggregated. The solvent was removed by vacuum from the reaction mixture, giving brownish sticky oil that turned to yellow solid upon stirring in hexane (30 ml) for 1 h. The solid was collected by decantation, dried under the vacuum and weighed into a new flask with the equivalence to Cp*$TiCl_3$ (0. 58 g, 2.0 mmol) in the Glove box. After the reaction flask was cooled to −78 °C, toluene (30 ml) was slowly added to it with stirring. The resulting red solution was stirred for 12 h at room temperature White solid residue obtained by removal of solvent under vacuum was redissolved in dichloromethane and filtered through a Celite bed. The evaporation of solvent from the dark red filtrate gave the desired product **1b**. The product was recrystallized by cooling to −20 °C overnight from dichloromethane/hexane, affording red crystals in 63% (0.65 g) yield. **1b**: ^{1}H-NMR ($CDCl_3$, 300.133 MHz); $\delta = 6.37$ (t, 2Hs, Cp*H proximal*), 5.90 (t, 2H, Cp*H distal*), 2.03 (s, 15H, Cp(CH_3)$_5$), 1.97 (s, 3H, $CB_{10}CCH_3$), 1.95 (s, 6H, C(CH_3)$_2$). ^{13}C-{^{1}H}-NMR ($CDCl_3$, 75.475 MHz); $\delta = 140.1$ (Cp(*C*)H), 130.6 (Cp*(*C*)), 125.6 (Cp(*C*)H), 111.2 (Cp(*C*)H), 90.4 (*C*B_{10}C), 77.8 (*C*B_{10}C), 45.1 (*C*(CH_3)$_2$), 29.9 (C(*C*H_3)$_2$), 26.2 ($CB_{10}C$$CH_3$), 13.6 (Cp-*C*$H_3$). ^{11}B-{^{1}H}-NMR ($CDCl_3$, 96.275 MHz); $\delta = -11.1$(6B), −9.0(2B), −5.6(1B), −3.1(1B). Anal. Calc. for $C_{21}H_{38}B_{10}Cl_2Ti$: C, 48.74; H, 7.39%. Found: C, 48.90; H, 7.45.

2.4.7. Synthesis of (η^5-Cp*)[η^5-(C_5H_4)CMe_2($CB_{10}H_{10}CMe$)]$ZrCl_2$ (**2b**)

A pale yellow solid **2b** was prepared in a yield of 49% (0.55 g) by reacting the lithium salt of **b** (0.60 g, 2.2 mmol) with Cp*$ZrCl_3$ (0.67 g, 2.0 mmol) in a manner analogous to the procedure for **1b**. Data for **2b**: ^{1}H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.3$ (t, 2H, Cp*H proximal*), 5.8 (t, 2H, Cp*H distal*), 2.0 (s, 15H, Cp(CH_3)$_5$), 1.96 (s, 3H, $CB_{10}CCH_3$), 1.91 (s, 6H, C(CH_3)$_2$). ^{13}C-{^{1}H}-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 138.2$ (Cp(*C*)H), 124.8 (Cp*(*C*)), 119.8 (Cp(*C*)H), 109.5 (Cp(*C*)H), 90.1 (*C*B_{10}C), 77.9 (*C*B_{10}C), 44.5 (*C*(CH_3)$_2$), 30.5 (C(*C*H_3)$_2$), 26.1 ($CB_{10}C$$CH_3$), 12.5 (Cp−*C*$H_3$). ^{11}B-{^{1}H}-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -3.2$(1B), −5.6(1B), −9.0(2B), −11.2(6B). Anal. Calc. for $C_{21}H_{38}B_{10}Cl_2Zr$: C, 44.97; H, 6.83%. Found: C, 44.62; H, 6.69.

2.4.8. Synthesis of (η^5-Cp*)[η^5-(C_5H_4)CMe_2($CB_{10}H_{10}CMe$)]$HfCl_2$ (**3b**)

A pale yellow solid **3b** was prepared in a yield of 43% (0.557 g) by reacting the lithium salt of **a** (0.60 g, 2.2 mmol) with Cp*$HfCl_3$ (0.84 g, 2.0 mmol) in a manner analogous to the procedure for **1b**. Data for **3b**: ^{1}H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.3$ (t, 2H, Cp*H proximal*), 5.8 (t, 2H, Cp*H distal*), 2.0 (s, 15H, Cp(CH_3)$_5$), 1.96 (s, 3H, $CB_{10}CCH_3$), 1.91 (s, 6H, C(CH_3)$_2$). ^{13}C-{^{1}H}-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 136.7$ (Cp(*C*)H), 122.6 (Cp*(*C*)), 118.5 (Cp(*C*)H), 107.8 (Cp(*C*)H), 90.3 (*C*B_{10}C), 77.9 (*C*B_{10}C), 44.6 (*C*(CH_3)$_2$), 30.4 (C(*C*H_3)$_2$), 26.2 ($CB_{10}C$$CH_3$), 12.2 (Cp-*C*$H_3$). ^{11}B-{^{1}H}-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -3.2$(1B), −5.6(1B), −8.9(2B), −11.2(6B). Anal. Calc. for $C_{21}H_{38}B_{10}Cl_2Hf$: C, 38.92; H, 5.91%. Found: C, 38.00; H, 6.14.

