

Another example of carborane based trianionic ligand: Syntheses and catalytic activities of cyclohexylamino tailed *ortho*-carboranyl zirconium and titanium dicarbollides

Zhu Yinghuai ^{a,*}, Shirley Lo Pei Sia ^a, Fethi Kooli ^a,
Keith Carpenter ^a, Richard A. Kemp ^{b,c}

^a Institute of Chemical and Engineering Sciences Ltd., 1 Pesek Road, Jurong Island, Singapore 627833, Singapore

^b Department of Chemistry, University of New Mexico, Albuquerque, NM 87131-2609, USA

^c Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, USA

Received 13 January 2005; received in revised form 18 March 2005; accepted 18 April 2005

Available online 25 July 2005

Abstract

In situ reaction of Li[*closo*-1-Ph-1,2-C₂B₁₀H₁₀] with 7-azabicyclo [4.1.0] heptane results in the formation of the disubstituted carborane, *closo*-1-Ph-2-(2'-aminocyclohexyl)-1,2-C₂B₁₀H₁₀ (**1**), in 63% yield. Decapitation of (**1**) with potassium hydroxide in refluxing ethanol produces the cage-opened *nido*-carborane, K[*nido*-7-Ph-8-(2'-aminocyclohexyl)-7,8-C₂B₉H₁₀]⁻ (**2**), in 80% yield. Deprotonation of the above monoanion with two equivalents of *n*-butyllithium followed by reaction with anhydrous MCl₄ · 2THF (M = Zr, Ti) provides *d*⁰-half-sandwich metallocarboranes, *closo*-1-M(Cl)-2-Ph-3-(2'-σ-(H)*N*-cyclohexyl)-2,3-η⁵-C₂B₉H₉ (3 M = Zr; 4 M = Ti) in 53% and 42% yields, respectively. The reaction of Li[*closo*-1,2-C₂B₁₀H₁₁] with 7-azabicyclo [4.1.0] heptane in THF affords *closo*-1-(2'-aminocyclohexyl)-1,2-C₂B₁₀H₁₀ (**5**) in 59% yield. Immobilization of the carboranyl amino ligand (**1**) to an organic support, Merrifield's peptide resin (1%), has been achieved by the reaction of the sodium salt of (**5**) with polystyryl chloride in THF to produce *closo*-1-(2'-aminocyclohexyl)-2-polystyryl-1,2-C₂B₁₀H₁₀ (**6**) in 87% yield. Further reaction of the dianion derived from (**6**) with anhydrous ZrCl₄ · 2THF led to the formation of the organic polystyryl supported *d*⁰-half-sandwich metallocarborane, *closo*-1-Zr(Cl)-2-(2'-σ-(H)*N*-cyclohexyl)-3-polystyryl-2,3-η⁵-C₂B₉H₉ (**7**), in 38% yield. These new compounds have been characterized by elemental analyses, NMR, and IR spectra. Polymerizations of both ethylene and vinyl chloride with (**3**) and (**7**) have been performed in toluene using MMAO-7 (13% ISOPAR-E) as the co-catalyst. Molecular weights up to 32.8 × 10³ (*M_w*/*M_n* = 1.8) and 9.5 × 10³ (*M_w*/*M_n* = 2.1) were obtained for PE and PVC, respectively.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Carborane trianion; Half-sandwich metallocarborane; Ligand immobilization; Olefin polymerization

1. Introduction

Although Ziegler-Natta polyolefin catalysts have been well-studied for the polymerization of simple olefins to obtain desired molecular weight polymers [1,2],

this field is still one of the most important and primarily interesting areas in polymer chemistry research and development. A major goal is to identify new generations of catalysts for the α-olefin polymerization process. Geometry constrained complexes, which contain at least one η⁵-ligand, such as cyclopentadienyl (Cp), indenyl ligand, etc., with a terminal σ-bonding group and group 3–6 transition metals, is a particular subgenus of Ziegler-Natta catalysts and belongs in the group of metallocene catalysts [3–5]. Although metallocene catalysts

* Corresponding author. Present address: ICES, Apply Cat. Ayer Rajah Crescent, Singapore 139959, Singapore. Tel.: +6568744217; fax: +6568734805.

E-mail address: zhu_yinghuai@ices.a-star.edu.sg (Z. Yinghuai).

have the advantage of often appearing to be “single-site” catalysts, giving a narrow range of molecular weight polymers of similar molecular structure, most of the known Ziegler-Natta catalyst systems fail to produce functionalized polyolefins directly. The reason for this is that the early transition metal centers in these catalysts are highly electrophilic, generally making it impossible to use olefins containing polar functional groups as monomers or co-monomers. Therefore, conventional free radical polymerization is still used industrially to produce a wide range of functionalized polymers [6]. However, the commonly used free radical process is unsuitable to prepare the polymers with precise molecular weight distribution. Thus, there is a need to generate new single-site catalysts for the polymerization of polar α -olefins in order to prepare homo- or copolymers with narrow molecular weight distributions.

It has been reported that the dicarbollide ligand $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ is isolobal and isoelectronic with Cp^- , and this ligand also coordinates with metal centers in an η^5 -fashion by contributing six delocalized π -electrons to form metallocarboranes [7–10]. Moreover, the carborane ligands are thermally stable and robust. The neutral icosahedral carborane cage can be heated to 600 °C without decomposition, and the C_2B_9 -cage ions can be recovered unchanged after several hours of heating in solution with aqueous acids and bases [11–13]. As these compounds are isoelectronic with their respective Cp analogues, one would expect similar, but polar group tolerable, catalytic behaviors in the polymerization of α -olefins. The coordination chemistry of carborane clusters derived from the carborane cages systems has been widely studied, and substituted and unsubstituted dicarbollide metal complexes have been reported [14–20]. However, to the best of our knowledge, the study of carborane trianion-based metallocene analogues is limited with only a few reported examples [21–26]. Following up on our former study, herein we report the synthesis and coordination chemistry of another carborane-based trianionic ligand, *ortho*-carboranyl dianion tailed with a cyclohexyl-bridged terminal nitrogen anion (N^-). The α -olefin polymerization results catalyzed by its group 4 metal complexes in the presence of co-catalyst MMAO-7 is also presented.

