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Dicarbollide Analogues of the Constrained-Geometry Polymerization Catalyst

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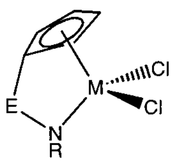
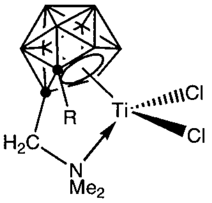
*Summary: A new type of constrained-geometry complex, [η^5:η^1-$RC_2B_9H_9{-}CH_2NMe_2$]$TiCl_2$ (**3**), based on the dimethylamino dicarbollyl ligand has been prepared and characterized by ^{11}B, ^{13}C, and ^{1}H NMR spectroscopy. This complex is the first example of a compound containing the "CGC-type" dicarbollyl ligand for titanium in its highest (4+) oxidation state. Complexes **3** in the presence of MMAO exhibit moderate catalytic activities for the ethylene polymerization but produce high-molecular-weight polymers.*

Chart 1



$(Cp^N)MCl_2$ **A**
E = CH_2, $SiMe_2$; M = Ti, Zr, Hf



$(Dcab^N)TiCl_2$ **3**

Much attention has been paid to constrained-geometry catalysts based on the cyclopentadienyl−amido ligand, e.g., **A**, due to their remarkable activity for the copolymerization of ethylene with α-olefins.[1] The sterically open nature of the catalyst center is considered to facilitate the incorporation of various α-olefins into growing polymer chains. As an extension of the structural variations[2] in the cyclopentadienyl derivatives of the group 4 metals, the dicarbollide moiety[3] has been employed as an η^5-coordinated group instead of the cyclopentadienyl ligand. The formal replacement of a monoanionic Cp^- ligand in $[CpM(IV)]^{3+}$ (**A**, Chart 1) by the isolobal, dianionic ligand $(Dcab^N)^{2-}$ in the $[(Dcab^N)Ti(IV)]^{2+}$ fragment (**3**, Chart 1) reduces the overall charge by one unit but leaves the gross structural and metal frontier orbital properties unchanged. Similar dianionic ligands such as aminoborollide,[4] trimethylenemethane,[5] and diene[6] have been synthesized and converted into the corresponding group 4 metal complexes. Consequently, the potential advantage of catalyst designs of this type would be the control of secondary metal/ligand interactions; the weaker π-donating character and the lower steric requirements of the pendant neutral amino group enhance the metal's Lewis acidity by the simultaneous reduction of the formal electron count and the steric crowding at the electrophilic metal center. Thus, it was anticipated that incorporation of the dicarbollyl fragment into the CGC ligand framework would provide interesting opportunities for the design of complexes with new metal/charge combinations and increased metal unsaturation. Herein we report the

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(1) (a) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (b) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (c) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4019. (d) Wang, W.; Yan, D.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E.; Sayer, B. G. *Macromol. Chem. Phys.* **1998**, *199*, 2409. (e) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836. (f) Eberle, T.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **1998**, 237. (g) Amor, F.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139. (h) Okuda, J.; Eberle, T. In *Metallocenes*; Halterman, R. L., Tongi, A.; Eds.; Wiley-VCH: Weinheim, Germany, 1998; p 415. (i) Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958. (j) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G. *Organometallics* **1996**, *15*, 2720. (k) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129. (l) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (m) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (n) Canich, J. A. M. U.S. Patent 5,026,798, 1991 (Exxon). (o) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. A.; Lai, S. Y. Eur. Pat. Appl. 0416815 A2, 1991 (Dow). (p) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59. (q) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649. (s) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(2) (a) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 1363. (b) Feng, S.; Klosin, J.; Kruper, W. J., Jr.; McAdon, M. H.; Neithamer, D. R.; Nickias, P. N.; Patton, J. T.; Wilson, D. R. *Organometallics* **1999**, *18*, 1159. (c) Brown, S. J.; Gao, X.; Harrison, D. G.; Koch, L.; Spence, R. E. v. H.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5445. (d) Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883. (e) de Boer, E. J. M.; Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A: Chem.* **1998**, *128*, 155. (f) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (g) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492. (h) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahamad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291.

(3) (a) Bei, X.; Kreuder, C.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 1085. (b) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508. (c) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (d) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (e) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630. (f) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (g) Uhrhammer, R.; Su, Y.-X.; Swenson, D. C.; Jordan, R. F. *Inorg. Chem.* **1994**, *33*, 4398. (h) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (i) Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098. (j) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

(4) Bazan, G. C.; Donnelly, S. J.; Rodriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671.

