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Syntheses and catalytic activities of Group 4 metal complexes derived from $C_{(cage)}$-appended cyclohexyloxocarborane trianion

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Abstract

The reaction of Li[*closo*-1-Me-1,2-$C_2B_{10}H_{10}$] with cyclohexene oxide produced *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**1**) in 86% yield. Decapitation of (**1**) with potassium hydroxide in refluxing ethanol gave the corresponding cage-opened potassium salt of the carborane anion, [*nido*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_9H_{10}$]$^-$ (**2**) in 82% yield. Deprotonation of (**2**) with two equivalents of *n*-butyllithium in THF at −78 °C, followed by its further reaction with anhydrous $MCl_4 \cdot 2THF$ (M = Ti, Zr) produced the corresponding d^0-half-sandwich metallacarboranes, *closo*-1-M(Cl)-2-Me-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**3** M = Zr; **4** M = Ti), in 59% and 51% yields, respectively. Reaction of Li[*closo*-1,2-$C_2B_{10}H_{11}$] with Merrifield's peptide resin (1%) in refluxing THF gave the *ortho*-carborane-functionalized polymer (**5**) in 88% yield. The corresponding *closo*-1-polystyryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**6**) was produced in 94% yield by refluxing a mixture of the lithium salt of (**5**) and cyclohexene oxide in THF for 2 days. Compound (**6**) was decapitated, deprotonated and then reacted with $ZrCl_4 \cdot 2THF$ to produce a polymer-supported d^0-half-sandwich metallacarborane *closo*-1-Zr(Cl)-2-polystyryl-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**7**) in 41% yield. Compounds (**3**) and (**7**), in the presence of MMAO-7 (13% ISOPAR-E), were found to catalyze the polymerization of ethylene and vinyl chloride in toluene to give high molecular weight PE (9.4×10^3 ($M_w/M_n = 1.8$)) and PVC (2.1×10^3 ($M_w/M_n = 1.6$)), respectively.

Keywords: Half-sandwich metallacarborane; Trianionic ligand; Ligand immobilization; Olefin polymerization; Group 4 metallacarborane; Ziegler–Natta catalysis

1. Introduction

The identification of new generations of polymerization catalysts remains one of the main avenues of current polymer research. The range, and success, of such studies is demonstrated in the area of Ziegler–Natta type polyolefin catalysis, especially involving the use of metallocenes as the active catalyst sites [1]. Catalytic activity has been shown to be function of the metal, plus the nature of the η^5-ligand as well as the other ligands [2–4]. Of particular interest are the so called constrained-geometry complexes in which an early transition metal is bonded to at least one η^5-ligand that has tethered to it a terminal σ-bonding group [5–9]. The advantages of the use of suitably modified metallocenes as "single site" polymerization catalysts include enhanced activities compared to conventional Ziegler–Natta catalysts and their ability to produce stereospecific polymers with narrow molecular weight distributions [2]. However, the

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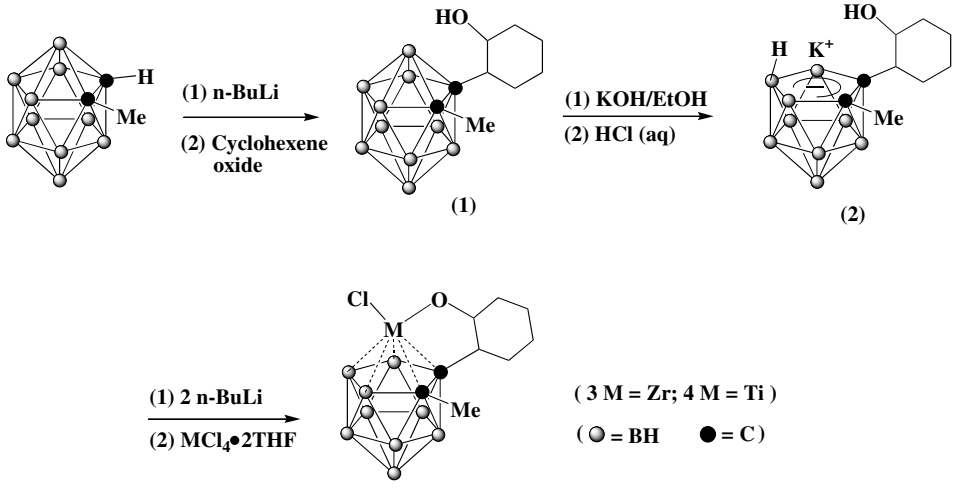
homogeneous nature of these catalysts limit their practical use, prompting investigations of supported catalysts [10,11]. Although the polymerization of vinyl chloride catalyzed by half-titanocene/MAO (MAO = methylaluminoxine) has been reported [12], the electrophilic nature of the metals prevents their wide spread use in the polymerization of monomers with polar groups. Therefore, conventional free radical polymerization is still used in industry to produce a wide range of functionalized polymers such as polyvinylacetate, polyvinylchloride (PVC), etc. [13]. However, such methods produce polymers containing a number of structural defects and are not conducive to the production of stereospecific polymers having narrow molecular weight distributions. Therefore, there is a need to generate new types of metal catalytic systems for the production of functionalized polymers or co-polymers that possess narrow molecular weight distributions.