2. Results and discussion

We previously reported the in situ synthesis and coordination chemistry of carborane trianions composed of dicarbollide dianion and methylene-bridged terminal heteroatom anion (Fig. 1) [24,25]. The disadvantages of high air-sensitivity and inconvenient synthetic methodology for these compounds made us look for a more feasible method to prepare additional stable carboranyl trianion-derived metal complexes.

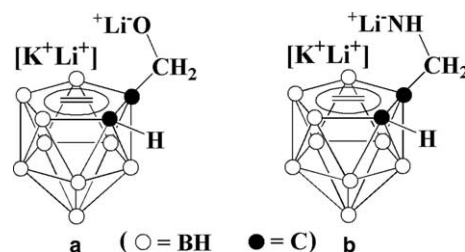
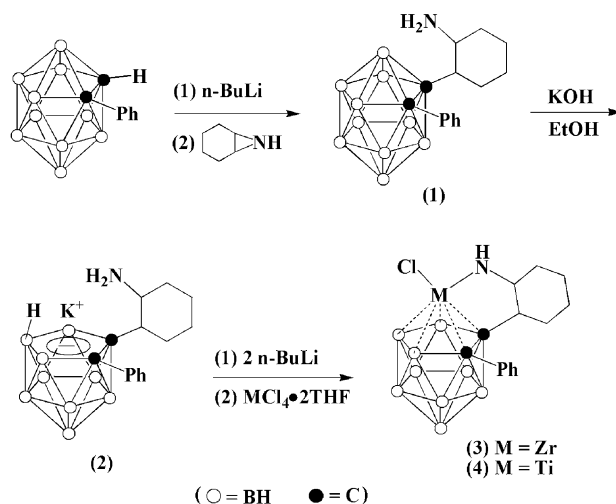


Fig. 1. CH_2 bridged carborane trianions.

Reaction of the lithium salt of the phenyl-substituted carborane monoanion with synthesized 7-azabicyclo [4.1.0] heptane followed by hydrolysis and purification produced *closo*-1-Ph-2-(2'-aminocyclohexyl)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (**1**) in 63% yield (Scheme 1). The ^1H , ^{13}C , and ^{11}B NMR spectra appear normal relative to other related structures. In the IR spectrum a strong absorption at $\nu = 2565\text{ cm}^{-1}$ is attributed to ν_{BH} . Further reaction of (**1**) with potassium hydroxide in refluxing ethyl alcohol led to the formation of the decapitated carborane monoanion $\text{K}[\textit{nido}$ -7-Ph-8-(2'-aminocyclohexyl)-7,8- $\text{C}_2\text{B}_9\text{H}_{10}]$ (**2**) in 80% yield after purification. Compound (**2**) easily dissolves in polar solvents such as THF, DMSO, acetone, DMF, ethyl alcohol, and the like. Compared with its precursor (**1**), the ^{13}C chemical shift of $-\text{CH}-\text{NH}_2$ in **2** shifted upfield 2.40 ppm, and the corresponding IR absorption of ν_{BH} blue shifted 31 cm^{-1} . After in situ deprotonation with two equivalents of *n*-BuLi in dry THF followed by reaction with $\text{MCl}_4 \cdot 2\text{THF}$ (pale yellow powder), cyclohexylamino tailed *ortho*-carboranyl trianionic ligand coordinated group 4 complexes, *closo*-1-M(Cl)-2-Ph-3-(2'- σ -(H)*N*-cyclohexyl)-2,3- η^5 - $\text{C}_2\text{B}_9\text{H}_9$ (**3**, M = Zr; **4**, M = Ti), were produced in 53% and 42% yields, respectively. Both (**3**) and (**4**) dissolve in benzene and permit purification by precipitation from corresponding benzene solution with pentane.



Scheme 1. Synthesis of carborane trianions group 4 compounds.

When exposed to air, the pale orange color of a benzene solution of (3) or (4) changed into a deep brown solution after 1 day. This is slower than the corresponding changes of known literature compounds [24,25]. The half-lives of decomposition of (3) and (4) are about 11 and 7 h, respectively, based on in situ NMR. These values are longer than the corresponding literature analogues under the same conditions ($t_{1/2} = 5, 8$ h, respectively, for ligand **b** in Fig. 1 for the titanium and zirconium complexes). This confirms that (3) and (4) are more stable than methylene bridged analogues. Compound (3) and (4) are also stable in polar solvents, such as THF, diethyl ether, DMSO, DMF, and absolute ethanol. There was no obvious change in their ^1H NMR spectra after dissolution in these solvents. It was noted that after metallization, the ^{13}C chemical shifts of $-\text{CHNH}-$ shifted dramatically upfield, 38.46 and 35.09 ppm for (3) and (4), respectively. This change supports the formation of M–N (M = Ti, Zr) bonds. Compared with the precursor ligand (2), the ^{11}B NMR spectra of (3) and (4) shifted significantly downfield to between $\delta -5.77$ and -25.30 ppm, is consistent with the literature values [24].

Immobilization of the new trianionic ligand has been successfully achieved by the reaction of the sodium salt of *closo*-1-(2'-aminocyclohexyl)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$, prepared in situ from the deprotonation of (5) with sodium hydride in THF at -30°C , with Merrifield's peptide resin (1%) to produce *closo*-1-(2'-aminocyclohexyl)-2-polystyryl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (6) in 87% yield (Scheme 2). The loading amount of ligand 1-(2'-aminocyclohexyl)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ reaches up to 1.28 mmol/g (Merrifield's peptide resin (1%)), based on the produced sodium chloride. Decapitation of (6) with potassium hydroxide in refluxing ethyl alcohol provided polymer supported *nido*-carborane. This species can be further deprotonated by *n*-BuLi to form a corresponding trianionic

intermediate. In situ reaction of the above intermediate with $\text{ZrCl}_4 \cdot 2\text{THF}$ produced polymer-supported carborane trianionic ligand coordinated zirconium complex (7) with loading amounts of zirconium species up to 0.46 mmol/g (Merrifield's peptide resin). Carborane cages in (6) and (7) exhibit typical ν_{BH} absorptions at 2576 and 2513 cm^{-1} , respectively. These data support the successful immobilization of carborane cages to Merrifield's peptide resin (1%).