2.4.9. Synthesis of (η^5-Cp*)[η^5;η^1-(C_5H_4)CMe_2($CB_{10}H_{10}C$)]TiCl (**4**)

A solution of a (0. 55 g, 2.2 mmol) in 150 ml of benzene/Et_2O (2:1) was added by syringe over 10 min to a cold (−78 °C) solution of *n*-BuLi (2.5 M, 1.8 ml) in hexane under N_2 atmosphere. The reaction flask was allowed to warm to room temperature over 12 h. The colorless solution turned yellowish solution and the brownish sticky precipitate was aggregated. The solvent was removed by vacuum from the reaction mixture, giving brownish sticky oil that turned to yellow solid upon stirring in hexane (30 ml) for 1 h. The solid was collected by decantation, dried under the vacuum and weighed into a new flask with the equivalence to Cp*$TiCl_3$ (0. 58 g, 2.0 mmol) in the Glove box. After the reaction flask was cooled to −78 °C, toluene was slowly added to it with stirring. The resulting dark red solution was stirred for 12 h at room temperature. White solid residue obtained by removal of solvent under vacuum was redissolved in dichloromethane and filtered through a Celite bed. The evaporation of solvent from the dark red filtrate gave the desired product **4**. The product was recrystallized from dichloromethane/hexane, affording dark red crystals in 49% yield. Data for **4**: ^{1}H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.9$ (q, 1H, Cp*H*), 6.2 (q, 1H, Cp*H*), 5.3 (q, 1H, Cp*H*), 5.1 (q, 1H, Cp*H*), 2.0 (s, 15H, Cp*C**H*$_3$), 1.6 (s, 3H, C(*C**H*$_3$)$_2$), 1.4 (s, 3H, C(*C**H*$_3$)$_2$). ^{13}C-{^{1}H}-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 160.1$ (Cp(*C*)H), 131.0 (Cp*(*C*)), 128.2 (CB_{10}*C*), 126.1 (Cp(*C*)H), 116.8 (Cp(*C*)H), 114.0 (Cp(*C*)H), 108.3 (Cp(*C*)H), 40.6 (*C*(CH_3)$_2$), 33.1 (C(*C*H_3)$_2$), 31.0 (C(*C*H_3)$_2$), 13.8 (Cp−*C*H_3). ^{11}B-{^{1}H}-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -2.4$(1B), −4.0(1B), −6.3(3B), −10.0(4B), −13.6(1B). Anal. Calc. for $C_{20}H_{35}B_{10}ClTi$: C, 51.44; H, 7.55%. Found: C, 50.18; H, 7.18.

2.4.10. Synthesis of (η^5-Cp*)[η^5;η^1-(C_5H_4)CMe_2($CB_{10}H_{10}C$)]ZrCl (**5**)

A pale green solid **5** was prepared in a yield of 44% (0.45 g) by reacting the dilithium salt of a (0.58 g, 2.2 mmol) with Cp*$ZrCl_3$ (0.67 g, 2.0 mmol) in a manner analogous to the procedure for **4**. Data for **5a**: ^{1}H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.6$ (q, 1H, Cp*H*), 5.9 (q, 1H, Cp*H*), 5.5 (q, 1H, Cp*H*), 5.4 (q, 1H, Cp*H*), 2.0

(s, 15H, $CpC\mathit{H}_3$), 1.6 (s, 3H, $C(C\mathit{H}_3)_2$), 1.5 (s, 3H, $C(C\mathit{H}_3)_2$). ^{13}C-{^{1}H}-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 158.3$ (Cp(*C*)H), 125.5 (Cp*(*C*)), 119.9 (Cp(*C*)H), 113.3 (*C*B_{10}C), 112.1 (Cp(*C*)H), 106.6 (Cp(*C*)H), 106.1 (CB_{10}*C*), 105.9 (Cp(*C*)H), 41.1 (*C*$(CH_3)_2$), 33.4 ($C(\mathit{C}H_3)_2$), 31.5 ($C(\mathit{C}H_3)_2$), 12.6 (Cp−$\mathit{C}H_3$). ^{11}B-{^{1}H}-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -1.5$(1B), −3.8(1B), −5.9(2B), −9.6(5B), −12.9(1B). Anal. Calc. for $C_{20}H_{35}B_{10}ClZr$: C, 47.07; H, 6.91%. Found: C, 45.17; H, 6.64.