(5) (a) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343. (b) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 10155.

(6) Pindado, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115.

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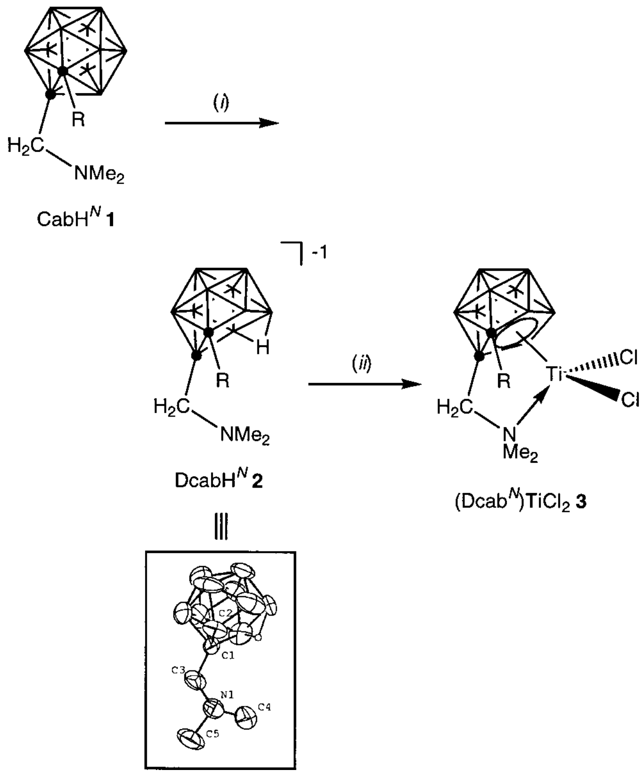
Scheme 1. Synthesis of Titanium Complexes Incorporating the Ligand 2 (R = H (a), Me (b))[a]



[a] Legend: (*i*) KOH, MeOH, 65 °C; (*ii*) (a) LiBu^n, THF, −78 °C, (b) $TiCl_4$, THF, −78 °C.

synthesis, characterization, and polymerization activity of dicarbollyl−amino group 4 metal complexes, which involve η^5- and η^1-bound dicarbollyl−amino moieties depending on the electronic nature of the group 4 metals.

The dicarbollide ligand DcabH^N [*nido*-7-NMe_2CH_2−7,8-$RC_2B_9H_{10}$]$^-$ (**2**; R = H (**a**), Me (**b**)) was prepared using a standard deborination procedure[7] involving the appropriate aminomethyl-*o*-carborane CabH^N (**1**). Thus, complex **1** undergoes facile degradation in methanollic KOH to selectively remove the boron atom and generate **2**. The spectroscopic characterization of this complex shows that the aminomethyl group is linked to the *nido* cage carborane. Indeed, the X-ray structure determination[8] of the complex **2** supports the spectral data (Scheme 1).

The reaction of the ligand **2a** with 1 equiv of Bu^{n}Li and subsequent reaction with $TiCl_4$ in toluene yielded the red dicarbollyl−amino titanium complex [η^5: η^1-$C_2B_9H_{10}$−CH_2NMe_2]$TiCl_2$ (**3a**; Scheme 1). Complex **3a** is only partially soluble in toluene. To increase the solubility of the titanium complex, we have developed the new Me-substituted dicarbollyl−amino ligand **2b** and synthesized the corresponding dicarbollyl−amino titanium complex [η^5:η^1-$MeC_2B_9H_{10}$−CH_2NMe_2]$TiCl_2$ (**3b**). As a consequence, the Me-substituted complex **3b** showed better solubility in aromatic solvents. The precise structure of this compound is unknown, due to our inability to obtain single crystals for X-ray analysis; the compound tended to dissolve out of the aromatic solvents employed and decomposed in chlorinated or donor solvents. However, elemental analysis and mass spectrometry confirmed the above formulation.[9] The ^{1}H and ^{13}C NMR spectra of the new dichloride complex is consistent with the structure shown in Scheme 1. Thus, the ^{1}H NMR spectra of **3** revealed two signals for the methyl groups at the nitrogen atom of the side chain due to the asymmetric titanium metal center. The methylene protons of the C*H*$_2$ group in **3** are diastereotopic, each giving rise to an AB spin pattern. The most significant change in the ^{1}H NMR spectra of **3** is caused by the low-field shift of the signals for the methylene hydrogen, while for complexes **2** these signals are observed at about 2.3 ppm, and **3** shows values of 2.7−3.5 ppm. In addition, the signals for the methyl groups at the nitrogen atom are shifted downfield (0.02−0.45 ppm). Corresponding downfield shifts for the methylene and methyl groups adjacent to the nitrogen atoms are observed in the ^{13}C NMR spectra. This observation is consistent with similar findings for the general intramolecularly coordinated metal complexes of the CabH^N (*closo*-1-NMe_2CH_2-1,2-$C_2B_{10}H_{11}$)[10] and CabH^P (*closo*-1-PPh_2CH_2-1,2-$C_2B_{10}H_{11}$)[11] ligand systems. In addition, the ^{11}B NMR spectra show the expected resonances for the dicarbollyl group in the highly asymmetric environments, due to the metal complexation. The ^{11}B chemical shifts are similar to those observed for other metal η^5-dicarbollide complexes and support the proposed η^5 coordination.[3,12]