In addition to the cycolpentadienyl based ligands, there is another class of 6π electron donors, namely the dinegative *nido*-carboranes, $[R_2C_2B_4H_4]^{2-}$ and $[R_2C_2B_9H_9]^{2-}$ (R=H or a single bonding group) [14]. Both the small and large cage metal complexes have been shown to catalyze olefin polymerization, but the results are limited [15,16]. There has been even less information as to the possible efficacy of constrained-geometry complexes as olefin catalysts; to date, most of the reports have only described their syntheses or ligand exchange reactions [17,18]. Herein we report the synthesis of $C_{(cage)}$-appended *nido*-carborane ligands, each containing an oxide anion in the terminal position of a hydrocarbyl bridge in the appended unit, along with their conversion to the corresponding Group 4 metallacarboranes. Their use as polymerization catalysts, both in homogeneous and heterogeneous phases, is also presented.

2. Results and discussion

The reaction of the lithium salt of the carborane monoanion, [*closo*-1-Me-1,2-$C_2B_{10}H_{10}]^-$, with commercially available cyclohexene oxide afforded the ligand precursor, *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**1**), in 86% yield (Scheme 1). The ^{1}H, ^{13}C and ^{11}B NMR spectra of (**1**) show normal group resonances that are consistent with a *closo*-$C_2B_{10}H_{11}$ cage with a hydroxycyclohexyl group bonded to one of the cage carbons, as depicted in Scheme 1 [19]. The IR spectrum of (**1**) shows the absorption band of ν_{BH} at the expected region (2588 cm^{-1}). The monoanion of the $C_{(cage)}$-appended carborane, [*nido*-7-Me-8-(2′-hydroxycyclohexyl)-7,8-$C_2B_9H_{10}]^-$ (**2**), was synthesized by the reaction of (**1**) with potassium hydroxide in refluxing ethanol in 82% yield after purification, following the literature procedures [20]. Compared with its precursor (**1**), the δ^{13}C of *C*H–OH in (**2**) down shifted 4.65 ppm. The ^{11}B NMR spectrum of (**2**) is essentially the same as those obtained for [*nido*-7-(CH_2NH_2)-7,8-$C_2B_9H_{11}]^-$ [18c] and [*nido*-7-(CH_2OH)-8-Me-7,8-$C_2B_9H_{10}]^-$ [18b]. The ^{1}H NMR spectrum of (**2**) showed resonances at δ 3.56 and −2.81 ppm corresponding to the hydroxy and bridging hydrogens, respectively, and its IR spectrum shows peaks at ν = 3524 cm^{-1} and ν = 2497 cm^{-1} that are assigned to the O–H and B–H stretches, respectively. The trianionic carborane ligand (Fig. 1), generated in situ from (**2**), was allowed to react with $MCl_4 \cdot 2THF$ to produce *closo*-1-M(Cl)-2-Me-3-[2′-σ-*O*-cyclohexyl]-η^5-2,3-$C_2B_9H_9$ in 59% (**3**, M = Zr) and 51% (**4**, M = Ti) yields (see Scheme 1), respectively. Compounds (**3**) and (**4**) could be easily purified by precipitation of the product in pentane. A comparison of the ^{11}B NMR spectra of (**3**) and (**4**) with their precursor, (**2**), shows that on metalation the apical boron



Scheme 1. Synthesis of constrained-geometry Group 4 metallacarboranes.

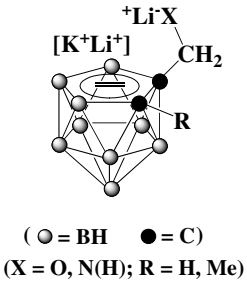


Fig. 1. Carborane trianionic ligands.

resonance shifts downfield from δ −38.10 ppm in the precursor to −27.70 ppm for (**3**) and −24.51 ppm for (**4**). This is consistent with the withdrawing of electron density by the bonded metal from the cage, thus deshielding the boron opposite to it [21]. ^{1}H NMR spectra of (**3**) and (**4**) are consistent with the molecular geometries shown in Scheme 1.