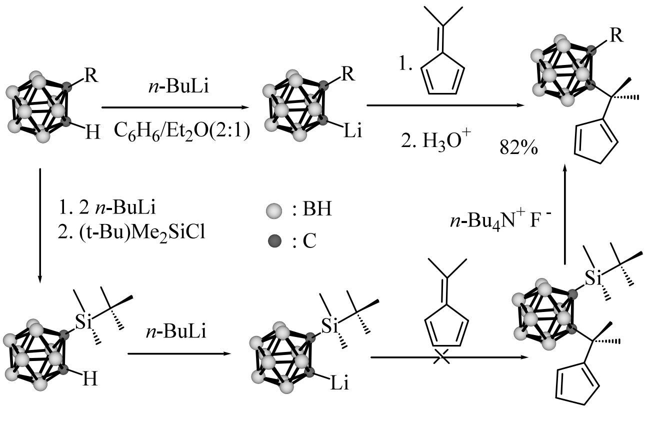
2.4.11. Synthesis of (η^5-Cp)[η^5;η^1-(C_5H_4)CMe_2($CB_{10}H_{10}C$)]HfCl (**6**)*

A pale green solid **6** was prepared in a yield of 45% (0.54 g) by reacting the dilithium salt of **a** (0.58 g, 2.2 mmol) with Cp^*HfCl_3 (0.84 g, 2.0 mmol) in a manner analogous to the procedure for **4**. Data for **6**: ^{1}H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 6.5$ (q, 1H, Cp*H*), 6.0 (q, 1H, Cp*H*), 5.4 (m, 2H, Cp*H*), 2.0 (s, 15H, $CpC\mathit{H}_3$), 1.6 (s, 3H, $C(C\mathit{H}_3)_2$), 1.5 (s, 3H, $C(C\mathit{H}_3)_2$). ^{13}C-{^{1}H}-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 154.1$ (Cp(*C*)H), 123.7 (Cp*(*C*)), 118.9 (Cp(*C*)H), 113.6 (*C*B_{10}C), 112.9 (Cp(*C*)H), 110.0 (Cp(*C*)H), 107.3 (CB_{10}*C*), 103.6 (Cp(*C*)H), 40.6 (*C*$(CH_3)_2$), 33.5 ($C(\mathit{C}H_3)_2$), 31.5 ($C(\mathit{C}H_3)_2$), 12.5 (Cp−$\mathit{C}H_3$). ^{11}B-{^{1}H}-NMR (96.275 MHz, $CDCl_3$, ppm): $\delta = -1.3$(1B), −3.8(1B), −5.7(2B), −7.4(1B), −9.6(4B), −13.3(1B). Anal. Calc. for $C_{20}H_{35}B_{10}ClHf$: C, 40.20; H, 5.90%. Found: C, 38.85; H, 5.71.

3. Results and discussion

3.1. Synthesis

The colorless crystalline compounds (C_5H_5)CMe_2($CB_{10}H_{10}CR$) (R = H, **a**; Me, **b**) were prepared according to the reaction Scheme 1 in 85 and 61% isolated yields, respectively. The use of $LiC_2B_{10}H_{11}$ in combination with a mixed solvent of benzene/Et_2O in 2:1 ratio, in which the equilibrium $2LiC_2B_{10}H_{11} \rightleftharpoons C_2B_{10}H_{12} + Li_2C_2B_{10}H_{10}$ shifts to the far left [19,20], is more efficient for the synthesis of a new ligand **a** compared to the use of $LiC_2B_{10}SiMe_2$(*t*-Bu) [21] or $Li_2C_2B_{10}H_{10}$ [22] since the former lacks reactivity with 6,6-dimethylfulvene and the latter leads to low yield. The analogous procedure for **a** with Li(1-Me-*o*-$C_2B_{10}H_{10}$) also works well for the synthesis of **b**.



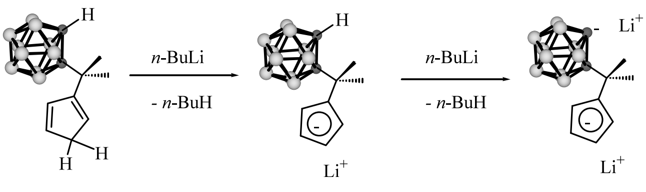
Scheme 1. Synthesis of $C_5H_5CMe_2CB_{10}CR$ (**a**; R = H, **b**; R = Me).

