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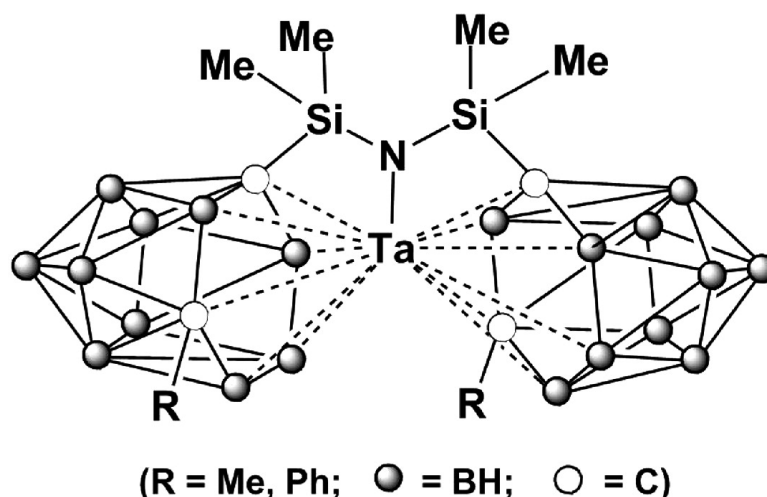
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Synthesis, Characterization, and Polymerization of a Neutral Tantalacarborane Sandwich Complex Derived from a Pentaanionic Exo-Polyhedrally Linked Bis(C₂B₁₀-carborane) Ligand

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Tetramethyldisilazane-bridged *closo*-carborane compounds, [(*closo*-1-R-1,2-C₂B₁₀H₁₀)Me₂Si]₂NH (R = Me (**1**), Ph (**2**)), and their tantalum complexes, [(*closo*-2-R-2,3-C₂B₁₀H₁₀)Me₂Si]₂N]Ta(V) (R = Me (**3**), Ph (**4**)), have been prepared and characterized. Compounds **3** and **4** were found to be active catalysts for the polymerization of ethylene in the presence of the cocatalyst MAO to produce two morphologically different polyethylenes with high molecular weight.

1. Introduction

It is well-known that metallocene complexes, such as sandwich and half-sandwich group 4 compounds, play important roles in ethylene polymerization, due to their ability to produce stereospecific polymers.^{1–7} The design and synthesis of structurally unique metallocenes are still attracting a great deal of attention.^{6,7} Such complexes can be used as “single site” catalysts for homo- or copolymerization of polar olefins, such as styrene, methyl methacrylate (MMA), vinyl chloride, etc., to produce functionalized polymers.^{6,7} It is well recognized that the *nido*-carborane dianions [R₂C₂B₉H₉]^{2–}, [R₂C₂B₄H₄]^{2–}, and [R₂C₂B₁₀H₁₀]^{2–} (R = H, alkyl, or aryl groups) (Figure 1)^{8–10} are isolable with the cyclopentadienides, in that they have six π electrons delocalized on the C₂B₃ or C₂B₄ open faces of the dianions that can coordinate metals in an η^5 or η^6 fashion. Because of this similarity and the high catalyst activity of activated metallocenes, the design and synthesis of stable carborane ligands for use in transition-metal complexes, with the possibility of high catalytic activity, has been an ongoing area of research.^{11–14} It was found that carboranyl trianionic

ligands coordinated to group 4 compounds (Figure 2a) are active precatalysts for olefin polymerization.^{13,14} Herein we report the syntheses of tetramethyldisilazane-bridged *closo*-carboranes, a novel pentaanionic precursor, and its conversation to a neutral tantalum(V) metallacarborane (Figure 2b). The tantalacarboranes were found to be active precatalysts for olefin polymerization.