An organic polymer substrate was introduced onto the *closo*-1,2-$C_2B_{10}H_{10}$ by reaction of its lithium salt with Merrifield's peptide resin (1%) that produced 1-polystyrenyl-1,2-$C_2B_{10}H_{11}$ (**5**), in 88% yield. Compound (**5**) reacts in situ with *n*-BuLi and cyclohexene oxide in THF to give the polymer-supported ligand, *closo*-1-polystyryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**6**) in 94% yield with the loading amounts up to 1.24 mmol/g (Merrifield's peptide resin (1%)) based on lithium chloride produced (Scheme 2). Decapitation of (**6**) with potassium hydroxide in refluxing ethanol, followed by deprotonation with *n*-BuLi in THF, produced the trianionic intermediate that reacts further with $ZrCl_4 \cdot 2THF$ to form the corresponding zirconium complex, *closo*-1-Zr(Cl)-2-polystyryl-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**7**) with loading amounts of zirconium moiety up to 0.48 mmol/g (Merrifield's peptide resin (1%)). The

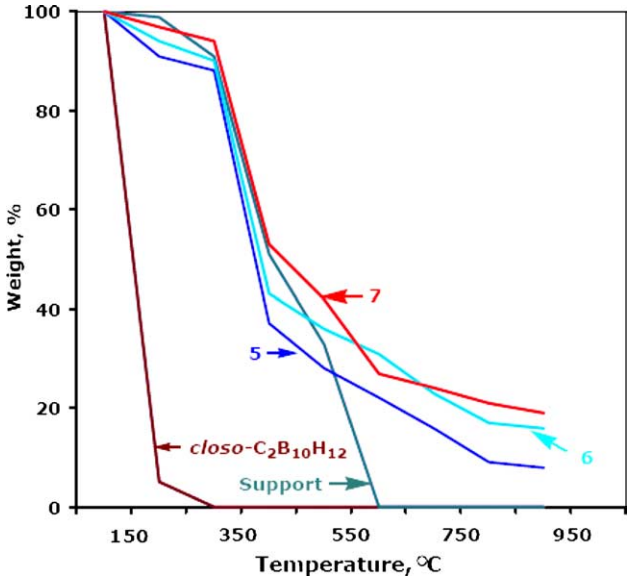
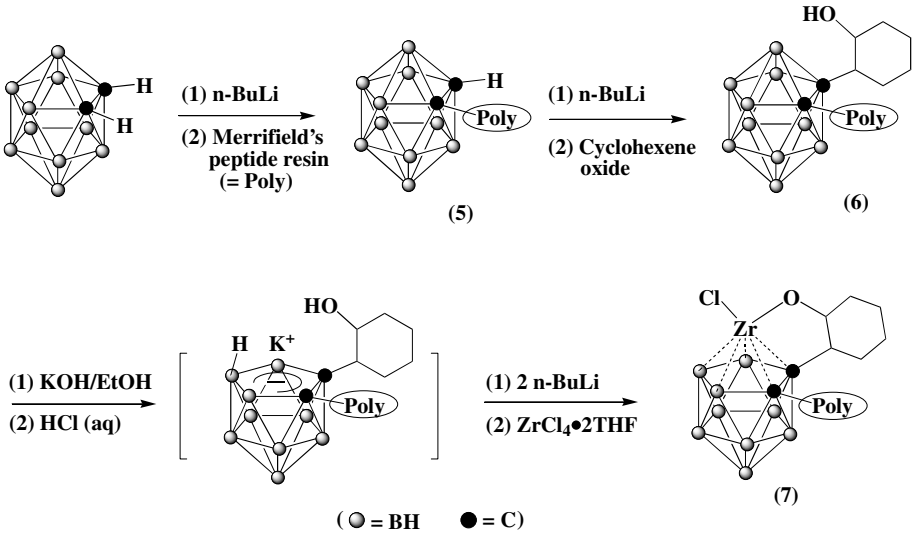


Fig. 2. TGA curves of Merrifield's peptide resin (support), *closo*-$C_2B_{10}H_{12}$, **5**, **6** and **7**.

presence of the ν_{BH} absorption bands in the range of 2590–2510 cm^{-1} in IR spectra of compounds **5**–**7**, coupled with the formation of LiCl, confirms the successful immobilization of carborane cages to the polymer support. Further support for successful immobilization of the carborane was furnished by thermogravimetric analyses of compounds **5**–**7** (see Fig. 2). The TGA plots show that, while both the *closo*-1,2-$C_2B_{10}H_{12}$ and the Merrifield's peptide resin precursors have completely reacted, or sublimed, by 900 °C, the supported carborane products (**5**–**7**) show mass residues of 8.13%, 15.77%, and 19.20%, respectively. Unfortunately, the chemical compositions of the residues could not be determined, so their masses could not be used for analysis purposes.