In view of its importance as a potential precursor for α-olefin polymerization catalysts, the synthesis of the alkylated derivatives of **3** was studied. The attempted reactions of **3** with methyllithium, trimethylaluminum, and methylmagnesium bromide resulted in either no reaction or the rapid decomposition of the possible alkylated species, which did not allow isolation or spectroscopic study. These observations were not com-

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(7) (a) Plesek, J.; Hermanek, S.; Stibr, B. *Inorg. Synth.* **1983**, *22*, 231. (b) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(8) Crystal structure analysis (CAD-4 diffractometer): **2a**, orthorhombic, $P2_12_12_1$, $a = 10.5791(7)$ Å, $b = 11.322(2)$ Å, $c = 14.9539(9)$ Å, $V = 1791.0(3)$ Å^3, $Z = 4$, 2006 observed reflections, 210 parameters. R1 = 0.1151, wR2 = 0.2779 ($I > 2\sigma(I)$), R1 = 0.2898, wR2 = 0.3566 (all data); **4b**, monoclinic, $P2_1/c$, $a = 18.030(1)$ Å, $b = 10.4035(6)$ Å, $c = 16.090(2)$ Å, $\beta = 96.555(9)$°, $V = 2998.3(5)$ Å^3, $Z = 4$, 6131 observed reflections, 367 parameters. R1 = 0.0385, wR2 = 0.1004 ($I > 2\sigma(I)$); R1 = 0.0754, wR2 = 0.1151 (all data).

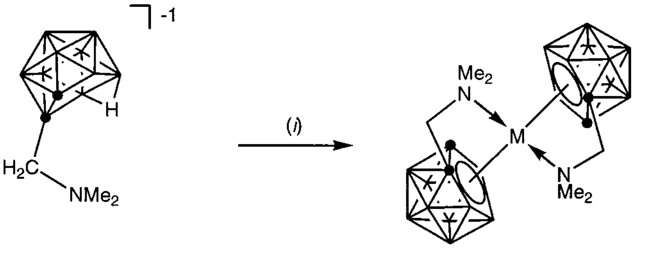
(9) **3a**: ^{1}H NMR (δ, 300.0 MHz, C_6D_6) 1.68 (s, 3H, N*Me*$_2$), 1.74 (s, 3H, N*Me*$_2$), 2.70 (d, 1H, 14 Hz, NC*H*$_2$), 3.43 (d, 1H, 14 Hz, NC*H*$_2$), 4.22 (s, 1H, C*H*$_{Cab}$); ^{13}C{^{1}H} NMR (δ, 75.4 MHz, C_6D_6) 54.36 (N*Me*$_2$), 58.63 (N*Me*$_2$), 69.76 (NC*H*$_2$); exact mass calcd for $^{12}C_5{}^{11}B_9{}^1H_{18}{}^{14}N^{48}Ti^{35}Cl_2$ 309.1133, found 309.1141; IR spectrum (KBr pellet, cm^{-1}) ν(C−H) 3188, ν(B−H) 2532. Anal. Found: C, 19.33; H, 5.75; N, 4.36. Calcd: C, 19.48; H, 5.89; N, 4.54. **3b**: ^{1}H NMR (δ, 300.0 MHz, C_6D_6) 1.52 (s, 3H, C*Me*$_{Cab}$), 2.09 (s, 3H, N*Me*$_2$), 2.11 (s, 3H, N*Me*$_2$), 3.20 (d, 1H, 14 Hz, NC*H*$_2$), 3.36 (d, 1H, 14 Hz, NC*H*$_2$); ^{13}C{^{1}H} NMR (δ, 75.4 MHz, C_6D_6) 34.47 (C*Me*$_{Cab}$), 53.25 (N*Me*$_2$), 57.86 (N*Me*$_2$), 69.85 (NC*H*$_2$); exact mass calcd for $^{12}C_6{}^{11}B_9{}^1H_{20}{}^{14}N^{48}Ti^{35}Cl_2$ 323.1290, found 323.1283; IR spectrum (KBr pellet, cm^{-1}) ν(C−H) 2960, ν(C−H) 2930, ν(C−H) 2872, ν(B−H) 2532. Anal. Found: C, 22.22; H, 6.12; N, 4.22. Calcd: C, 22.36; H, 6.25; N, 4.35.

