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# Carboranylimine-complexed titanium (IV) organometallics: An investigation of synthesis, structure and catalytic polymerization

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### 1. Introduction

A three-dimensional aromatic and highly thermally stable bulky carborane cage, has been used to construct various metal complexes [1-3] since the first report on a metalladicarbollide complex by Hawthorne and co-workers [1]. Subsequently, Group IV metal complexes derived from functionalized ansa-ligands with cyclopentadienyl [4,5], pyridinyl [6], phosphino [7], sulfano [8,9], alkyloxo [10,11] and alkylamino [12-16] moieties, have been developed and their reasonable activity for olefin polymerization was demonstrated. On the other hand, the titanium complexes derived from the phenoxy-imine ligands, popularly named as Ti-FI catalysts, have been well recognized as highly active catalysts for  $\alpha$ -olefin polymerization [17–26]. Despite the fact that the titanium complexes are recognized as being highly oxophilic and easily poisoned by a polar monomer, the prototype Ti-FI catalysts have demonstrated good activity for copolymerization of ethylene and unsymmetrical olefins to form functional polymers [24]. Nonetheless, the designable phenoxy-imine functionality plays an important role in catalysis and, ultimately, it alters the polymer

### ABSTRACT

The condensation reaction of carboranylmethyl ammonium chloride,  $1-(CH_2NH_3Cl)-1,2-C_2B_{10}H_{11}$  (1) with phenyl aldehydes produced phenyl(carboranylmethyl)imine ligands,  $1-(CH_2N = CC_6H_4R-2)-1,2-C_2B_{10}H_{11}$  (2 R = H; 3 R = OH). Deprotonation of 2 and 3 with *n*-BuLi followed by metalation with TiCl<sub>4</sub> led to the formation of phenyl(carboranylmethyl)imidotitanium (IV) chlorides,  $[1-(CH_2N = CC_6H_4R-2)-1,2-C_2B_{10}H_{10}]$ TiCl<sub>3</sub> (4 R = H; 5 R = O). Compounds 4 and 5 were found to catalyze the polymerization of ethylene in the presence of co-catalyst MAO to produce high molecular weight polyethylene. In addition, compounds 4 and 5 were also active for copolymerization of ethylene and methyl-10-undecannoate to generate corresponding copolymers.

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properties [17–26]. Therefore, the incorporation of a carborane cage with the 3D-aromaticity by substituting the benzene ring in the phenoxy–imine ligands should lead to a new class of carboranylimines. Consequently, the metalation of the carboranylimines with the Group IV metals should produce unique analogues of Ti–FI catalysts. Thus, the carboranylimines, synthesized by dehydration of carboranylaldehyde and anilines were first decapitated and then metalated to form  $\eta^{1}_{(C=N)}$ ,  $\eta^{5}_{(nido-cage)}$ -coordinated constrained-geometry Group IV complexes [27]. However, neither the exopolyhedral metalation of the *closo*-carboranylimine ligands with the  $\eta^{1}_{(C=N)}$ ,  $\sigma_{(closo-cage)}$ -functionalities to form the corresponding Group IV metal complexes nor its catalytic activities has been investigated. Herein, we report the synthesis and crystal structure of the *closo*-carboranylimine ligands along with the catalytic activity of the corresponding titanium complexes.

### 2. Results and discussion

### 2.1. Ligands

Reaction of the carboranylmethyl ammonium salt with commercially available phenyl aldehyde in the presence of NaHCO<sub>3</sub> and molecular sieve (4 Å) followed by purification produced airstable waxy solid, phenyl(carboranylmethyl)imines **2** and **3**, 1- $(CH_2N = CC_6H_4R-2)$ -1,2- $C_2B_{10}H_{11}$  (**2** R = H; **3** R = OH) in 53% and



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Scheme 1. Synthesis of carboranylimine and derived titanium metal complexes.

64% yield, respectively (Scheme 1). Compounds **2** and **3** were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B NMR and FT–IR spectroscopy as well as elemental analyses. The <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra of **2** and **3** appear normal relative to other related structures. In the <sup>11</sup>B NMR spectra, both **2** and **3** showed a splitting model of 1:1:3:2:3. In the IR spectra, strong absorptions at ~2600 cm<sup>-1</sup> are attributed to  $\nu_{BH}$ .