Scheme 2. Synthesis of Merrifield's peptide resin-supported constrained-geometry zirconacarborane.

Table 1
Polymerization results of ethylene and vinyl chloride with **3** and **7**

Polymer[a]	Activity[b]	M_w ($\times 10^3$/mol)[c]	M_w/M_n
Polyethylene	53(A) 31(B)	9.4(A) 3.8(B)	1.8(A) 1.3(B)
Polyvinyl chloride	22(A) 14(B)	2.1(A) 1.3(B)	1.6(A) 1.2(B)

[a] A results are for (**3**) and B results are for (**7**), polymerization conditions: ratio of catalyst and co-catalyst ([Al]/[Zr]) = 2000, solvent = toluene, temperature = 50 °C, pressure = 1.5 bar (polyethylene) and 1.2 bar (polyvinyl chloride), polymerization time = 4 h.

[b] Activity = kg polymer per mol catalyst per h per bar.

[c] Molecular weight and molecular weight distribution of the polymers were determined by means of gel-permeation chromatography (GPC: Waters 150 °C) at 145 °C using 1,2,4-trichlorobene as a solvent. The weight average molecular weight and polydispersity index (M_w and M_w/M_n, respectively) were calculated on the basis of polystyrene standards.

Therefore, the loading amounts of anchored carborane was determined by titration of the lithium chloride produced in their formation reactions with standard $AgNO_3$.

The polymerization reactions of ethylene and vinyl chloride in the presence of (**3**) or (**7**) and MMAO-7 cocatalyst were studied. The catalytic runs were carried out in toluene with an [Al]/[Zr] = 2000 at 50 °C under pressures of 1.5 bar of ethylene or 1.2 bar of vinyl chloride. The polymerization data are presented in Table 1. As can be seen from the table, both (**3**) and (**7**), in the presence of MMAO-7 are moderately active catalysts for olefin polymerization affording polymers with narrow molecular mass distributions (M_w/M_n = 1.2–1.8). Even though the activity of the homogeneous olefin (ethylene) is greater than that of vinyl chloride, the activity of the latter is sufficiently high to warrant further investigations of these systems, including their mechanisms. Such studies are currently underway in our laboratories.

3. Conclusions

The hydroxycyclohexyl-appended carborane, *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ have been synthesized in high yields, decapitated with alcoholic KOH and reacted with *n*-BuLi to give a trianionic *ansa*-carborane ligand. The reaction of this ligand with anhydrous $MCl_4 \cdot 2THF$ (M = Ti, Zr) afforded the corresponding d^0-half-sandwich metallocarboranes, *closo*-1-M(Cl)-2-Me-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**3**, M = Zr; **4**, M = Ti) in good yields. The polymer-supported metallacarborane, *closo*-1-Zr(Cl)-2-polystyryl-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ was prepared in a three-step sequence. First, *closo*-1,2-$C_2B_{10}H_{12}$ was immobilized on Merrifield's peptide resin (1%) and then reacted with cyclohexene oxide to give *closo*-1-polystyryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$. The polymer-linked carborane was found to undergo a standard decapitation reaction to yield the corresponding *nido*-carborane ligand that was further reacted with $ZrCl_4 \cdot 2THF$ to afford the polymer-supported zirconacarborane, *closo*-1-Zr(Cl)-2-polystyl-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$. Both the supported and the unsupported zirconacarboranes in the presence of MMAO-7 were found to be active catalysts for the polymerization of ethylene and vinyl chloride.

4. Experimental

All syntheses were carried out in an inert atmosphere with standard Schlenk techniques or in a glove box. Tetrahydrofuran (THF), diethyl ether, toluene, benzene, pentane and *n*-hexane were heated over sodium and benzophenone until a blue color was obtained, and then distilled under argon just before use. *n*-Butyllithium (1.6M in hexanes), zirconium (IV) chloride tetrahydrofuran complex (1:2), titanium (IV) chloride tetrahydrofuran complex (1:2), cyclohexene oxide, Merrifield's peptide resin (1%) (contains 1.97 mmol Cl^-/g), ethylene, vinyl chloride, and organic solvents were used as received from Aldrich. Modified methylaluminoxane 7 (MMAO-7, 13% ISOPAR-E) was obtained from Akzo Chemicals Inc. 1-Me*closo*-1,2-$C_2B_{10}H_{11}$ and *closo*-1,2-$C_2B_{10}H_{12}$ were provided by Katchem Ltd. Proton, carbon-13 and boron-11 NMR spectra were recorded on a Bruker Fourier-transform multinuclear spectrometer at 400.13, 100.62 and 128.38 MHz, respectively. Chemical shifts for ^1H NMR and ^{13}C NMR spectra were referenced to $SiMe_4$ (0.00 ppm) and measured with respect to residual protons in the deuterated solvent. Chemical shift values for ^{11}B NMR spectra were referenced relative to $BF_3 \cdot OEt_2$ (0.00 ppm). Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets techniques and presented in a sequence of signal strength and peak mode in brackets, in which s = strong, vs = very strong, m = middle and w = weak for signal strength and s = single, m = multiple and br = broad for peak model. Elemental analyses were determined by a Perkin–Elemer 2400 CHN elemental analyzer. The TGA analyses were carried out on an SDT 2960 Simultaneous DSC-TGA analyzer.