In simultaneous DSC–TGA analysis, the residue weight of (6) and (7) increases noticeably when compared to that of Merrifield's peptide resin (1%), which is completely combusted when heated to 600°C in air (Fig. 2). Unfortunately, the amount of immobilized carborane cannot be determined by calculation from the changes of the residual weight like other polymer analyses, because both the starting material (5) and Merrifield's peptide resin (1%) completely combust in air at 900°C . In addition, compound (5) sublimates when heated and this property also makes it impossible for

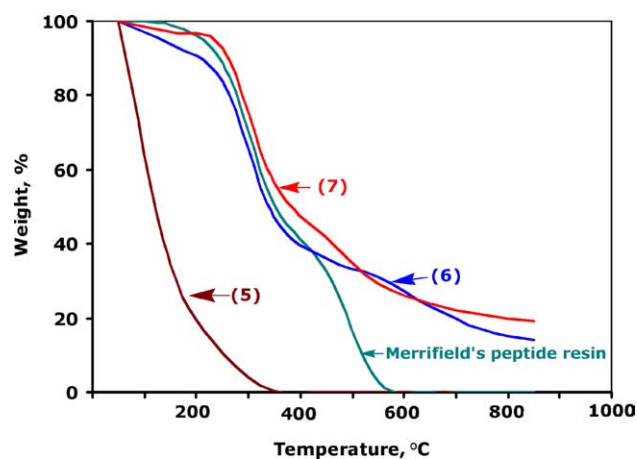
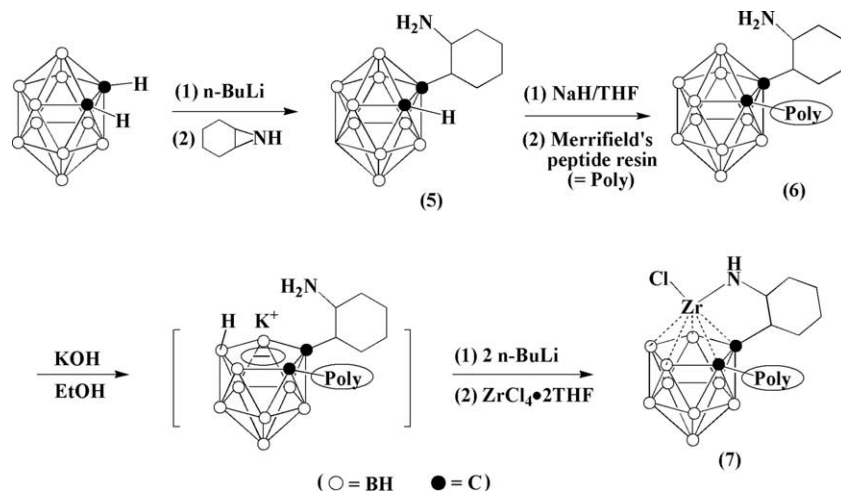


Fig. 2. TGA curves of Merrifield's peptide resin, 5, 6 and 7.



Scheme 2. Synthesis of polymer supported carborane trianion zirconium complex.

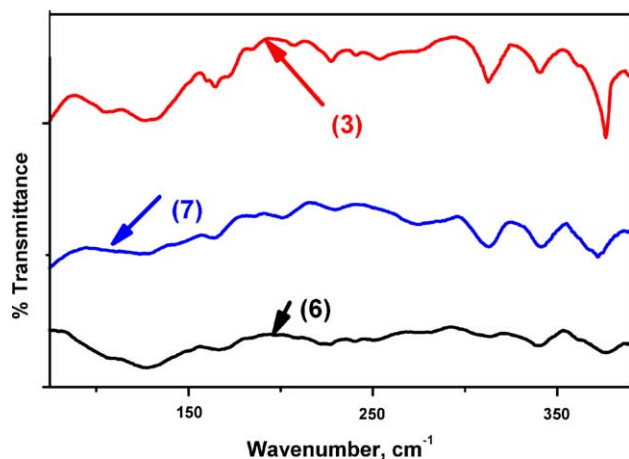


Fig. 3. Far-IR spectra of **3**, **6** and **7**.

the quantitative determination of carborane attached to Merrifield's peptide resin even under nitrogen atmosphere by simultaneous DSC–TGA analysis, due to unavailable reference. Hence, we determined the amount of anchored carborane by titration of the sodium or lithium chloride produced in the reactions with AgNO_3 and further confirmed the zirconium contents with ICP–MS analysis.

To confirm the exact structure of the zirconium species in the Merrifield's peptide resin (1%) supported trianionic ligand coordinated zirconium dicarbollide (**7**), the far-IR spectra of (**3**), (**6**) and (**7**) have been analyzed (Fig. 3). The broad peaks in the solid-state ^{13}C NMR spectra of (**6**) and (**7**), as well as the pale yellow color of (**3**) and (**7**), make it impossible to use either solid-state NMR or Raman spectroscopy to analyze the detailed coordination modes. However, far infrared techniques have been developed that allow us to probe lower frequencies. Much information related to the metal–ligand bond stretching frequencies $\nu_{\text{M-L}}$ is available. The fundamental absorptions of $\nu_{\text{Zr-N}}$, $\nu_{\text{Zr-Cl}}$ and $\nu_{\text{Zr-Cp}}$ have been assigned at 300, 310, and 360 cm^{-1} , respectively [27,28]. Obviously, owing to the possibility of various coupling stretching vibrations, it may be difficult to distinguish the fundamental metal–ligand stretching vibrations from low-frequency infrared spectra. However, the far-IR spectra of compounds (**3**), (**6**) and (**7**) clearly

show difference vibrations. Having the isolobal concept of carboranyl dianion with Cp^- in mind, we tentatively assign the vibrations at 311, 337, and 376 in the far-IR spectrum of (**3**) to $\nu_{\text{Zr-NH}}$, $\nu_{\text{Zr-Cl}}$ and $\nu_{\text{Zr-Cage}}$ stretching vibrations, respectively. Compared with the relatively smooth absorption curve of (**6**), (**7**) presented a similar absorption model with free complex (**3**). This suggests that the zirconium species in (**7**) has the same coordination fashion as the unsupported compound (**3**).