(10) (a) Lee, J.-D.; Kim, S.-J.; Yoo, D.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1695. (b) Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514. (c) Lee, H.-S.; Bae, J.-Y.; Ko, J.; Kang, Y. S.; Kim, H. S.; Kim, S.-J.; Chung, J.-H.; Kang, S. O. *J. Organomet. Chem.* **2000**, *614−615*, 83. (d) Lee, J.-D.; Baek, C.-K.; Ko, J.; Park, K.; Cho, S.; Min, S.-K.; Kang, S. O. *Organometallics* **1999**, *18*, 2189.

(11) Lee, T.; Lee, S. W.; Jang, H. G.; Ko, J.; Kang, S. O. *Organometallics* **2001**, *20*, 741.

(12) (a) Su, Y.-X.; Reck, C. E.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2000**, *19*, 4858. (b) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163. (c) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964. (d) Manning, M. J.; Knobler, C. B.; Khatter, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009. (e) Siriwardane, U.; Zhang, H.; Hosmane, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9637.

Scheme 2. Synthesis of Bis(dicarbollylamino) Group 4 Metal Complexes 4 (M = Ti (a), Zr (b), Hf (c))[a]



DcabH^N **2a** (Dcab^N)$_2$M **4**

[a] Legend: (*i*) (a) LiBu^n, THF, −78 °C, (b) MCl$_4$, THF, −78 °C.

pletely unanticipated in light of the high electrophilicity of the boron centers in the dicarbollyl ligand backbone.[3j,13]

At the outset of these studies we expected to synthesize the dichloro−zirconium and −hafnium complexes in a way analogous to that for the corresponding titanium complex **3**. However, the reaction of **2a** and MCl$_4$ (M = Zr, Hf) in toluene results in (Dcab^N)$_2$M, [η^5:η^1-$C_2B_9H_{10}$−CH_2NMe_2]$_2$M (M = Zr (**4b**), Hf (**4c**); Scheme 2). The first evidence for the formation of the 1:2 complexes **4b**,**c** came from their ^{1}H NMR spectra. In contrast to the 1:1 complex **3a**, the methylene protons in **4b**,**c** show different chemical shifts at around δ 2.7−2.9 (doublet, J_{H-H} = 14 Hz) in benzene-d_6 solution at room temperature. For an unequivocal structural characterization, we decided to determine the structure by X-ray crystallography.

Thus, the X-ray crystal structure of **4b**, shown in Figure 1, reveals that the Zr atom essentially adopts an η^5 bonding posture with the dicarbollyl rings and an η^1 bonding posture with the dimethylamino side groups. Overall, the structure of **4b** adopts the distorted-tetrahedral coordination geometry of [Zr(η^5:η^1-$C_2B_9H_{10}$−CH_2NMe_2)$_2$], consisting of 2-fold rotational symmetry. The Zr−N$_{\text{amino}}$ distance of 2.46−2.49 Å confirms that the N-donor atom is complexed to the metal in a strain-free manner. This distance is consistent with a Zr−N(sp^3) single bond.[3e,14] The noticeable shortening of the Zr−C_2B_3(cent) distance (2.079 Å) (where C_2B_3(cent) is the centroid of the dicarbollyl ring) and the expansion of the C_2B_3(cent)−Zr−C_2B_3(cent) (138.05°) and N−Zr−N (103.40(1)°) angles in **4b** can be explained by the chelating effect introduced by the η^5:η^1-$C_2B_9H_{10}$−CH_2NMe_2 ligand. The preferred formation of a bis(dicarbollyl) over a mono(dicarbollyl) complex can be ascribed to the greater ionic radii of zirconium and hafmium as compared with that of titanium.[3a,f,15]