4.1. Synthesis of *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**1**)

A solution of 1.00 g (6.32 mmol) of 1-Me-1,2-$C_2B_{10}H_{11}$, dissolved in a mixture of 40 ml diethyl ether and 20 ml benzene, was cooled to −78 °C and 4.20 ml (6.72 mmol) of *n*-BuLi (1.6 M in *n*-hexane) was added with syringe. After addition and half an hour of further

stirring, the mixture was allowed to warm to room temperature and stirring was continued for 4 h. After that time, 0.70 ml (6.78 mmol) of cyclohexene oxide was added with a syringe at 0 °C and the reaction was continued at room temperature for another 6 h before hydrolysis with 10 ml water. The mixture was transferred to a separatory funnel where the organic phase was separated and the aqueous phase was extracted with 2×25 ml ethyl ether. After drying with $MgSO_4$, the solvent was removed under reduced pressure and the residue was re-crystallized with *n*-hexane to obtain 1.40 g sticky residue identified as *closo*-1-Me-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (**1**) in 86% yield. Analytical data: Calcd. (Found) for $C_9H_{24}B_{10}O$ (**1**): C, 42.16 (42.11); H, 9.44 (9.40). ^{1}H NMR ($CDCl_3$, ppm), $\delta = 3.40$ (m, 1H, C*H*–O), 2.90–0.63 (m, br, 20H, $B_{10}H_{10}$, –C*H*, 4CH_2, O*H*), 1.80 (s, 3H, C_{cage}–CH_3). ^{13}C NMR ($CDCl_3$, ppm), $\delta = 83.20$ and 75.71 (C_{cage}), 71.64 (–*C*H–O), 47.03, 35.99, 33.56, 25.62, 23.60, 23.01 (–*C*H–C_{cage}, 4*C*H_2, *C*H_3–C_{cage}). ^{11}B NMR ($CDCl_3$, ppm), $\delta = -3.65$ (1B, $^1J_{BH} = 160$ Hz), -5.01 (1B, $^1J_{BH} = 149$ Hz), -8.52 (2B, $^1J_{BH} = 85$ Hz), -9.11 (2B, $^1J_{BH} = 103$ Hz), -9.95 (4B, $^1J_{BH} = 150$ Hz). IR (KBr pellet, cm^{-1}), $\upsilon = 3062$(s, s), 2588(vs, s), 1447(m, s), 1390(m, s), 1229(w, s), 1133(m, s), 1094(m, s), 1017(s, s), 934(m, s), 722(s, s).