The catalytic properties of the complexes (**3**) and (**7**) have been evaluated for the olefin polymerization process using commercially available ethylene and vinyl chloride in toluene with MMAO-7 co-catalyst. Table 1 summarizes the dual polymerization results of ethylene and vinyl chloride with carborane trianionic ligand coordinated zirconium complexes. It can be seen that (a) the synthesized zirconium complexes are active α -olefin polymerization catalysts whose catalytic efficiencies demonstrate a higher activity for ethylene than vinyl chloride; (b) under the same conditions, the homogeneous catalytic system is more active than corresponding heterogeneous system, which may be caused by the diminished diffusion of monomer into the interior pores of the supported catalyst, or the result of fewer active centers present in the heterogeneous variant [29]; and (c) the obtained polymers have a well-defined molecular architecture with relatively narrow molecular weight distributions (M_w/M_n are in the range 1.6–2.2).

To further elucidate the structure of the obtained polyvinyl chloride (PVC), selected PVC samples produced from the homogeneous catalyst systems were reduced to saturated hydrocarbon polymer using Bu_3SnH and AIBN in THF according to the literature [30,31]. Branched structures cannot be determined from NMR spectra of PVC. The ^{13}C NMR spectra of the reduced polymer no longer contained any PVC signals but only showed the main peak of the CH_2 groups (δ 29.02 ppm), signals of remaining Bu_3SnH , and no detectable amounts of branches. This indicates that side reactions leading to branches do not occur under these polymerization conditions, and the resulting PVC is free of structural defects.

The tacticity of the PVC obtained from the polymerization of vinyl chloride with (**3**) was determined by the

Table 1
Results of ethylene and vinyl chloride polymerization by **3** and **7**

Polymer ^a	Activity ^b	M_w ($\times 10^3/\text{mol}$) ^c	M_w/M_n
Polyethylene	47(A) 21(B)	32.8(A) 10.2(B)	1.8(A) 1.6(B)
Polyvinyl chloride	9(A) 4(B)	8.8(A) 9.5(B)	2.2(A) 2.1(B)

^a A result is for (**3**) and B result is for (**7**), polymerization conditions: ratio of catalyst and co-catalyst ($[\text{Al}]/[\text{Zr}]$), 2000; solvent, toluene; temperature, 50 °C; pressure, 1.5 bar (polyethylene) and 1.2 bar (polyvinyl chloride); polymerization time, 2 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-trichlorobenzene 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.

^{13}C NMR spectra obtained in a mixed solvent of benzene- d_6 and *o*-dichlorobenzene from the area of each split peak of the methine carbon [32]. The tacticity of the PVC thus determined was: mm = 16%, mr = 47%, rr = 37%, respectively, which are close to those obtained with the conventional radical polymerization reported (mm = 12%, mr = 49%, rr = 39%) [32].

Although a few examples of vinyl chloride polymerization catalyzed by group 4 metallocene complexes in the presence of cocatalysts have been described, the mechanism studies are very limited and not definitive [30,33]. On the other hand, zirconocene complexes also have been reported to be inactive for vinyl chloride polymerization due to the rapid β -Cl elimination by the alkylated metallocene intermediate formed from insertion of vinyl chloride to in situ produced metallocene cation species [34]. Considering the decapitated *ortho*-carborane dianion ([7-R-8-R'-C₂B₉H₉]) isoelectronic with Cp⁻ [7–10], we anticipate the complexes will show similar chemical properties with corresponding metallocene analogues. Thus, it is reasonable for us to propose the vinyl chloride polymerization is caused by a radical polymerization process, initiated by the carboranyl zirconium complexes in our conditions. This consideration raises the intriguing question of whether it might be possible to produce group 4 carborane based trianion complexes more capable for polar homo- or comonomer polymerization than those produced via a living radical polymerization process. The detailed mechanistic study is undergoing in our lab using in situ NMR.

3. Conclusions

A new carborane based trianionic ligand, composed of a dicarbollide dianion and cyclohexyl bridged terminal amino group, has been coordinated with group 4 metals via a convenient, three-step process from commercially available 1-Ph-1,2-C₂B₁₀H₁₁ and 7-azabicyclo[4.1.0]heptane. The new ligand has been successfully immobilized onto Merrifield's peptide resin (1%), which in turn could be metallized to give supported zirconium metallocarboranes. Both free and anchored zirconium carborane complexes were found to be efficient olefin polymerization catalysts. Their activities are greater for unsubstituted monomers than for substituted ones such as vinyl chloride.

4. Experimental

All synthetic procedures were carried out in inert atmosphere with standard Schlenk techniques or glove box. Tetrahydrofuran, diethyl ether, toluene, benzene, pentane and *n*-hexane were heated over sodium and ben-

zophenone until a blue color was obtained, and then distilled under argon just before use. *N*-butyllithium (1.6 M in hexanes), sodium hydride (60% dispersion in mineral oil), zirconium (IV) chloride bis(tetrahydrofuran), titanium (IV) chloride bis(tetrahydrofuran). Merrifield's peptide resin (1%) (contains 1.97 mmol Cl⁻/g, 100–200 mesh, cross-linked), ethylene, vinyl chloride, AIBN and organic solvents were used as received from Aldrich. Modified methylaluminoxane 7 (MMAO-7, 13% ISO-PAR-E) was obtained from Akzo Chemicals Inc. *Ortho*-carborane and 1-phenyl-*ortho*-C₂B₁₀H₁₁ were provided by Katchem Ltd. 7-Azabicyclo[4.1.0]heptane was prepared according to the literature [35]. Tri(*n*-butyl)tin hydride (Bu₃SnH) was synthesized according to the literature [36]. ^1H , ^{13}C and ^{11}B NMR were recorded on a Bruker Fourier-Transform multinuclear spectrometer at 400, 100.6 and 128.4 MHz, relative to external Me₄Si (TMS) and BF₃·OEt₂ standards. Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets technique and presented in the sequence of signal strength as strong (s), middle (m) and weak (w), and peak model as single (s), multiple (m) and broad (br). Far-infrared spectra were recorded on a Nicolet-7199B spectrophotometer with CsI pellets technique. Elemental analyses were determined by a Perkin-Elmer 2400 CHN elemental analyzer. The TGA analyses were carried out on an SDT 2960 Simultaneous DSC-TGA analyzer. ICP analysis was determined by a VISTA-MPX, CCD Simultaneous ICP-OES analyzer.