The molecular structure of **2** was characterized by single-crystal X-ray diffraction as shown in Fig. 1. Fig. 1 reveals that compound **2** exhibits a *trans*-configuration with a normal C—N bond length. The C–B and B–B bond lengths are consistent with the literature values [27]. The angles of the C(1)-C(7)-N(1) and C(8)-N(1)-C(7) are 123.0(1) and 116.7(1), respectively. The selected bond lengths and angles are summarized in Table 1.

### 2.2. Titanium complexes

In situ deprotonation with *n*-BuLi at -78 °C in toluene followed by reaction with TiCl<sub>4</sub> led to the formation of the phenyl(carboranylmethyl)imido titanium (IV) chlorides 4 and 5, [1- $(CH_2N = CC_6H_4R-2)-1,2-C_2B_{10}H_{10}$ TiCl<sub>3</sub> (**4** R = H; **5** R = O), in 49% and 51% yields, respectively, as illustrated in Scheme 1. Compounds 4 and 5 are highly soluble in polar solvents such as THF, DCM, DMF, and also in benzene, thus permitting purification by precipitation from the corresponding benzene solution with *n*-pentane. In comparison with their precursors **2** and **3**, the <sup>1</sup>H chemical shifts of -CH = N in **4** and **5** were shifted downfield from ~0.30 ppm to 8.52 and 8.51 ppm, respectively, indicating significant involvement of this moiety in coordination to the metal. Similarly, the <sup>13</sup>C chemical shift ( $\delta$ ) of –CH=N moiety in **2**, after metalation, shifted downfield by 5.5 ppm. In contrast, the  $\delta_{CH=N}$  in **3** was shifted upfield by 11.6 ppm after metalation. This observation can be rationalized based on the fact that the formation of a stable six-membered ring



**Fig. 1.** A perspective view showing the molecular structure of **2**, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Table 1
Selected bond lengths, angles (°) for carbonylimine
$\mathbf{D}_{\mathbf{a}} = \mathbf{d} 1_{\mathbf{a}} = \mathbf{d} \mathbf{b} \mathbf{a}$

Bond lengths (A)	
N(1)-C(7)	1.265(2)
N(1)-C(8)	1.458(2)
C(8)-C(9)	1.528(2)
C(9)-C(10)	1.643(2)
Angles (°)	
C(7)-N(1)-C(8)	116.7(1)
C(1)-C(7)-N(1)	123.0(1)

in **5** causes the reverse shift and thus reduced the intra-molecular strain leading to enhanced electron delocalization. Similar phenomenon was also observed in the corresponding IR absorptions. In comparison with the  $v_{BH}$  of the corresponding precursors, the red shifts of 27 and 7 cm<sup>-1</sup> were observed for the metalation of **2** and **3**, respectively. In the <sup>11</sup>B NMR spectra, **4** and **5** showed the splitting patterns of 1:1:1:3:2:2 and 1:1:3:2:3, respectively in a range of -3.17--15.21 ppm. No peaks beyond -30 ppm were observed. In far-IR spectra (Fig. 2), compounds **4** and **5** show strong absorptions in the range of 425–500 cm<sup>-1</sup>, which are consistent with the reported  $v_{Ti-CI}$  and  $v_{Ti-O}$  absorptions [28,29]. In comparison with **4**, compound **5** shows one more peak that could be due to the vibration of Ti–O bond in **5**. Neither **2** nor **3** shows such absorptions (Fig. 2).

These results clearly indicate the presence of the Ti–Cl and Ti–O bonds in **4** and **5**, respectively. The MS (ESI) analysis showed  $[M - H]^+$  peaks further confirming the molecular composition of the complexes.

### 2.3. Ethylene and ethylene/methyl-10-undecannoate polymerization

The catalytic properties of the complexes **4** and **5** have been examined for the olefin polymerization processes using commercially available ethylene and methyl-10-undecannoate in toluene with MAO, trimethylaluminum (MA) and tris(pentafluorophenyl) borane co-catalysts. Table 2 summarizes the homo- and copolymerization results of ethylene with carboranylimine-coordinated titanium complexes with MAO co-catalyst. It has been observed that (a) both **4** and **5** are active catalysts for homo- and co-polymerization of ethylene with an activity of 5.2–57 kg polymer (molTi)<sup>-1</sup>h<sup>-1</sup> bar<sup>-1</sup> The results are comparable with FI catalyst, bis[*N*-(3-phenylsalicylidene)-3',5'-bis-*tert*-butylanilinato] titanium(IV)dichloride showing an activity of 41.6 and 5.1 kg polymer (molTi)<sup>-1</sup>h<sup>-1</sup> bar<sup>-1</sup> for homo- and co-polymerization of



Fig. 2. Far-IR spectra of compounds 2-5.