The lithiation study with *n*-BuLi indicates that the ligand **a** can be lithiated in a stepwise manner as outlined in Scheme 2, indicating that the CH proton of the carborane cage is less acidic than the cyclopentadienyl proton. Such acidity trend of two acidic protons in a new *ansa*-ligand **a** is consistent with the relative acidity of individual *o*-carborane and cyclopentadiene whose pK_a values are 23 and 18, respectively [23]. The metathetic reactions of lithiated ligands with Cp^*MCl_3, outlined in Schemes 3 and 4, gave metallation products **1**–**6** in 35–60% yields. Route A in Scheme 4 represents the synthetic procedures for the compounds **4**–**6** described in the Section 2. The stepwise lithiation behavior of the ligand **a** also afforded additional reaction route, Route B in Scheme 4, for the compounds **4**–**6** via the formation of **1a**–**3a**. The compounds **1**–**6** are stable in air and soluble in polar solvents such as THF and dichloromethane.

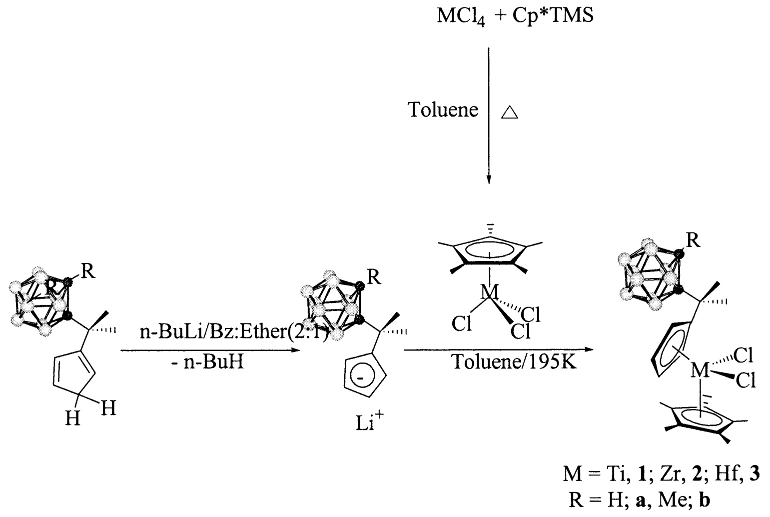
3.2. X-ray structures

Among nine new Group 4 *o*-carborane-based complexes reported in this paper, the molecular structures of all compounds except **3b** were determined by single-crystal X-ray diffraction studies. The selected structural data are listed in Tables 3 and 4. For the purpose of presenting ORTEP diagrams, only three diagrams of **2a**, **2b** and **5** are given below since these compounds are the members of three isostructural classes of the type (η^5-Cp*)[η^5-(C_5H_4)CMe_2($CB_{10}H_{10}CH$)]MCl_2 (**1a**–**3a**), (η^5-Cp*)[η^5-(C_5H_4)CMe_2($CB_{10}H_{10}CMe$)]MCl_2 (**1b**–**2b**) and (η^5-Cp*)[η^5;η^1-(C_5H_4)CMe_2($CB_{10}H_{10}C$)]MCl (**4**–**6**) (M = Ti, Zr and Hf), respectively.

1a, **2a** and **3a**. These compounds are isostructural and their molecular structures are collectively presented in Fig. 1 by utilizing the ORTEP drawing of **2a**. The metal centers are η^5-bonded to both cyclopentadienyl rings, symmetrically with the Cp* ring and unsymmetrically with the $C_5H_4CMe_2(CB_{10}H_{10}CH)$ ring (Cp′). The Cp′(cent)−M−Cp*(cent) bond angle range of 128.7–



Scheme 2. Lithiation behavior of $C_5H_5CMe_2CB_{10}CH$(**a**).

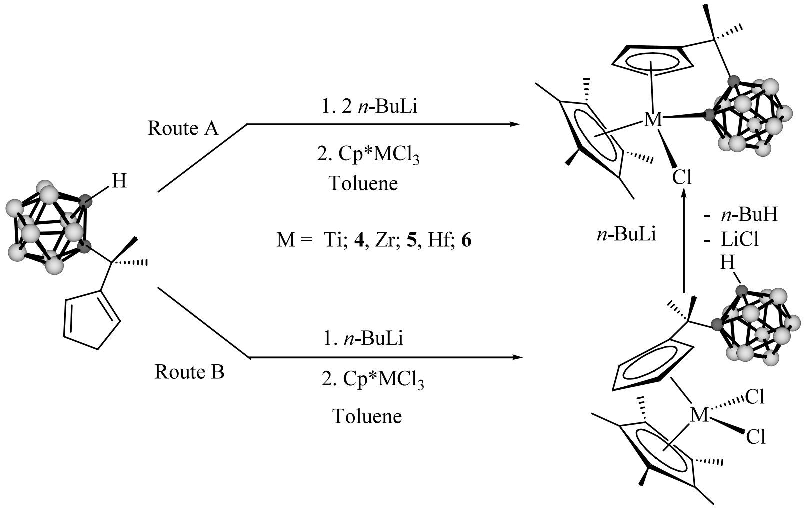


Scheme 3. Synthesis of (η^5-Cp*)(η^5-$CpCMe_2CB_{10}H_{10}CR$)MCl_2.