4.1. Synthesis of *closo*-1-Ph-2-(2'-aminocyclohexyl)-1,2-C₂B₁₀H₁₀ (1)

A solution of 1.40 g (6.32 mmol) of 1-Ph-1,2-C₂B₁₀H₁₁ dissolved in a mixture of 60 ml diethyl ether and 30 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 a half hour further stirring, the mixture was warmed to room temperature spontaneously and continued stirring for 5 h followed by addition of 0.67 g (6.84 mmol) of 7-azabicyclo[4.1.0]heptane with a syringe at 0 °C, then the reaction was proceeded at room temperature for another 12 h before hydrolysis with 10 ml of water. The organic phase was separated with a separating funnel, and the aqueous phase was extracted with 2 × 40 ml diethyl ether. The combined organic phase was dried with MgSO₄ and filtered, the filtrate was dried under reduced pressure and the resulting residue was recrystallized with *n*-hexane to obtain 1.26 g waxy solid (1) in yield 63%. Analytic data: Calc. (Found) for C₁₄H₂₇B₁₀N (1): C, 52.96 (53.01); H, 8.57 (8.54); N, 4.41 (4.38%). ^1H NMR (CDCl₃, ppm), δ = 7.35–6.80 (m, 5H, C₆H₅), 3.34 (m, 1H, CH-N), 2.90–0.64 (m, br, 21H, CH, B₁₀H₁₀, 4CH₂, NH₂). ^{13}C NMR (DMSO- d_6 , ppm), δ = 141.06, 130.93, 128.89 and 126.93 (C₆H₅), 87.09

and 74.78 (C_{cage}), 56.00 ($-\text{CH}-\text{N}$), 35.99, 32.31, 25.40, 24.96, 23.06 ($-\text{CH}-C_{\text{cage}}$, 4CH_2). ^{11}B NMR (DMSO- d_6 , ppm), $\delta = -2.34$ (1B, $^1J_{\text{BH}} = 153$ Hz), -4.84 (1B, $^1J_{\text{BH}} = 141$ Hz), -9.37 (2B, $^1J_{\text{BH}} = 93$ Hz), -11.11 (6B, $^1J_{\text{BH}} = 160$ Hz). IR (KBr pellet, cm^{-1}), 3548(m, s), 3208(s, s), 2936(s, s), 2859(s, s), 2565(vs, s), 1701(m, s), 1598(m, s), 1492(s, s), 1447(s, s), 1390(m, s), 1328(s, s), 1195(m, s), 1095(m, s), 1051(s, s), 1003(s, s), 963(m, br), 900(m, s), 820(m, br), 760(m, s), 694(s, s), 551(w, s), 490(w, s).

4.2. Synthesis of *K*[nido-7-Ph-8-(2'-aminocyclohexyl)-7,8- $C_2B_9H_{10}$] (2)

1.86 g (5.85 mmol) of (1) was added to a clear solution of 2.00 g (32.08 mmol) potassium hydroxide in 65 ml of 95% ethanol with continuous stirring. When all solids dissolved, the obtained solution was heated to reflux for 20 h. The vessel was cooled to room temperature, bubbled with carbon dioxide and filtered. The filtrate was dried under reduced pressure and the sticky residue was then extracted with anhydrous THF. After filtration and drying in vacuum, 1.62 g of colourless sticky residue (2) was obtained in 80% yield. Analytic data: Calc. (Found) for $C_{14}H_{27}B_9KN$ (2): C, 48.63 (48.60); H, 7.87 (7.89); N, 4.05 (4.03%). ^1H NMR (DMSO- d_6 , ppm), $\delta = 7.43$ – 6.92 (m, 5H, C_6H_5), 3.29 (m, 1H, $CH-\text{N}$), 2.10–0.15 (m, br, 20H, B_9H_9 , $-\text{CH}$, 4CH_2 , NH_2), -2.73 (br, 1H, $\text{BH}_{\text{bridge}}$). ^{13}C NMR (DMSO- d_6 , ppm), $\delta = 139.10$, 127.97, 126.61 and 124.84 (C_6H_5), 85.34 and 72.10 (C_{cage}), 53.60 ($-\text{CH}-\text{N}$), 34.31, 30.34, 24.32, 24.05, 22.62 ($-\text{CH}-C_{\text{cage}}$, 4CH_2). ^{11}B NMR (DMSO- d_6 , ppm), $\delta = -36.50$ (1B, $^1J_{\text{BH}} = 145$ Hz), -31.20 (1B, $^1J_{\text{BH}} = 104$ Hz), -19.30 (1B, $^1J_{\text{BH}} = 110$ Hz), -17.22 (2B, $^1J_{\text{BH}} = 114$ Hz), -14.29 (1B, $^1J_{\text{BH}} = 121$ Hz), -9.90 (2B, $^1J_{\text{BH}} = 135$ Hz), -6.04 (1B, $^1J_{\text{BH}} = 143$ Hz). IR (KBr pellet, cm^{-1}), 3504(m, br), 3210(m, s), 3061(w, s), 2933(s, s), 2856(m, s), 2534(vs, s), 1599(m, s), 1445(s, s), 1379(m, s), 1195(m, s), 1092(m, s), 1045(s, s), 963(m, s), 903(m, s), 755(m, s), 701(m, s), 548(w, s).