Similarly, the reaction of TiCl$_4$ with 2 equiv of **2a** in THF gave complex **4a** as yellow crystals. Thus, the reaction of MX$_4$ (M = Ti, Zr, Hf) with 2 equiv of **2a** in THF afforded the novel bis(dicarbollyl) complexes **4** in good yields as colorless to slightly yellow crystals (Scheme 2). Consistent with the proposed structure, the ^{1}H NMR spectra of **4** at room temperature show two signals for the methyl protons of the dimethylamino groups and two signals for the C−H signals on the dicarbollyl groups. The two protons in each of the CH$_2$ links are diastereotopic and give rise to an AB coupling pattern.

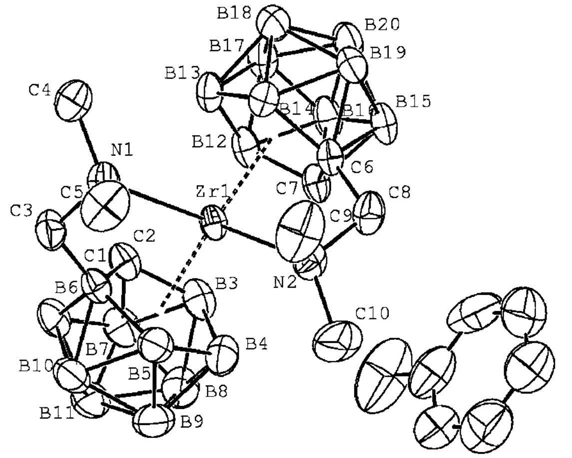


Figure 1. Molecular structure of **4b** with atom labeling. Ellipsoids show 30% probability levels, the unlabeled atoms are carbon atoms, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)−N(1) = 2.460(3), Zr(1)−N(2) = 2.487(3), Zr(1)−C(1) = 2.469(4), Zr(1)−C(2) = 2.490(4), Zr(1)−B(3) = 2.579(4), Zr(1)−B(4) = 2.591(5), Zr(1)−B(5) = 2.498(5), Zr(1)−C(6) = 2.467(4), Zr(1)−C(7) = 2.504(4), Zr(1)−B(12) = 2.593(5), Zr(1)−B(13) = 2.572(5), Zr(1)−B(14) = 2.474(4); N(1)−Zr(1)−N(2) = 103.40(1), C(1)−C(3)−N(1) = 108.0(3), N(2)−C(8)−C(6) = 108.3(3).

The activities of catalysts **3** were studied during the polymerization of ethylene in the presence of the cocatalyst MMAO (500/1Al/Ti) in hexane at 40 °C (1 atm of ethylene). The activity of **3a** was relatively low at 85 kg of PE (mol of catalyst)$^{-1}$ h^{-1}, compared to an activity of 323 kg of PE (mol of catalyst)$^{-1}$ h^{-1} with Cp$_2$TiCl$_2$ under the same conditions. The introduction of a methyl group at the 8-position of the dicarbollyl ligand resulted in no significant change with respect to the catalytic performance, though it somewhat lowered the polymerization activity. Thus, complex **3b** (R = Me) afforded an activity of 55 kg of PE (mol of catalyst)$^{-1}$ h^{-1}. The melting temperatures of the polyethylenes prepared with these catalysts **3** were between 129 and 131 °C, values typical for linear high-density polyethylene. Also, the IR spectra of the polyethylenes made with catalysts **3** showed no sign of branching in the polyethylenes, supporting the linear structure. The molecular weights of the produced polymers are very high, and their molecular weight distributions are broad (**3a**, M_w = 1156 000 and M_w/M_n = 147.8; **3b**, M_w = 1010 000 and M_w/M_n = 63.8). Further studies on the reactivity and α-olefin polymerization characteristics of **3** are being investigated.

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Supporting Information Available: Text giving spectroscopic data and text and tables giving crystallographic data (excluding structure factors) for the structures (**2a** and **4b**) reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Yang, X.; King, W. A.; Sabat, M.; Marks, T. J. *Organometallics* **1993**, *12*, 4254. (b) Grimes, R. N. *Carboranes*; Academic: New York, 1970.

(14) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572.

(15) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.