131.4° is essentially the same as the corresponding angles in (η^5-C_5H_5)$_2MCl_2$ (129.2–131.0°) [24], (η^5-$^tBuC_5H_4$)$_2MCl_2$ (M = Ti, 130.9°; Zr, 128.9°) [25] and [η^5-$C_5H_4C(Me)_2C(H)Me_2$]$_2MCl_2$ (129.8–132.4°) [26,27]. The Cl–M–Cl angles range 93.14–97.57° that are similar to that (92.5–97.1°) found in (η^5-C_5H_5)$_2MCl_2$ [24]. The carborane cage is situated such that the overall molecular symmetry approaches to C_s point group and the CH proton of the carborane cage forms the non-classical hydrogen-bond with the Cp′ ring. The distance (2.594 Å in **1a**, 2.579 Å in **2a** and 2.537 Å in **3a**) between the centroid of the Cp′ ring and the H atom on the carborane carbon is indicative of the presence of such interaction. Similar type of the non-classical hydrogen-bonding interaction between carborane and π-bound ligand was seen in the adduct of o-$C_2B_{10}H_{12}$ with cyclotriveratrylene [28] and [η^5-$Me_2Si(C_5H_4)(C_2B_{10}H_{11})$]$_2Yb(THF)_2$ [29].

1b and **2b**. The ORTEP drawing of **2b** is employed in Fig. 2 to illustrate the collective feature of the molecular structures for these isostructural complexes. The overall molecular symmetry also approaches to C_s point group. The carborane methyl group is staggered with respect to the dimethyl groups of isopropyl bridging unit. The Cp′(cent)–M–Cp*(cent) angles and the M–Cp′(cent) distances are comparable to those for the analogous systems with **a**.

4, **5** and **6**. The representative structure, the ORTEP drawing of **5**, of these compounds is shown in Fig. 3. The X-ray structures clearly reveal that these compounds are asymmetric. The metal centers adopt distorted tetrahedral coordination sphere. The average Cl–M–carborane carbon angle of 94.1° and the average Cp′(cent)–M–Cp*(cent) angle of 129.5° reflect the extent of the distortion. The Cp* and Cp′ rings are staggered relative to each other.



Scheme 4. Synthesis of (η^5-Cp*)(η^5;η^1-$CpCMe_2CB_{10}H_{10}C$)MCl.

Table 3
Selected bond lengths (Å) and angles (°) for **1a**, **1b**, **2a**, **2b**, and **3a**

	1a	**1b**	**2a**	**2b**	**3a**
Bond lengths					
M–Cl(1)	2.3317(13)	2.348(2)	2.380(2)	2.4408(14)	2.406(3)
M–Cl(2)	2.3645(13)	2.366(2)	2.481(2)	2.4525(15)	2.424(3)
M–cent(Cp′)	2.132	2.146	2.309	2.262	2.252
M–cent(Cp*)	2.101	2.104	2.231	2.226	2.203
M–C(6)	2.597	2.610	2.712	2.682	2.680
M–C(7)	2.459(3)	2.502(7)	2.621(9)	2.568(4)	2.586(11)
M–C(8)	2.354(3)	2.359(6)	2.549(9)	2.462(4)	2.462(11)
M–C(9)	2.328(3)	2.328(6)	2.518(9)	2.480(3)	2.449(11)
M–C(10)	2.468(3)	2.476(6)	2.598(8)	2.597(4)	2.567(11)
M–C(11)	2.409(3)	2.451(6)	2.554(9)	2.552(4)	2.522(12)
M–C(12)	2.415(3)	2.451(6)	2.566(9)	2.551(4)	2.490(12)
M–C(13)	2.421(3)	2.392(7)	2.531(9)	2.504(5)	2.516(11)
M–C(14)	2.412(3)	2.452(7)	2.551(9)	2.534(4)	2.486(12)
M–C(15)	2.441(3)	2.398(6)	2.469(9)	2.515(4)	2.529(12)
C(1)–C(2)	1.733(4)	1.725(9)	1.716(13)	1.730(6)	1.671(14)
C(2)–C(3)	1.591(4)	1.602(8)	1.632(13)	1.604(6)	1.601(16)
C(3)–C(6)	1.522(4)	1.535(9)	1.539(13)	1.535(6)	1.517(16)
Bond angles					
cent(Cp*)–M–cent(Cp′)	131.41	131.44	128.71	129.23	129.92
Cl(1)–M–Cl(2)	93.14(3)	95.79(6)	97.50(8)	97.76(5)	97.57(10)
C(1)–C(2)–C(3)	119.5(2)	122.6(4)	120.4(7)	123.0(3)	119.9(9)
C(2)–C(3)–C(6)	107.4(2)	105.7(4)	105.4(7)	105.7(3)	107.6(8)
C(4)–C(3)–C(5)	108.9(3)	108.5(5)	107.2(8)	108.3(3)	109.0(9)
C(1)–C(2)–C(3)–C(6)	−8.6(3)	157.5(5)	−5.0(9)	157.3(3)	−4.6(12)