4.3. Synthesis of *closo-1-Zr(Cl)-2-Ph-3-(2'- σ -(H)N-cyclohexyl)-2,3- η^5 - $C_2B_9H_9$* (3)

1.83 g (5.28 mmol) of (2) was dissolved in 80 ml of dry tetrahydrofuran, the obtained mixture was cooled to -78°C and 6.93 ml (11.09 mmol) of *n*-BuLi (1.6 M in hexanes) was added with syringe carefully. After addition, the mixture was kept reacting at that temperature for 30 min before warmed to room temperature for 8 h. Stirring was then stopped and the reaction mixture was allowed to cool to 0°C and 2.00 g (5.25 mmol) $\text{ZrCl}_4 \cdot 2\text{THF}$ was added. The colour of the mixture changed quickly from pale yellow into red brown during the addition process. After reaction about 30 min at

0°C , the mixture was stirred at room temperature for 3 days. After filtration and removal of all the solvents under reduced pressure, the obtained residue was recrystallized with a mixture of benzene/pentane (v:v = 2:1) to give 1.21 g (3) in 53% yield. Analytic data: Calc. (Found) for $C_{14}H_{25}B_9ClNzr$ (3): C, 38.98 (38.95); H, 5.84 (5.80); N, 3.25 (3.22). ^1H NMR (DMSO- d_6 , ppm), $\delta = 7.23$ – 6.68 (m, 5H, C_6H_5), 3.11 (m, 1H, $-\text{CH}-\text{N}$), 2.07–0.25 (m, br, 19H, B_9H_9 , $-\text{CH}-C_{\text{cage}}$, 4CH_2 , NH). ^{13}C NMR (DMSO- d_6 , ppm), $\delta = 138.83$, 127.75, 126.58 and 124.68 (C_6H_5), 75.84 and 62.61 (C_{cage}), 38.46 ($-\text{CH}-\text{N}$), 36.51, 27.36, 23.88, 22.14, 20.14 ($-\text{CH}-C_{\text{cage}}$, 4CH_2). ^{11}B NMR (C_6D_6 , ppm), $\delta = -25.30$ (1B, $^1J_{\text{BH}} = 107$ Hz), -16.71 (2B, $^1J_{\text{BH}} = 130$ Hz), -9.02 (4B, $^1J_{\text{BH}} = 126$ Hz), -6.27 (2B, $^1J_{\text{BH}} = 95$ Hz). IR (KBr pellet, cm^{-1}), 3433(m, s), 2905(vs, s), 2854(s, s), 1722(m, s), 1623(s, s), 1490(s, s), 1438(s, s), 1388(m, s), 1315(s, s), 992(m, s), 803(m, br), 759(m, s), 688(s, s), 535(w, s).

4.4. Synthesis of *closo-1-Ti(Cl)-2-Ph-3-(2'- σ -(H)N-cyclohexyl)-2,3- η^5 - $C_2B_9H_9$* (4)

A similar process of the preparation of (3) was used to synthesize 0.97 g (4) in 42% yield from 2.06 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) $\text{TiCl}_4 \cdot 2\text{THF}$ in 75 ml dry THF. Analytic data: Calc. (Found) for $C_{14}H_{25}B_9ClNTi$ (4): C, 43.34 (43.31); H, 6.50 (6.47); N, 3.61 (3.63). ^1H NMR (DMSO- d_6 , ppm), $\delta = 7.15$ – 6.53 (m, 5H, C_6H_5), 3.25 (m, 1H, $-\text{CH}-\text{N}$), 2.07–0.15 (m, br, 19H, B_9H_9 , $-\text{CH}-C_{\text{cage}}$, 4CH_2 , NH). ^{13}C NMR (DMSO- d_6 , ppm), $\delta = 140.16$, 127.83, 126.74 and 124.90 (C_6H_5), 76.20 and 62.35 (C_{cage}), 35.09 ($-\text{CH}-\text{N}$), 34.40, 28.45, 25.48, 23.37, 22.26 ($-\text{CH}-C_{\text{cage}}$, 4CH_2). ^{11}B NMR (C_6D_6 , ppm), $\delta = -23.15$ (1B, $^1J_{\text{BH}} = 117$ Hz), -15.67 (2B, $^1J_{\text{BH}} = 125$ Hz), -8.29 (4B, $^1J_{\text{BH}} = 121$ Hz), -5.77 (2B, $^1J_{\text{BH}} = 107$ Hz). IR (KBr pellet, cm^{-1}), 3488(m, s), 3105(s, s), 3010(s, s), 2894(s, s), 2700(vs, s), 1680(s, s), 1518(s, s), 1401(s, s), 1299(w, br), 953(m, br), 713(m, s), 457(s, s).

4.5. Synthesis of *closo-1-(2'-aminocyclohexyl)-1,2- $C_2B_{10}H_{11}$* (5)

A similar process of the preparation of (1) was used to produce 1.98 g (5) in 59% yield from 2.00 g (13.87 mmol) *ortho*-carborane, 9.10 ml (14.56 mmol) *n*-BuLi (1.6 M in hexanes) and 1.41 g (14.51 mmol) 7-azabicyclo[4.1.0]heptane in 60 ml THF. Analytic data: Calc. (Found) for $C_8H_{23}B_{10}N$ (5): C, 39.81 (39.79); H, 9.60 (9.53); N, 5.80 (5.77%). ^1H NMR (DMSO- d_6 , ppm), $\delta = 3.30$ (m, 1H, $CH-\text{N}$), 0.53–2.80 (m, br, ill-defined, 22H, $B_{10}H_{10}$, $CH-C_{\text{cage}}$, $C_{\text{cage}}H$, 4CH_2 , NH_2). ^{13}C NMR (DMSO- d_6 , ppm), $\delta = 80.23$ and 72.53 (C_{cage}),

52.36 (–CH–N), 35.07, 31.93, 25.25, 25.09, 24.61 (–CH–C_{cage}, 4CH₂). ¹¹B NMR (DMSO-*d*₆, ppm), $\delta = -4.47$ (1B, ¹J_{BH} = 127 Hz), -5.80 (1B, ¹J_{BH} = 114 Hz), -9.11 (2B, ¹J_{BH} = 124 Hz), -9.74 (2B, ¹J_{BH} = 103 Hz), -10.62 (4B, ¹J_{BH} = 104 Hz). IR (KBr pellet, cm⁻¹), 3450(s, s), 3089(s, s), 2937(s, s), 2859(s, s), 2573(s, s), 2527(vs, s), 1640(s, sz), 1449(s, s), 1396(m, s), 1274(w, s), 1213(m, s), 1075(s, s), 1051(s, s), 962(m, s), 915(m, s), 860(m, s), 727(m, s), 615(m, br), 553(m, s), 506(m, s), 416(m, s).