Table 2 Results of ethylene and ethylene/methyl-10-undecannoate polymerization by  ${\bf 4}$  and  ${\bf 5}^{\rm a}.$ 

Polymer	Cat	Activity (kg/mol h bar)	$M_{ m w}  (10^6) \ (g/ m mol)^{ m b}$	$M_{\rm w}/M_{\rm n}$
Polyethylene	4	41	1.26	4.84
	5	57	1.44	4.63
Poly(ethylene/	4	5.2	0.54	4.52
methyl 10-undecannoate)	5	12.3	1.26	3.64

<sup>a</sup> Polymerization conditions: ratio of catalyst and co-catalyst ([A1]/[Ti]) = 2000, solvent = toluene, temperature = 50 °C,  $P_{\text{ethylene}}$  = 1.5 bar, methyl-10-undecannoate (1.0 M in toluene, 10 mmol), polymerization time = 2 h.

<sup>b</sup> Molecular weight and molecular weight distribution of the polymers were determined by means of gel-permeation chromatography (GPC: Waters 150) at 145 °C using 1,2,4-trichlorobenezene 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.

ethylene, respectively [24]. However, with the co-catalysts trimethylaluminum and tris(pentafluorophenyl)borane, both 4 and 5 demonstrate low activity (<0.01 kg polymer (molTi)<sup>-1</sup>h<sup>-1</sup> bar<sup>-1</sup>) for ethylene polymerization because of the relatively strong Ti-Cl bonds; (b) under the same conditions, complex 5 is more active than the corresponding analogue 4, which may be caused by the formation of the six-membered ring (Scheme 1) that enhances the intramolecular electron delocalization and reconstruct the molecule configuration differing from 4, the resulting unique bis(cyclo)coordination model may benefit the olefin polymerization procedure [26]; (c) the obtained polymers have a high molecular weight with reasonable molecular weight distributions  $(M_w/M_p)$  are in the range 3.64–4.84) To further elucidate the structure of the obtained ethylene/methyl-10-undecannoate copolymer, products obtained from catalyst **5** have been analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectra at 110 °C in 1,2-dichlorobenzene- $d_4$ . According to the <sup>1</sup>H NMR spectra, an incorporation ratio of 4.7 mol% methyl-10-undecannoate has been reached in the copolymers; and (d) although the mechanism for the carboranylimine-complexed titanium(IV)/MAO catalytic process is not known in control experiments, neither 2 nor 3 produced polymers in the presence of MAO.

These results suggest that the catalytic activity is sensitive to initiator and the titanium cations could be the active species. Similar to other titanium based FI catalysts [21], the active titanium cations can be generated in situ by a reaction of MAO with precursor 4 or 5 leading to a metal-ligand bond rupture. On the other hand the Ti-Cl bond could be broken to form the catalytically active species.  $[1-(CH_2N=CC_6H_4)-1,2-C_2B_{10}H_{10}]Ti(IV)Me_2$ or [1- $(CH_2N=CC_6H_4O-2)-1,2-C_2B_{10}H_{10}]$ Ti(IV)Me, upon coordination with the ethylene or methyl-10-undecannoate monomer. In the processes, a single-site polymerization mechanism of the conventional "Ziegler-Natta" catalysts may be operable [30]. More detailed mechanistic studies are currently underway in our laboratory, using FT-IR and NMR spectroscopy.

### 3. Conclusions

The new carborane-based imine ligands have been synthesized conveniently and coordinated with titanium to form phenyl(-carboranylmethyl)imido titanium(IV) chlorides. The resulting titanium complexes were found to be efficient  $\alpha$ -olefin polymerization catalysts to produce high molecular weight polyethylene and poly(ethylene/methyl-10-undecannoate). We expect the catalysts to find broader applications in both academia and materials industry. A study of the mechanism of the catalysts is currently underway in our laboratories.