Table 4
Selected bond lengths (Å) and angles (°) for **4**, **5**, and **6**

	4	**5**	**6**
Bond lengths			
M–Cl	2.347(3)	2.440(2)	2.418(3)
M–C(1)	2.328(9)	2.389(7)	2.364(1)
M–cent(Cp′)	2.067	2.193	2.183
M–cent(Cp*)	2.12	2.233	2.213
M–C(4)	2.423(8)	2.539(8)	2.528(12)
M–C(5)	2.401(10)	2.524(8)	2.511(11)
M–C(6)	2.358(10)	2.473(8)	2.467(13)
M–C(7)	2.374(10)	2.482(10)	2.481(13)
M–C(8)	2.358(10)	2.475(9)	2.479(12)
M–C(11)	2.467(10)	2.564(9)	2.527(12)
M–C(12)	2.434(10)	2.533(9)	2.521(13)
M–C(13)	2.399(10)	2.505(8)	2.491(13)
M–C(14)	2.430(11)	2.532(9)	2.505(13)
M–C(15)	2.451(11)	2.558(9)	2.540(13)
C(1)–C(2)	1.751(12)	1.730(11)	1.731(15)
C(2)–C(3)	1.551(13)	1.569(11)	1.564(16)
C(3)–C(4)	1.538(12)	10514(12)	1.519(16)
Bond angles			
cent(Cp*)–M–cent(Cp′)	129.48	129.40	129.60
Cl–M–C(1)	92.0(2)	95.9(2)	94.5(2)
M–C(1)–C(2)	117.7(6)	118.4(5)	119.1(6)
C(1)–C(2)–C(3)	115.1(7)	116.2(6)	115.9(8)
C(2)–C(3)–C(4)	108.8(7)	109.4(7)	109.1(9)
C(9)–C(3)–C(10)	107.2(7)	106.8(7)	107.4(9)
C(1)–C(2)–C(3)–C(4)	−1.2(10)	−2.2(9)	−2.0(12)

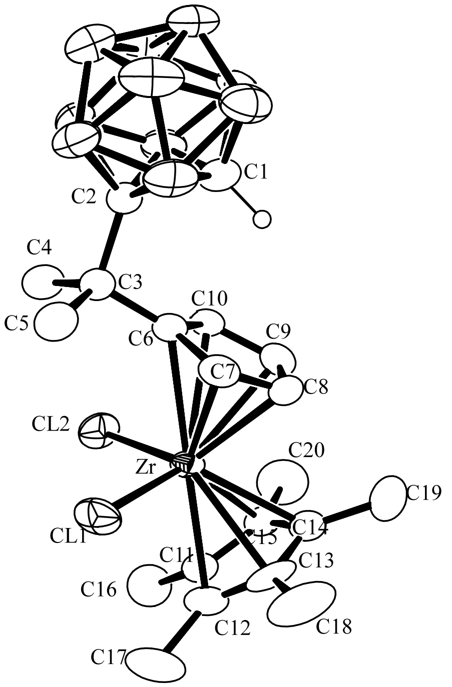


Fig. 1. Molecular structure of **2a** with 50% probability and numbering scheme. For clarity, all hydrogens except that at C(1) are omitted.

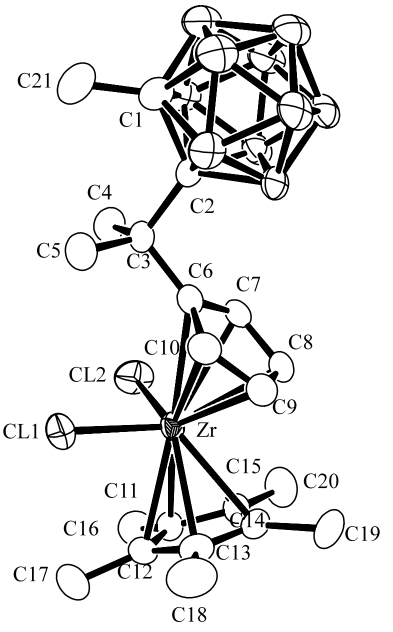


Fig. 2. Molecular structure of **2b** with 50% probability and numbering scheme. For clarity, all hydrogens are omitted.