4.6. Synthesis of *closo*-1-(2'-aminocyclohexyl)-2-polystyryl-1,2-C₂B₁₀H₁₀ (6)

0.97 g (4.02 mmol) of (5) was added to a 250 ml two-necked round bottom flask equipped with a magnetic stirring bar and dissolved with 100 ml THF. The resulting solution was cooled to -30 °C and 0.16 g (4.00 mmol) NaH was added carefully. After addition, the mixture was kept reacting at that temperature for 30 min followed by warming up to room temperature spontaneously and reacting further 6 h. Merrifield's peptide resin (1%), 2.00 g (contains 3.94 mmol Cl⁻), was added and kept stirring at room temperature for two days. At the end of the reaction process, the mixture was heated to reflux for 10 h before cooled to room temperature and quenched with 5.00 ml methanol. The solvents was then removed under reduced pressure and the obtained crude product was washed with deionized water (2 × 10 ml) and *n*-hexane (2 × 20 ml) to remove any trace of NaCl and starting material *closo*-1-(2'-aminocyclohexyl)-1,2-C₂B₁₀H₁₁, and dried in high vacuum for two days to give 2.72 g pale yellow solid *closo*-1-(2'-aminocyclohexyl)-2-polymeryl-1,2-C₂B₁₀H₁₀ (6) in 87% yield. The collected aqueous solution was combined and concentrated to 5.0 ml and subjected to titration with AgNO₃ to detect the amount of the produced NaCl as 0.204 g. The loading amount of aminocyclohexyl carborane reached up to 1.28 mmol (carborane cage)/g (Merrifield's peptide resin). IR (KBr pellet, cm⁻¹): 3430(m, s), 3013(s, s), 2916(s, s), 2576(vs, s), 1934(s, s), 1800(m, s), 1611(s, s), 1485(s, s), 1422(m, s), 1364(s, s), 1304(m, s), 1252(s, s), 1178(m, s), 1150(m, s), 1109(m, s), 1060(s, s), 1022(s, s), 905(s, s), 816(s, s), 748(s, s), 690(s, s), 536(s, s).

4.7. Synthesis of *closo*-1-Zr(Cl)-2-(2'-σ-(H)N-cyclohexyl)-3-polystyryl-2,3-η²-C₂B₉H₉ (7)

2.27 g (contains carborane ligand 2.90 mmol) (6) was suspended in a solution of 1.10 g (16.66 mmol) potassium hydroxide in 150 ml of 95% ethanol, the mixture was stirred at room temperature for 30 min before refluxing for 2 days. The reaction mixture was then cooled to room temperature, bubbled and

saturated with carbon dioxide and filtered. The resulting solid was washed with deionized water (3 × 10 ml) to remove any trace of KCl, and dried in high vacuum for two days before resuspended in 120 ml THF. The mixture was cooled to -78 °C and 6.5 ml (10.40 mmol) *n*-BuLi in hexanes was added with continuous stirring. After 30 min at -78 °C, the vessel was warmed to room temperature spontaneously and kept stirring for 1 day. Solvent was removed under reduced pressure and the resulting residue was washed with *n*-hexane (2 × 15 ml) to remove unreacted *n*-BuLi. The residue was resuspended in 150 ml THF and ZrCl₄ · 2THF 1.10 g (2.89 mmol) was added at 0 °C. The reaction was continued at room temperature for 3 days before filtration. The collected solids was washed with absolute ethyl alcohol (2 × 10 ml) to remove lithium chloride followed by dried in high vacuum for 2 days to give 2.40 g (7) (38% yield) as a pale yellow solid. The collected alcohol solutions were combined and dried in vacuum. The obtained residue was dissolved in 5.0 ml deionized water and subjected to titration with AgNO₃ to determine the amount of the produced LiCl as 0.246 g. The loading amount of zirconium species reached up to 0.46 mmol (zirconium species)/g (Merrifield's peptide resin). The result is consistent with data derived from ICP analysis which give 42.00 mg (zirconium)/g (Merrifield's peptide resin (1%)). IR (KBr pellet, cm⁻¹): 3428(m, br), 3019(s, s), 2928(s, s), 2850(s, s), 2513(s, s), 1641(s, s), 1525(s, s), 1490(s, s), 1408(m, s), 1358(s, s), 1161(s, s), 1088(m, s), 1010(s, s), 745(s, s), 701(s, s), 520(s, s).

4.8. Polymerization procedures

The polymerization of ethylene and vinyl chloride catalyzed by compounds (3) and (7) was performed for 2 h in 80 ml toluene in the presence of modified methylaluminoxane 7 (MMAO-7, 13% ISOPAR-E) in Schlenk tubes. The argon pressure inside the Schlenk tubes was reduced by applying vacuum. Monomer pressure was then applied to the tubes and the reactor was adjusted to constant temperature and pressure. During the polymerization process, 1 μmol catalyst (3 or 7) based on zirconium species and 2000 μmol MMAO-7 were used to give a concentration ratio of [Al]/[Zr] = 2000. The reaction temperature was 50 °C under 1.5 and 1.2 bar for polyethylene and polyvinyl chloride, respectively. After polymerization process, the reaction was carefully quenched with 10 ml mixture of 10% HCl solution of MeOH. The polymer was then precipitated with 150 ml methanol, collected by filtration, washed with MeOH (4 × 20 ml) and *n*-hexane (2 × 20 ml) in sequence and dried at 60 °C in high vacuum to a constant weight. Polymerization results are summarized in Table 1.

4.9. Characterization of PVC

The reduction of PVC to the corresponding hydrocarbon polymer was carried out by following process, 0.80 g of above produced PVC, 5.0 g (17.18 mmol) Bu_3SnH , 24 mg (1.46×10^{-4} mol) of AIBN, and 60 mL of THF were added to a 100-mL glass autoclave, the mixture was then degassed three time and filled with argon at last. After stirring for 8 h at 100 °C, the reaction solution was cooled to 80 °C and added into 200 mL hot methanol (62 °C) and then cooled until room temperature. The product was collected by filtration and purified by threefold precipitation from hot THF to MeOH. The purified product was dried for 2 days in high vacuum to a constant weight of 0.29 g (81%). The tacticity of obtained PVC was analyzed from ^{13}C NMR spectra measured in the mixed solvent of benzene- d_6 and *o*-dichlorobenzene at 120 °C.