4.2. Synthesis of K[nido-7-Me-8-(2′-hydroxycyclohexyl)-7,8-$C_2B_9H_{10}$] (2)

A 1.50-g (5.85 mmol) sample of (**1**) was added to a clear solution of 2.00 g (32.08 mmol) potassium hydroxide in 50 ml of 95% ethanol with continuous stirring. After all of the solid dissolved, the mixture was heated to reflux for 16 h. The vessel was cooled to room temperature, neutralized with aqueous HCl and the solvent was removed under reduced pressure. The resulting residue was extracted with anhydrous THF. After filtration and drying in vacuum, 1.36 g of sticky solid, K[*nido*-7-Me-8-(2′-hydroxycyclohexyl)-7,8-$C_2B_9H_{10}$] (**2**) was obtained in 82% yield. Analytical data: Calcd. (Found) for $C_9H_{24}B_9KO$ (**2**): C, 37.97 (37.93); H, 8.50 (8.48). ^{1}H NMR (DMSO-d_6, ppm), $\delta = 3.56$ (br, 1H, –O*H*), 3.18 (m, 1H, C*H*–O), 2.00–0.95 (m, br, 22H, B_9H_9, –C*H*, 4CH_2, C_{cage}–CH_3, O*H*), -2.81(br, 1H, BH_{bridge}). ^{13}C NMR (DMSO-d_6, ppm), $\delta = 76.29$ (–*C*H–O), 45.59, 36.90, 33.63, 26.71, 25.21, 24.05 (–*C*H–C_{cage}, 4*C*H_2, *C*H_3–C_{cage}). ^{11}B NMR (DMSO-d_6, ppm), $\delta = -8.10$ (1B, $^1J_{BH} = 147$ Hz), -11.47 (2B, $^1J_{BH} = 138$ Hz), -16.32 (1B, $^1J_{BH} = 103$ Hz), -19.52 (2B, $^1J_{BH} = 124$ Hz), -21.75 (1B, $^1J_{BH} = 120$ Hz), -34.90 (1B, $^1J_{BH} = 110$ Hz), -38.10 (1B, $^1J_{BH} = 135$Hz). IR (KBr pellet, cm^{-1}), $\upsilon = 3524$(vs, s), 3040(m, s), 2931(s, s), 2857(s, s), 2497(vs, s), 1477(s, s), 1449(s, s), 1388(s, s), 1273(m, s), 1212(m, s), 1036(vs, s), 978(s, s), 860(m, s), 472(m, s).

4.3. Synthesis of closo-1-Zr(Cl)-2-Me-3-(2′-σ-O-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (3)

A 1.50-g (5.27 mmol) sample of (**2**) was dissolved in 75 ml of dry tetrahydrofuran, the resulting mixture was cooled to -78 °C and 6.60 ml (10.56 mmol) *n*-BuLi (1.6 M in hexanes) was carefully added with a syringe. After addition, the system was kept reacting at -78 °C for 30 min before being warmed to room temperature and stirred for 6 h. The reaction mixture was cooled to 0 °C and 2.00 g (5.25 mmol) $ZrCl_4 \cdot 2THF$ was added to the THF solution under argon. The colour of the mixture changed from pale yellow to red-brown during the addition of $ZrCl_4 \cdot 2THF$. After 30 min at 0 °C, the mixture was then stirred at room temperature for 2 days. After filtration and removal of the solvent under reduced pressure, the residue was re-crystallized from a mixture of benzene/pentane (v:v = 2:1) to give 1.15 g of *closo*-1-Zr(Cl)-2-Me-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**3**) in 59% yield. Analytical data: Calcd. (Found) for $C_9H_{22}B_9ClOZr$ (**3**): C, 29.20, (29.18); H, 6.00, (5.95). ^{1}H NMR (DMSO-d_6, ppm), $\delta = 3.10$ (m, 1H, C*H*–O), 1.90–0.43 (m, br, 18H, B_9H_9, –C*H*, 4CH_2), 1.66 (s, 3H, C_{cage}–CH_3). ^{13}C NMR (DMSO-d_6, ppm), $\delta = 69.94$, 68.20 (C_{cage}), 56.18 (–*C*H–O), 49.63, 32.71, 26.37, 26.32, 23.92, 23.74 (–*C*H–C_{cage}, 4*C*H_2, *C*H_3–C_{cage}). ^{11}B NMR (C_6D_6, ppm), $\delta = -8.31$ (2B, $^1J_{BH} = 113$ Hz), -10.56 (4B, $^1J_{BH} = 128$ Hz), -17.52 (2B, $^1J_{BH} = 139$ Hz), -27.70 (1B, $^1J_{BH} = 117$ Hz). IR (KBr pellet, cm^{-1}), $\upsilon = 3413$(s, s), 2919(vs, s), 2851(s, s), 1637(m, s), 1457(s, s), 1305(s, s), 963(m, s), 423(m, s).