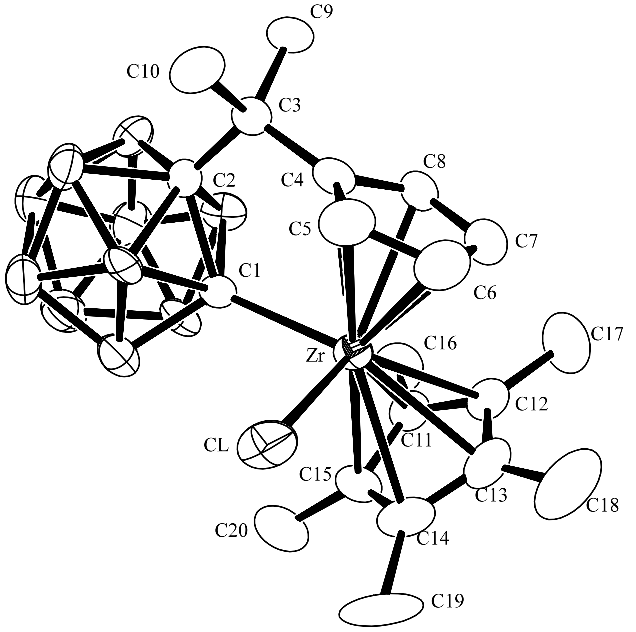


Fig. 3. Molecular structure of **5** with 50% probability and numbering scheme. For clarity, all hydrogens are omitted.

3.3. Ethylene polymerization

Ethylene polymerization with the newly synthesized catalytic metallocene precursors **1a**, **1b**, **2a**, **2b**, **4** and **5** were carried out in the presence of MMAO cocatalyst at various temperatures under 1 bar of ethylene. All the hafnium complexes were ruled out as catalytic precursors based on the preliminary polymerization experiments. The polymerization data are summarized in Table 5. These catalytic systems produce high-density polyethylenes with the activity range of about 10^3–10^4 g PE (mol of M bar h)$^{-1}$. For a given type of complexes, the zirconium analogue gives higher activity than the titanium analogue. The Ti-based systems, **1a**, **1b** and **4**, do not show any particular temperature-activity dependence while the activities of the Zr-based systems, **2a**, **2b** and **5**, increase with increasing temperature, indicating the thermal stability of the latter catalytic systems.

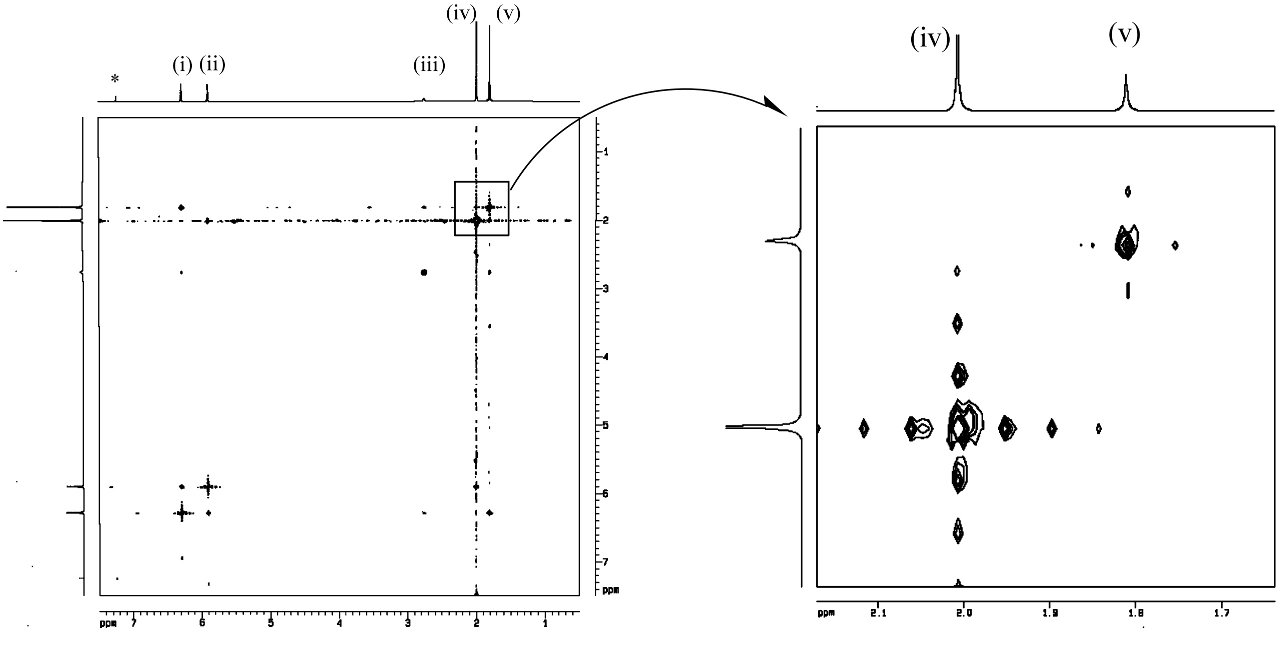


Fig. 4. (a) ^{1}H-^{1}H-NOESY spectrum of **2a**: Signals marked with *, (i), (ii), (iii), (iv) and (v) are due to residual solvent proton, *proximal* protons of Cp′, *distal* protons of Cp′, CH proton of the carborane cage, methyl protons of Cp* and *geminal* methyl protons, respectively. (b) Enlarged sectional view of the NOESY spectrum of **2a**.