Acknowledgments

We thank ICES in Singapore for support of the work. We also acknowledge Professor Narayan S. Hosmane in the Department of Chemistry and Biochemistry in Northern Illinois University, and Professor John A. Maguire in the Department of Chemistry, Southern Methodist University, for their helpful discussions. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE's National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

References

- [1] U. Siemeling, Chem. Rev. 100 (2000) 1495.
- [2] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
- [3] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
- [4] H.G. Alt, A. Reb, K. Kundu, J. Organomet. Chem. 628 (2001) 211.
- [5] J. Klosin Jr., W.J. Kruper, P.W. Nickias, G.R. Roof, P.De. Waele, K.A. Abbound, Organometallics 20 (2001) 2663.
- [6] F. Stephen, in: Plastic: The Making of a Synthetic Century, HarperCollins, New York, 1996.
- [7] D.J. Crowther, N.C. Baenziger, R.F. Jordan, J. Am. Chem. Soc. 113 (1991) 1455.
- [8] S. Saccheo, G. Gioia, A. Grassi, D.E. Bowen, R.F. Jordan, J. Mol. Cat. A 128 (1998) 111.
- [9] T. Doge, M.A. Curtis, J.M. Russell, M. Sabat, M.G. Finn, R.N. Grimes, J. Am. Chem. Soc. 122 (2000) 10573.
- [10] G.C. Bazan, W.P. Schaefer, J.E. Bercaw, Organometallics 12 (1993) 2126.
- [11] G. Henrici-Olive, S. Olive, Angew. Chem., Int. Ed. 6 (1967) 790.
- [12] H.A. Schroeder, Inorg. Macromol. Rev. 1 (1970) 45.
- [13] A.M. Thayer, Chem. Eng. News 11 (1995) 15.
- [14] R. Uhrhammer, Y.-X. Su, D.C. Swenson, R.F. Jordan, Inorg. Chem. 33 (1994) 4398.
- [15] C.K. Broder, A.E. Goeta, A.K. Howard, A.K. Hughes, A.L. Johnson, J.M. Malget, K. Wade, J. Chem. Soc., Dalton Trans. (2000) 3526.
- [16] A.K. Saxena, J.A. Maguire, N.S. Hosmane, Chem. Rev. 97 (1997) 2421.
- [17] Y.-X. Su, C.E. Reck, I.A. Guzei, R.F. Jordan, Organometallics 19 (2000) 4858.
- [18] X. Bei, C. Kreuder, D.C. Swenson, R.F. Jordan, V.G. Young Jr., Organometallics 17 (1998) 1085.
- [19] Z. Xie, Z. Liu, K. Chiu, F. Xue, T.C.W. Mak, Organometallics 16 (1997) 2460.
- [20] X. Bei, V.G. Young Jr., R.F. Jordan, Organometallics 20 (2001) 355.
- [21] J.-S. Park, D.-H. Kim, S.-J. Kim, J. Ko, S.H. Kim, S. Cho, C.-H. Lee, S.O. Kang, Organometallics 20 (2001) 4483.
- [22] (a) W. Kwong, H. Chan, Y. Tang, Z. Xie, Organometallics 23 (2004) 4301;
(b) Y. Wang, H. Wang, H.-W. Li, Z. Xie, Organometallics 21 (2002) 3311.
- [23] J.-S. Park, D.-H. Kim, J. Ko, S.H. Kim, S. Cho, C.-H. Lee, S.O. Kang, Organometallics 20 (2001) 4632.
- [24] Y. Zhu, K. Vyakaranam, J.A. Maguire, W. Quintana, F. Teixidor, C. Vinas, N.S. Hosmane, Inorg. Chem. Commun. 4 (2001) 486.
- [25] Y. Zhu, J.A. Maguire, N.S. Hosmane, Inorg. Chem. Commun. 5 (2002) 296.
- [26] D.-H. Kim, J.H. Won, S.-J. Kim, J. Ko, S.H. Kim, S. Cho, S.O. Kang, Organometallics 20 (2001) 4298.
- [27] (a) R.J.H. Clark, C.S. Williams, Spectrochim. Acta 22 (1966) 1081;
(b) C.F. Robert, J.P. Thomas, Inorg. Chem. 7 (1968) 508.
- [28] J. Zheng, Z. Xu, S. Chen, Beijing Daxue Xuebao, Ziran Kexueban 35 (1999) 855.
- [29] P.J.T. Tait, M.G.K. Monteiro, M. Yang, J.L. Richardson, Proceedings of MetCon 1996, Houston, TX, 12–13 June 1996 (available from Catalyst Consultants, P.O. Box 637, Spring House PA 19477).
- [30] K. Endo, M. Saitoh, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 248.
- [31] W.H. Starnes Jr., R.L. Hartless, F.C. Schilling, F.A. Bovey, Polym. Prep. (AM. Chem. Soc. Div. Polym. Chem.) 18 (1977) 499.
- [32] M.W. Crowther, N.M. Szevernyi, G.C. Levy, Macromolecules 19 (1986) 1333.
- [33] (a) K. Taeji, T. Uozumi, K. Soga, Polym. Prep. Jpn. 44 (1995) 2;
(b) T. Matsukawa, R. Kiba, T. Ikeda, Japan Patent 08208736;
T. Matsukawa, R. Kiba, T. Ikeda, Chem. Abstr. 125 (1996) 276902.
- [34] R.A. Stockland Jr., R.F. Jordan, J. Am. Chem. Soc. 122 (2000) 6315.
- [35] J. Christoffers, Y. Schulze, J. Pickardt, Tetrahedron 57 (2001) 1765.
- [36] J. Szammer, L. Otvos, Chem. Ind. (London, United Kingdom) 23 (1988) 764.