### 4. Experimental

All synthetic procedures were carried out in inert atmosphere with standard Schlenk techniques or glove box. Tetrahydrofuran, diethyl ether, toluene, pentane and hexane were heated over sodium and benzophenone until a blue color was obtained, and further distilled under argon just before use. The reagents, nbutyllithium (1.6 M in hexanes), titanium (IV) chloride, benzaldehyde, methylaluminoxane (MAO, 1.7 M in toluene), trimethylaluminum (MA, 2.0 M in toluene), tris(pentafluorophenyl)borane and organic solvents, were used as received from Aldrich. The precursor 1-(CH<sub>2</sub>NH<sub>3</sub>Cl)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (1) was prepared according to the literature procedure [31]. The <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectra were recorded on a Bruker Fourier-Transform multinuclear NMR spectrometer at 400, 100.6 and 128.4 MHz, respectively, relative to external Me<sub>4</sub>Si (TMS) and BF<sub>3</sub> $\cdot$ OEt<sub>2</sub> 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). Elemental analyses were determined by a Perkin Elemer 2400 CHN elemental analyzer. MS (ESI) analyses were carried out on a Thermo Finnigan MAT XP95 analyzer using ESI model.

## 4.1. Synthesis of phenyl(carboranylmethyl)imine, $1-(CH_2N=CC_6H_5)-1,2-C_2B_{10}H_{11}$ , (2)

A mixture of 1-(CH<sub>2</sub>NH<sub>3</sub>Cl)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (1), (1.5 g, 7.2 mmol), NaHCO<sub>3</sub> (35.0 g, 416.7 mmol), benzaldehvde (3.8 g, 35.1 mmol) and 30.0 g 4 Å MS in 250 mL toluene was heated to reflux for 2 days under argon. After reaction, the mixture was cooled to room temperature and filtered. The solid residue was washed with dichloromethane (50 mL  $\times$  2). The combined organic phase was reduced under reduced pressure resulting in a yellow sticky residue which was further washed with pentane to remove unreacted benzaldehyde to obtain 0.99 g waxy solid (2) in 53% yield. Analytic data: Calcd. (Found) for C<sub>10</sub>H<sub>19</sub>B<sub>10</sub>N (**2**): C, 45.95 (46.33); H, 7.33 (7.25); N, 5.36 (5.24). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm),  $\delta = 8.12$  (s, 1H, C<u>H</u>=N), 7.66-7.35 (m, 5H, C6H5), 4.10 (s, 2H, CH2-N), 4.05 (s, 1H, HCcage), 2.72–1.48 (m, br, 10H,  $B_{10}H_{10}$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm),  $\delta = 164.14$ (C=N), 134.80, 131.92, 128.86, 128.58 (C<sub>6</sub>H<sub>5</sub>), 73.48 and 63.64  $(\underline{C}_{cage})$ , 57.94 (-<u>C</u>H<sub>2</sub>-N). <sup>11</sup>B NMR (CDCl<sub>3</sub>, ppm),  $\delta = -2.96$  (1B,  ${}^{I}_{JBH} = 152 \text{ Hz}$ , -5.19 (1B,  ${}^{I}_{JBH} = 150 \text{ Hz}$ ), -9.07 (3B,  ${}^{I}_{JBH} = 150 \text{ Hz}$ ), -11.15 (2B,  ${}^{I}_{JBH} = 109 \text{ Hz}$ ), -13.07 (3B,  ${}^{I}_{JBH} = 167 \text{ Hz}$ ). IR (KBr pellet, cm<sup>-1</sup>), 3649 (w, m), 3278 (w, s), 3069 (s, s), 2880 (m, br), 2604 (vs, s), 2566 (vs, s), 1646 (vs, s), 1445 (m, s), 1386 (m, s), 1335 (m, s), 1016 (s, s), 752 (s, s), 689 (s, s), 526 (w, s), 465 (w. s).

### 4.2. Single crystal X-ray diffraction of (2)

A suitable quality single crystal of **2** was chosen under a Leica microscope and placed on a fibre needle which was then mounted on the goniometer of the X-ray diffractometer. The crystal was purged with a cooled nitrogen gas stream at 110 K throughout the data collection. X-ray reflections were collected on a Rigaku Saturn CCD area detector with graphite monochromated Mo-*K* $\alpha$  radiation ( $\lambda = 0.71073$ Å). Data were collected and processed using Crystal-Clear (Rigaku) software. Crystal structure was solved by direct methods and SHELX-TL was used for structure solution and least-squares refinement. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either fixed at idealized positions or located from the difference Fourier map and allowed to ride on their parent atoms in the refinement cycles. Data collection and refinement details are given in Table S-1.