4.4. Synthesis of closo-1-Ti(Cl)-2-Me-3-(2′-σ-O-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (4)

A method similar to that described in the preparation of (**3**) was used to produce 0.99 g of *closo*-1-Ti(Cl)-2-Me-3-(2′-σ-*O*-cyclohexyl)-η^5-2,3-$C_2B_9H_9$ (**4**) (51% yield) from 1.70 g (5.96 mmol) (**2**), 7.65 ml (12.24 mmol) *n*-BuLi (1.6 M in hexanes) and 2.05 g (5.95 mmol) $TiCl_4 \cdot 2THF$ in 70 ml dry THF. Analytical data: Calcd. (Found) for $C_9H_{22}B_9ClOTi$ (**4**): C, 33.07, (33.05); H, 6.78, (6.76). ^{1}H NMR (DMSO-d_6, ppm), $\delta = 3.30$ (m, 1H, C*H*–O), 2.10–0.20 (m, br, 18H, B_9H_9, –C*H*, 4CH_2), 1.48 (s, 3H, C_{cage}–CH_3). ^{13}C NMR (THF-d_8, ppm), $\delta = 70.49$, 68.26 (C_{cage}), 51.81 (–*C*H–O), 35.50, 33.49, 29.73, 26.80, 26.54, 26.43 (–*C*H–C_{cage}, 4*C*H_2, *C*H_3–C_{cage}). ^{11}B NMR (C_6D_6, ppm), $\delta = -7.42$ (2B, $^1J_{BH} = 122$ Hz), -9.10 (4B, $^1J_{BH}$ = unresolved), -16.48 (2B, $^1J_{BH} = 126$ Hz), -24.51 (1B, $^1J_{BH} = 131$ Hz). IR (KBr pellet, cm^{-1}), $\upsilon = 3490$(m, s), 3117(s, s), 3039(s, s), 2901(s, s), 2705(vs, s), 1685(s, s), 1528(s, s), 1410(s, s), 1292(m, br), 959(m, s), 703(s, s), 455(m, s).

4.5. Synthesis of Merrifield's peptide resin supported ortho-carborane (5)

A 0.58-g (4.02 mmol) sample of 1,2-$C_2B_{10}H_{12}$ was taken in a 250 ml two-necked round-bottom flask equipped with a magnetic stirring bar to which 100 ml of dry THF was then added to dissolve the carborane compound producing a clear solution. The solution was cooled to −78 °C and 2.6 ml (4.16 mmol) *n*-BuLi (1.6 M in hexane) was added using a syringe with continuous stirring. After the addition, the mixture was maintained at that temperature for 30 min followed by warming to room temperature spontaneously and reacted further for 4 h. Merrifield's peptide resin (1%), 2.0 g (3.94 mmol Cl^-), was added and the resulting mixture was stirred at room temperature under argon for 2 days. At the end of the reaction process, the mixture was heated to reflux for 4 h before cooling down to room temperature and quenching with 3.0 ml methanol. The solvents were removed under reduced pressure and the crude product was washed with de-ionized water (2 × 10 ml) and *n*-hexane (2 × 20 ml) to remove any trace of LiCl and starting material 1,2-$C_2B_{10}H_{12}$, then dried in high vacuum for 2 days to give 2.39 g of a pale yellow solid of 1-polystyryl-*closo*-1,2-$C_2B_{10}H_{11}$ in 88% yield. The collected aqueous solution was combined and concentrated to 5.0 ml and titrated with $AgNO_3$ that determined 0.150 g (3.54 mmol) of LiCl was produced in the reaction. Titration procedure: The 5.0 ml of concentrated aqueous washing was pipetted into a 250-ml volumetric flask and diluted with de-ionized water to 250 ml and titrated with standard silver nitrate solution (0.1 M in water) using five drops of 5% potassium chromate as an indicator. Titrant was added until a pinkish yellow color persisted at the end point to consume 35.38 ml of $AgNO_3$. The loading amount of carborane reached to 1.48 mmol (carborane cage)/g (Merrifield's peptide resin).

IR (KBr pellet, cm^{-1}): υ = 3440(m, br), 3024(s, s), 2920(vs, s), 2583(vs, s, υ_{BH}), 1944(m, s), 1802(m, s), 1601(s, s), 1490(s, s), 1420(s, s), 1374(m, s), 1314(m, s), 1265(s, s), 1182(m, s), 1154(m, s), 1111(m, s), 1069(s, s), 1024(s, s), 907(s, s), 824(s, s), 756(s, s), 698(s, s), 545(s, s).

4.6. Synthesis of closo-1-polystyryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_{10}H_{10}$ (6)

A 2.00 g of (**5**) (containing 2.96 mmol carborane) was suspended in 60 ml of THF. The resulting mixture was cooled to −78 °C and 2.50 ml (4.00 mmol) *n*-BuLi (1.6 M in hexanes) was added with a syringe carefully. After addition, the mixture was maintained at that temperature for 30 min, followed by warming to room temperature spontaneously and reacted further for 8 h. After removal of all volatiles, the residue was washed with *n*-hexane to remove any unreacted *n*-BuLi. The solid was re-suspended in 60 ml THF with vigorous stirring followed by addition of 0.36 ml (3.49 mmol) of cyclohexene oxide with a syringe at 0 °C, then the reaction mixture was stirred at room temperature for another 4 h before heating to reflux for 2 days. After cooling to room temperature and quenching with 4.0 ml mixture of 20% HCl solution of methanol, the solvent was removed under reduced pressure and the crude product was washed with de-ionized water (2 × 10 ml) to remove any trace quantity of LiCl, then dried in high vacuum for 3 days to collect 2.25 g of a pale yellow solid, identified as *closo*-1-polymeryl-2-(2′-hydroxycyclohexyl)-1,2-$C_2B_9H_{10}$] (**6**) in 94% yield. The collected aqueous solution was combined and concentrated to 5.0 ml and subjected to titration with $AgNO_3$ to determine that 0.118 g of LiCl was produced with a consumption of 27.83 ml $AgNO_3$ standard. The loading amount of carborane reached to 1.24 mmol (functionalized carborane cage)/g (Merrifield's peptide resin).

