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A Neutral Group 4 Poly(methyl methacrylate) Catalyst Derived from *o*-Carborane

Eunkee Hong, Youngjo Kim, and Youngkyu Do*

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

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Summary: rac-Zr(η^5:η^1-CpCMe$_2$CB$_{10}$H$_{10}$C)$_2$, prepared from the reaction of the dilithium salt of the new isopropyl-bridged cyclopentadienyl o-carboranyl ligand CpHCMe$_2$CB$_{10}$H$_{10}$CH with ZrCl$_4$, catalyzes the formation of syndiotactic poly(methyl methacrylate) in THF in the absence of any alkylating reagent or cationic center generator.

Since the use of organolanthanides and zirconocene catalytic precursors in the polymerization of methyl methacrylate (MMA), a polar monomer, was independently reported by the groups of Yasuda[1] and Collins,[2] respectively, in 1992, extensive efforts have been directed toward the expansion of the organolanthanide systems,[3] the synthesis of new catalytic systems,[4-7] stereocontrol in the polymerization,[8] and an understanding of the polymerization machanism.[9] Nonetheless, the types of the catalytic precursors are mainly limited to organolanthanide metallocenes,[1,3-8] while Me$_2$C=C(OMe)OZrCp$_2$Cl[10] and [Cp$_2$ZrMe(THF)][BPh$_4$]/Cp$_2$ZrMe$_2$[2,9] constitute rare examples of the group 4 complex type. We now report here the synthesis, structure and MMA polymerization behavior of the new group 4 neutral complex *rac*-Zr(η^5:η^1-CpCMe$_2$CB$_{10}$H$_{10}$C)$_2$ (**2**), prepared from the new ligand CpHCMe$_2$CB$_{10}$H$_{10}$CH (**1**).

The colorless crystalline compounds **1** and **2** were prepared, according to the reaction given in Scheme 1, in 83 and 61% isolated yields, respectively.[11] The use of both LiC$_2$B$_{10}$H$_{11}$ and benzene, in which the equilibrium 2LiC$_2$B$_{10}$H$_{11}$ $\rightleftharpoons$ C$_2$B$_{10}$H$_{12}$ + Li$_2$C$_2$B$_{10}$H$_{10}$ shifts to the far left,[12] turned out to be efficient in the synthesis of the new ligand **1** compared to the use of LiC$_2$B$_{10}$H$_{10}$-

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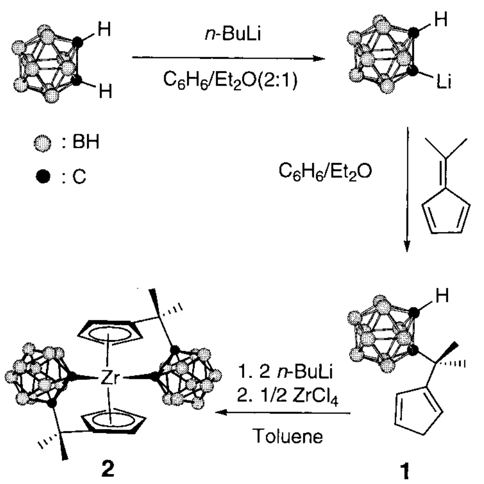
Scheme 1



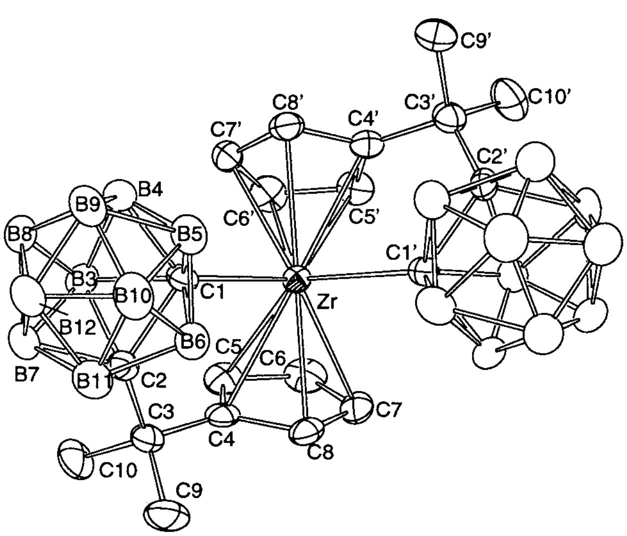


Figure 1. Perspective view of **2** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Zr−C1, 2.369(5); Zr−C1′, 2.384(3); Zr−C4, 2.536(4); Zr−C5, 2.485(4); Zr−C6, 2.483(4); Zr−C7, 2.497(4); Zr−C8, 2.507(4); C1−C2, 1.740(6); C1−Zr−C1′, 110.83(15); Zr−C1−C2, 118.6(3).