2. Experimental Section

2.1. General Methods. All operations were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox. The solvents diethyl ether, *n*-hexane, and tetrahydrofuran (THF) were dried with sodium. All other reagents were purchased from Sigma-Aldrich Pte. Ltd. or Katchem Spolo. s.r.o. and used as received. 1,3-Dichloro-1,1,3,3-tetramethyldisilazane¹⁵ and Cl₄-TaN(SiMe₃)₂¹⁶ were prepared according to literature methods. Elemental analyses were measured in a Euro EA elemental analyzer and melting points determined by a Büchi melting point analyzer. ¹H, ¹³C, and ¹¹B NMR were recorded on a Bruker Advance 400 MHz spectrometer. Chemical shifts were measured in ppm relative to a TMS standard (¹H, 400.2 MHz; ¹³C, 100.6 MHz; ¹¹B, 128.4 MHz). Near-infrared (IR) spectra were measured using a Bio-Rad spectrophotometer with KBr pellets. Far-infrared spectra were measured using a Bruker FT-IR Vertex 70 spectrophotometer with THF film. Molecular weights and molecular weight distributions of the polymers were determined by means of gel-permeation chromatography (GPC; Polymer Laboratories, PC-GPC-220) at 160 °C, using 1,2,4-trichlorobenzene stabilized with 0.0125% BHT as eluent with a column set of 2 \times PLgel 10 μ m MIXED-B (300 \times 7.5 mm). The weight average molecular weight and polydispersity index (*M_w* and *M_w/M_n*, respectively) were calculated on the basis of polystyrene standards: flow rate 1.0 mL/min, injected volume 200 μ L. The Scanning electron microscopy (SEM) images were obtained

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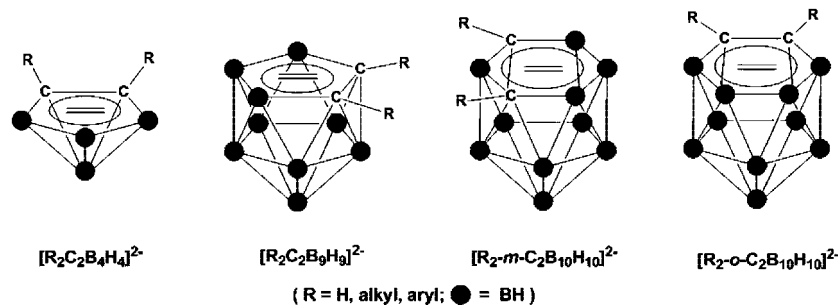
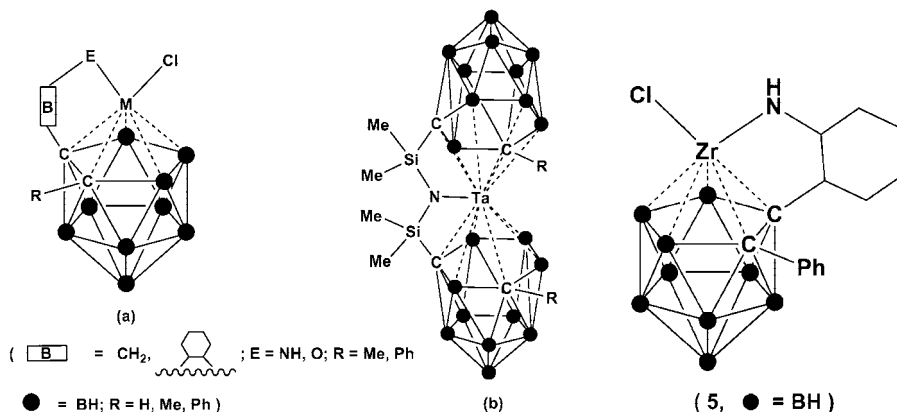
Figure 1. *nido*-Carborane-derived ligands.

Figure 2. Carboranyl trianion (a), pentaanionic coordinated Ta(V) complex (b), and 5.

on a JSM-6700F field-emission microscope. The Raman scattering spectra were measured at room temperature using a JY Horiba LabRAM Raman microscope. The high-resolution MS was measured on a Thermo Finnigan MAT XP95 analyzer using the EI-HR model (70 eV, source temperature 150 °C).