Table 5
Ethylene polymerization results with catalysts **1a**, **1b**, **2a**, **2b**, **4** and **5**/MMAO

Run [a] No.	Catalyst	Tp (°C)	Al/Cat	tp (min)	Crude PE (g)	Activity [b] (× 10^{-3})	Tm [c] (°C)
1	**1a**	30	1500	30	0.30	7.1	137.7
2		50	1500	30	0.33	7.8	132.3
3		70	1500	30	0.060	1.5	131.3
4	**1b**	30	1500	30	0.070	1.7	136.5
5		50	1500	30	0.15	3.6	133.9
6		70	1500	30	0.18	4.3	132.1
7	**4**	30	1500	30	0.050	1.2	133.7
8		50	1500	30	0.020	0.53	134.4
9		70	1500	30	0.040	0.93	131.7
10	**2a**	50	1500	30	0.74	18	132.2
11		70	1500	30	1.1	25	133.6
12		90	1500	30	1.5	36	134.3
13	**2b**	50	1500	30	0.22	5.3	133.3
14		70	1500	30	1.0	25	133.7
15		90	1500	30	3.1	75	132.9
16	**5**	50	1500	30	0.18	4.3	135.0
17		70	1500	30	0.21	5.0	134.4
18		90	1500	30	0.22	5.3	134.0

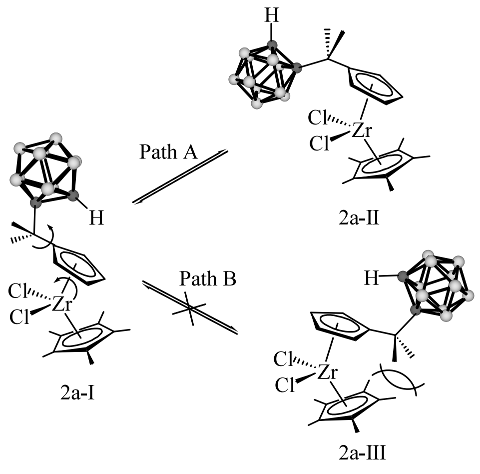
[a] Polymerization condition: P(ethylene) = 1 bar; [Cat] = 2.158 mM.
[b] Activity = g PE per mol of M bar h.
[c] Determined by DSC.

Overall, the new Group 4 complexes derived from *o*-carborane show relatively lower activities than other known bent metallocenes [1a,1d].

The observed lower polymerization activities of the foregoing catalytic systems may be ascribed to the steric hindrance of the carborane cage coupled with possible involvement of the activation of a σ-M–C(carborane) bond. In order to probe the steric influence of the carborane cage on the catalytic site, the through-space relationship among the ligand moieties in solution was examined by performing NOE experiments on a representative catalytic precursor [(η^5-Cp*){η^5-(C_5H_4)CMe_2($CB_{10}H_{10}CH$)}$ZrCl_2$] (**2a**). The NOESY spectrum, given in Fig. 4a, reveals the presence of three kinds of correlations: The first is between the *geminal* dimethyl protons ($\delta = 1.84$) and the *proximal* protons ($\delta = 6.27$) of C_5H_4 ring (Cp′), the second is between the Cp* methyl protons ($\delta = 2.03$) and the *distal* Cp′ protons ($\delta = 5.92$), and the third is between the carborane CH proton ($\delta = 2.96$) and the *proximal* Cp′ protons. These correlations can be explained in terms of two conformers **2a-I** and **2a-II** that are interrelated via the free rotation of isopropylcarboranyl unit with respect to Cp′-isopropyl C–C bond as shown in Path A of Scheme 5. The first correlation indicates the presence of the conformer **2a-II** while the second and the third correlations are consistent with the conformer **2a-I** whose structure is similar to the solid state structure of **2a**. The carborane cage of the conformer **2a-II** situates toward front-side of metal center and thus clearly imposes the steric hindrance onto the catalytic site. It is also worth to note that the correlation between the *geminal* dimethyl protons and the Cp* methyl protons is absent in the NOESY spectrum (Fig. 4b) thereby the conformer **2a-III** is not existing in solution and thus the rotation (Path B in Scheme 5) of the Cp′ ring with respect to Zr–Cp′ centroid vector is restricted.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic



Scheme 5. Rotational behavior of **2a** in solution.

Data Centre, CCDC nos. 207913–207920 for compounds **1a**, **1b**, **2a**, **2b**, **3a**, **6**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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