Table 1. Polymerization of MMA Catalyzed by 2[a]

temp (°C)	time (h)	% conv	10^{-3} M_n[b]	M_w/M_n	% rr[c]
25	2	5.4	37	1.63	66.7
25	12	14	43	2.10	66.0
25	24	42	41	2.10	65.7
50	2	4.7	52	1.68	63.1
75	2	4.8	58	1.60	59.4

[a] All polymerizations were performed with 100 mmol of MMA and 0.02 mmol of **2** in 50 mL of THF. [b] From GPC relative to polystyrene standards. [c] From ^{1}H and ^{13}C{^{1}H} NMR in $CDCl_3$ at 20 °C.

$SiMe_2(t\text{-}Bu)$[13] or $Li_2C_2B_{10}H_{10}$,[14] since the former lacks reactivity with 6,6-dimethylfulvene and the latter leads to low yields. It is interesting to note that the dimethylsilyl-bridged analogue of **1** was prepared from the reaction of $Li_2C_2B_{10}H_{10}$ and $(C_5H_5)SiMe_2Cl$ in high yield and utilized in developing organolanthanide chemistry.[15] A lithiation study of **1** using *n*-BuLi indicates that the CpH proton is more acidic than the carborane CH proton and both protons can be removed. Treatment of the dilithiated product of **1**, $Li_2[CpCMe_2CB_{10}H_{10}C]$, with $ZrCl_4$ in a 2:1 ratio in toluene affords **2**. Solid **2** is stable in air for an extended period of time, and isostructural[16] lighter and heavier congeners of **2** can be prepared analogously.

The X-ray crystal structure of **2**,[16] shown in Figure 1, reveals that the Zr atom adopts essentially an η^5-bonding posture with Cp rings and an η^1-bonding posture with carborane cages. The average Zr to Cp carbon distance of 2.50 Å is in a reasonable range for Zr−Cp distances.[17] The Zr−carboranyl carbon distances of 2.369(5) and 2.384(3) Å, which are similar to Zr−alkyl distances,[17] are longer than the average metal−*o*-carborane carbon distances found in mercuracarborands (2.10 Å)[18] and bis(*o*-carborane)−late-transition-metal complexes (2.00−2.07 Å)[19] but shorter than the Nd−carboranyl carbon distances of 2.701(1) and 2.583(1) Å in $[Nd\{Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2][Li(THF)_4]$.[15] The bent-metallocene structural feature, involving a distorted-tetrahedral arrangement of the ligands around the metal with a Cp−Zr−Cp′ angle of 128.7° and C1−Zr−C1′ angle of 110.8°, approaches C_2 symmetry. The isopropyl-bridged nature of the ligand leads to two possible racemic conformers for **2**. For a given single crystal, the X-ray analysis reveals that only one form of racemic conformer exists, raising an engaging possibility that **2** may show piezoluminescence and/or nonlinear optical effect.

The catalytic activity of **2** toward polar monomer has been initially tested with MMA in THF, for solubility reasons, at various temperature. The use of polar THF as an MMA polymerization solvent is rather unusual in metallocene catalytic systems, since the retardation of polymerization by THF was reported in organolanthanide systems.[3b] Preliminary polymerization data are summarized in Table 1. The rr triads of 60−70% indicates that the poly(MMA) (PMMA) produced with

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(11) Data for **1**: ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ 1.53 (s, 6H, $C(CH_3)_2$), 3.01 (m, 2H, $Cp(H_2)$), 3.35 (br, 1H, $CB_{10}C(H)$), 6.21 (m, 1H, Cp(*H*)), 6.34∼6.47 (m, 3H, Cp(*H*)); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.475 MHz) δ 30.78($C(CH_3)_2$), 40.23 ($Cp(CH_2)$), 41.17 ($C(CH_3)_2$), 63.64 ($CHB_{10}C$), 84.55($CHB_{10}C$), 129.35 (Cp(*C*)H), 132.06 (Cp(*C*)H), 134.88 (Cp(*C*)H), 150.20 (Cp(*C*)C); ^{11}B{^{1}H} NMR ($CDCl_3$, 96.275 MHz) δ −4.30 (2B), −9.27 (2B), −11.61 (2B), −14.06 (4B); IR (KBr, cm^{-1}) ν(B−H) 2640 (vs), 2596 (vs), 2556 (vs), 2362 (s). Anal. Calcd for $C_{10}H_{22}B_{10}$: C, 47.97; H, 8.86. Found: C, 49.13; H, 8.96. Data for **2**: ^{1}H NMR (THF-d_8, 300.133 MHz) δ 1.52 (s, 3H, $C(CH_3)_2$), 1.58 (s, 3H, $C(CH_3)_2$), 6.00 (dd, 1H, Cp(*H*)), 6.46 (m, 2H, Cp(*H*)), 6.66 (dd, 1H, Cp(*H*)); ^{13}C{^{1}H} NMR (THF-d_8, 75.475 MHz) δ 32.51 ($C(CH_3)_2$), 32.98 ($C(CH_3)_2$), 42.71 ($C(CH_3)_2$), 106.99 ($CB_{10}C$), 109.16 (Cp(*C*)H), 111.04 (Cp(*C*)H), 116.15 (Cp(*C*)H), 118.35 (Cp(*C*)H), 157.27 (Cp(*C*)C). ^{11}B{^{1}H} NMR (THF-d_8, 96.275 MHz) δ −11.35 (br), −8.01(br), −5.48(br), −4.58(br), −2.46(br), −0.39(br); IR (KBr, cm^{-1}) ν(B−H) 2624 (s), 2610 (vs), 2588 (vs), 2572 (vs), 2551 (vs), 2538 (vs). Anal. Calcd for $C_{20}H_{40}B_{20}Zr$: C, 40.72; H, 7.18. Found: C, 40.86; H, 7.27.