IR (KBr, pellet, cm^{-1}): υ = 3328(w, br), 3063(w, s), 2938(s, s), 2844(s, s), 2547(vs, s, υ_{BH}), 1781(m, s), 1500(m, s), 1453(s, s), 1391(m, s), 1359(m, s), 1047(s, s), 906(m, s), 875(m, s), 766(s, s), 688 (s, s), 656(s, s), 477(m, s), 438(m, s).

4.7. Synthesis of closo-1-Zr(Cl)-2-polystyryl-3-(2′-σ-O-cyclohexyl)-η⁵-2,3-$C_2B_9H_9$ (7)

A 2.33-g (contains 2.89 mmol of carborane) sample of **6** was suspended in a clear solution of 1.10 g (16.66 mmol) potassium hydroxide in 150 ml 95% ethanol, the mixture was stirred at room temperature for 30 min before refluxing for 2 days. Then the reaction mixture was cooled to room temperature, neutralized with aqueous HCl and filtered. The resulting solid was washed with de-ionized water (3 × 10 ml) to remove any traces of KCl, dried in high vacuum for 2 days and then suspended in 120 ml dry THF. The mixture was cooled to −78 °C and 6.5 ml (10.40 mmol) *n*-BuLi in hexanes was added under argon atmosphere with continuous stirring. After reacting at −78 °C for 30 min, the mixture was warmed to room temperature spontaneously and kept stirring for 1 day, the solvent was then removed under reduced pressure and the resulting residue was washed with *n*-hexane (2 × 15 ml) to remove any traces of unreacted *n*-BuLi. The residue was re-suspended in 150 ml THF and 1.10 g (2.89 mmol) of $ZrCl_4 \cdot 2THF$ was added at 0 °C. After the addition, the reaction was continued at room temperature for 2 days, the mixture was filtered and the collected solid was washed with absolute ethanol (2 × 10 ml) to remove lithium chloride followed by drying in high vacuum for 2 days to collect *closo*-1-Zr(Cl)-2-polystyryl-3-(2′-σ-*O*-cyclohexyl)-η⁵-2,3-$C_2B_9H_9$ (**7**) as a pale yellow solid (2.48 g, 41% yield). The collected alcohol solutions were combined, dried and the resulting residue was dissolved in 5.0 ml de-ionized water and subjected to titration with

$AgNO_3$ to determine that 0.101g of LiCl was produced with a consumption of 23.82 ml $AgNO_3$ standard. The loading amount of zirconium moiety reached up to 0.48 mmol (zirconium moiety)/g (Merrifield's peptide resin).

IR (KBr pellet, cm^{-1}): υ = 3435(w, br), 3026(s, s), 2913(s, s), 2850(m, s), 2515(s, s, υ_{BH}), 1630(s, s), 1528(s, s), 1491(m, s), 1410(m, s), 1365(s, s), 1163(m, s), 1096(w, s), 1015(s, s), 743(s, s), 703(s, s), 527(s, s).

4.8. Evaluation of the catalytic activity of (3) and (7)

The polymerizations of ethylene and vinyl chloride catalyzed by compound (**3**) or (**7**) were carried out for 4 h in 80 ml toluene in the presence of modified methylaluminoxane 7 (MMAO-7, 13% ISOPAR-E) in Schlenk tubes. The argon pressures inside the Schlenk tubes were reduced by applying vacuum. Monomer pressure was then applied to the tubes and the reactor was adjusted to constant temperature and pressure for reaction. The detailed polymerization conditions are as follow: catalysts (**3**, **7**) 1 μmol based on zirconium carborane species, MMAO-7 amount is 2000 mol to give a ratio of [Al]/[Zr] = 2000. The reaction temperature was 50 °C and the pressures of polyethylene and polyvinyl chloride were 1.5 and 1.2 bars, respectively. After the allotted time, the reactions were quenched with a 50-ml mixture of 10% HCl solution of MeOH. The polymers were then precipitated with 150 ml methanol, collected by filtration, washed with MeOH (4×20 ml), *n*-hexane (2×20 ml) and dried at 60 °C in high vacuum for 2 days to constant weight. Polymerization results are summarized in Table 1.

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