### 4.3. Synthesis of 1-(CH<sub>2</sub>N=CC<sub>6</sub>H<sub>4</sub>(OH)-2)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**3**)

A similar process, adopted for the preparation of (**2**), was used to synthesize 1.27 g of (**3**) in 64% yield from 1.5 g of (7.2 mmol) (**1**), 9.92 g of (36.0 mmol) salicyladehyde, NaHCO<sub>3</sub> (35.0 g, 416.7 mmol) and 30.0 g of 4 Å MS in 250 mL toluene. Analytic data: Calcd. (Found) for C<sub>10</sub>H<sub>19</sub>B<sub>10</sub>NO: C, 43.3 (43.50); H, 6.90 (6.89); N, 5.05 (4.89). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm),  $\delta = 12.06$  (s, 1H, -OH), 8.20 (s, 1H, CH=N), 7.35–6.85 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 4.15 (s, 2H, CH<sub>2</sub>–N), 3.68 (s, 1H,  $HC_{cage}$ ), 2.74–1.18 (m, br, 10H, B<sub>10</sub>H<sub>10</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm),  $\delta = 168.37$  (C=N), 160.79, 133.91, 132.35, 119.41, 117.81, 117.32 (C<sub>6</sub>H<sub>4</sub>), 72.58 and 63.74 (C<sub>cage</sub>), 58.45 ( $-CH_2$ –N). <sup>11</sup>B NMR (CDCl<sub>3</sub>, ppm),  $\delta = -2.45$  (1B, <sup>1</sup>J<sub>BH</sub> = 150 Hz), -4.96 (1B, <sup>1</sup>J<sub>BH</sub> = 150 Hz), -8.96 (3B, <sup>1</sup>J<sub>BH</sub> = 143 Hz), -11.31 (2B, <sup>1</sup>J<sub>BH</sub> = 104 Hz), -13.05 (3B, <sup>1</sup>J<sub>BH</sub> = 175 Hz). IR (KBr pellet, cm<sup>-1</sup>), 3671 (w, br), 3649 (w, m), 3057 (m, s), 2911 (w, br), 2599 (vs, s), 2574 (vs, s), 1948 (w, m), 1626 (vs, s), 1559 (m, s), 1457 (m, s), 1400 (m, s), 1275 (s, s), 1208 (m, s), 1117 (m, s), 1019 (s, m), 935 (w, s), 820 (m, s), 756 (s), s3, 723 (m, s), 639 (w, s), 592 (w, s), 455 (w, s).

### 4.4. Synthesis of phenyl(carboranylmethyl)imidotitanium (IV) chloride, $[1-(CH_2N=CC_6H_5)-1,2-C_2B_{10}H_{10}]TiCl_3$ (**4**)

A 1.0 g (3.8 mmol) of (2) was dissolved in 120 mL of dry toluene and the resulting solution was cooled to -78 °C and to which 2.51 ml (4.02 mmol) of *n*-BuLi (1.6 M in hexanes) was carefully added with syringe. After addition, the mixture was kept at that temperature for 30 min before warming to room temperature for 4 h. The reaction mixture was then allowed to cool to 0 °C and 0.76 g (4.01 mmol) of TiCl<sub>4</sub> was added. After 30 min at 0 °C, the mixture was stirred at room temperature for 2 days. After filtration and removal of all the solvents under reduced pressure, the obtained residue was precipitated with a mixture of benzene/pentane (v:v = 1:2) to collect 0.51 g of (4) in 32% yield. MS (ESI) for  $C_{10}H_{18}B_{10}Cl_3NTi$  (5):  $m/z = 413.27 [M - H]^+$ . <sup>1</sup>H NMR (CD<sub>3</sub>CN, ppm),  $\delta = 8.52$  (s, 1H, CH=N), 7.80–7.42 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 4.41 (s, 2H, CH<sub>2</sub>-N), 3.12-1.28 (m, br, 10H, B<sub>10</sub>H<sub>10</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, ppm),  $\delta = 169.6 \text{ (C=N)}, 131.99, 131.18, 129.80, 129.21 \text{ (C}_{6}H_{5}), 78.1 \text{ and}$ 66.69 (<u>C<sub>cage</sub></u>), 58.0 (–<u>CH</u><sub>2</sub>–N). <sup>11</sup>B NMR (CD<sub>3</sub>CN, ppm),  $\delta$  = –3.17 (1B,  ${}^{I}_{JBH} = 148$ , -5.37 (1B,  ${}^{I}_{JBH} = 159$  Hz), -6.73 (1B,  ${}^{I}_{JBH} = 163$  Hz), -9.99 (3B,  ${}^{I}_{JBH} = 167$  Hz), -12.13 (2B,  ${}^{I}_{JBH} = 98$  Hz), -13.22 (2B,  ${}^{I}_{JBH} = 136.1$  Hz). IR (KBr pellet, cm<sup>-1</sup>), 3397 (s, br), 2593 (s, s), 1632 (s, br), 1457 (m, s), 1339 (m, br), 1209 (m, s), 1167 (m, s), 1089 (w, s), 911 (s, s), 846 (s, br), 759 (m, s), 729 (m, s), 694 (m, s), 490 (m, s).