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(16) Crystal data for **2**: formula $C_{20}H_{40}B_{20}Zr$, fw 587.94, monoclinic, $P2_1$, $a = 9.3393(8)$ Å, $b = 9.8329(11)$ Å, $c = 16.551(2)$ Å, $\beta = 102.595(14)°$, $V = 1483.4(3)$ Å^3, $Z = 2$, R1 = 0.025, $wR_2 = 0.057$. The 2580 independent reflections ($2\theta < 50°$; $I > 2\sigma(I)$) were collected using Mo Kα radiation on an Enraf-Nonius CAD4TSB diffractometer using $\omega-2\theta$ scans. The Flack X parameter of 0.01 indicates the right choice of absolute configuration.

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2 is predominantly syndiotactic with a molecular weight distribution of 1.6−2.1. The decrease of syndiotacticity with an increase of polymerization temperature is as expected; however, conversion of MMA remains essentially the same even if the molecular weight (MW) is increased up to 57%. This is presumably due to the fact that the equilibrium constant for the initiation step is larger at lower temperature while the propagation rate is faster at higher temperature. For ambient-temperature runs, the percentage of monomer conversion increases with the polymerization time while the MW remains constant as expected for single-site catalytic systems. Triad tests[20] give 4[mm][rr]/[mr]^2 values of 0.67−0.80, suggesting that propagation proceeds mainly via a chain-end control mechanism. The characteristics worthy of mention for the catalyst **2** are its air and thermal stability and its neutral nature, which makes unnecessary any additional use of alkylating regents or cationic center generators such as MAO, AlR_3, and $[Ph_3C]^+[B(C_6F_5)_4]^-$ in MMA polymerization. The details of the polymerization mechanism are certainly of considerable interest and remain as yet to be established, but ^{11}B NMR and IR spectral data for well-rinsed PMMA may suggest the involvement of the cleavage of a Zr−carboranyl carbon bond followed by the coordination of MMA and 1,4-addition as initial steps.

Compound **2** clearly constitutes the first example of a group 4 neutral s-PMMA catalyst. In addition, the formation of Ti and Hf analogues of **2** and the various lithiation extent of **1** to monoanion, dianion, and potentially trianion clearly manifest the versatile complexation behavior of isopropyl-bridged cyclopentadienyl *o*-carboranyl ligand **1**. Indeed, the 1:1 reaction of the dianion $[CpCMe_2CB_{10}H_{10}C]^{2-}$ as the lithium salt with $ZrCl_4$ in toluene generates $Zr(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)Cl_2$,[21] a constrained-geometry catalyst type[22] containing carborane. The derivative chemistry of **1** and the detailed catalytic behavior of its complexes will be the subject of future reports.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complex **2** (16 pages). Ordering information is given on any current masthead page.

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[21] Data for $Zr(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)Cl_2$: ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ 1.66 (s, 3H, C(C*H*$_3$)$_2$), 6.36 (dd, 1H, Cp(*H*)), 6.45 (dd, 2H, Cp(*H*)), 6.72 (dd, 1H, Cp(*H*)), 6.85(dd, 1H, Cp(*H*)); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.475 MHz) δ 32.07 (C(*C*H$_3$)$_2$), 32.58 (C(*C*H$_3$)$_2$), 42.31 (*C*(CH$_3$)$_2$), 104.42 (*C*B$_{10}$C), 109.90 (Cp(*C*)H), 117.18 (Cp(*C*)H), 118.25 (Cp(*C*)H), 120.03 (Cp(*C*)H), 156.75 (Cp(*C*)C); ^{11}B{^{1}H} NMR ($CDCl_3$, 96.275 MHz) δ −9.21 (br), −6.54 (br), −3.91 (br); IR (KBr, cm^{-1}) ν(B−H) 2562 (vs), 2596 (vs); high-resolution MS (EI) *m*/*z* calcd 410.0920, found 410.0953.

[22] Dow Chemical Co. European Patent 0416815A2, 1990.