### 4.5. Synthesis of [1-(CH<sub>2</sub>N=CC<sub>6</sub>H<sub>4</sub>(0)-2)-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]TiCl<sub>2</sub> (**5**)

A similar process, described above for the preparation of (**4**), was used to synthesize 0.73 g of (**5**) in 51% yield from 1.0 g of (3.6 mmol) (**3**), 4.73 mL of (7.57 mmol) *n*-BuLi (1.6 M in hexanes) and 0.72 g of (3.80 mmol) TiCl<sub>4</sub> in 120 mL dry toluene. MS (ESI) for C<sub>10</sub>H<sub>17</sub>B<sub>10</sub>Cl<sub>2</sub>NOTi (**5**): *m*/*z* = 391.28 [M – 3H]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm),  $\delta$  = 8.51 (s, 1H, CH=N), 7.57–7.01 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 4.41 (s, 2H, CH<sub>2</sub>–N), 2.90–0.95 (m, br, 10H, B<sub>10</sub>H<sub>10</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm),  $\delta$  = 156.8 (C=N), 155.5, 129.9, 129.3, 124.3, 119.7, 117.1 (C<sub>6</sub>H<sub>4</sub>), 74.2 and 68.3 (C<sub>cage</sub>), 60.7 (-CH<sub>2</sub>–N). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm),  $\delta$  = -4.39 (1B, <sup>1</sup>J<sub>BH</sub> = 148 Hz), -7.23 (1B, <sup>1</sup>J<sub>BH</sub> = 144 Hz), -11.41 (3B, <sup>1</sup>J<sub>BH</sub> = 146 Hz), 14.09 (2B, <sup>1</sup>J<sub>BH</sub> = 149 Hz), -15.21 (3B, <sup>1</sup>J<sub>BH</sub> = 154 Hz). IR (KBr pellet, cm<sup>-1</sup>), 3397 (s, br), 2960 (s, s), 2931 (s, s), 2581 (s, s), 1610 (s, br), 1553 (s, s), 1447 (m, s), 1401 (m, s), 1288 (m, s), 1234 (m, s), 1125 (w, s), 1034 (w, s), 911 (m, s), 758 (s, s), 729 (s, s), 635 (s, s), 515 (m, s).

#### 4.6. Polymerization procedures

The polymerization of ethylene and methyl-10-undecannoate catalyzed by compounds 4 and 5 were performed for 2 h in 70 mL toluene in the presence of methylaluminoxane (MAO, 1.7 M in toluene) or trimethylaluminum (MA, 2.0 M in toluene) or tris(pentafluorophenyl)borane in Parr reactor. The argon pressure inside the reactor was reduced by applying vacuum. Monomer pressure was then applied to the reactor which was adjusted to constant temperature and pressure. During the polymerization process, 3.0 µmol catalyst (4 or 5) based on titanium species and 2000 µmol MAO or MA were used to give a concentration ratio of [Al]/[Ti] = 2000. For initiator tris(pentafluorophenyl)borane, a mole ratio of 3 for [B]/[Ti] was used. The co-monomer methyl-10undecannoate (1 M in toluene, 10 mmol) was charged with syringe. The reaction temperature was 50 °C under 1.5 bar pressure. 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  $\times$  20 ml) and n-hexane (2  $\times$  20 ml) in sequence and dried at 60 °C in high vacuum to a constant weight. Polymerization results are summarized in Table 2.

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### Appendix A. Supplementary material

CCDC 883306 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

### Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012. 07.010.

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