2.2. Synthesis of [(*closo*-1-Me-1,2- $C_2B_{10}H_{10}$) Me_2Si_2NH (1). A 1.59 g (10.05 mmol) sample of *closo*-1-Me-1,2- $C_2B_{10}H_{11}$ was dissolved in 30 mL of THF to produce a clear solution, which was cooled to -78 °C. A 6.35 mL (10.16 mmol) amount of *n*-BuLi solution (1.6 M in hexane) was slowly added to the THF solution at -78 °C with syringe. After addition, the mixture was stirred at -78 °C for 30 min before being warmed to room temperature spontaneously and the reaction continued for 4 h. The solution was then cooled to -10 °C and added dropwise to a solution of $HN(SiMe_2Cl)_2$ (1.01 g, 4.99 mmol) in 10 mL of THF. After addition, the solution was warmed to room temperature spontaneously for 2 h followed by heating to 80 °C for 10 h. The mixture was then cooled to room temperature and concentrated to about 5 mL under reduced pressure. The resulting light brown residue was purified by thin-layer chromatography (TLC; SiO_2) and developed with a mixed solvent of pentane and ethyl ether (10/1 v/v). The main product was collected and dried under high vacuum to give a colorless solid of **1**: yield 1.14 g (2.56 mmol), 51.2% (mp 87–89 °C). Anal. Calcd for $C_{10}H_{39}B_{20}NSi_2$ (**1**): C, 26.94; H, 8.82; N, 3.14. Found: C, 26.90; H, 8.80; N, 3.10. 1H NMR (THF- d_8 , ppm): δ 0.04 (s, 12H, 4 \times Si- CH_3); 1.13–3.20 (m, 20H, 2 \times $C_2B_{10}H_{10}$); 2.02 (s, 6H, 2 \times C_{cage} - CH_3). ^{13}C NMR (THF- d_8 , ppm): δ 1.65 (Si- CH_3); 26.65 (C_{cage} - CH_3); 62.92 and 70.32 (C_{cage}). ^{11}B NMR (THF- d_8 , ppm): δ = -2.39 (1B, $^1J_{BH}$ = 148 Hz); -6.96 (1B, $^1J_{BH}$ = 154 Hz); -9.47 (2B, $^1J_{BH}$ = 155 Hz); -10.51 (2B, $^1J_{BH}$ = 74 Hz); -11.29 (2B, $^1J_{BH}$ = 122 Hz); -12.77 (2B, $^1J_{BH}$ = 174 Hz). ^{29}Si NMR (THF- d_8 , ppm): δ -107.93 (s). IR (KBr pellet, cm^{-1} , vs = very strong, s = strong, m = middle, w = weak, br = broad): ν 3272 (br, vs), 2963 (s, s), 2521 (ν_{BH} , s, m), 2296 (s, w), 2229 (s, w), 1642 (s, vs), 1509 (s, s), 1449 (s, s), 1413 (s, vs), 1315 (s, m), 1255 (s, w), 1180 (s, w), 1128 (s, w), 1068 (s, w), 938 (s, vs), 865 (s, w), 784 (s, m), 604 (br, s), 550 (s, m), 454 (s, m).

2.3. Synthesis of [(*closo*-1-Ph-1,2- $C_2B_{10}H_{10}$) Me_2Si_2NH (2). A procedure similar to that used in the preparation of **1** was used to prepare [(*closo*-1-Ph-1,2- $C_2B_{10}H_{10}$) Me_2Si_2NH (**2**). After purification, complex **2** (mp 103–105 °C) was obtained in 42.1% yield from the reaction of 2.21 g (10.03 mmol) of *closo*-1-Ph-1,2- $C_2B_{10}H_{11}$, 6.35 mL of *n*-BuLi (1.6 M in hexane), and $HN(SiMe_2Cl)_2$ (1.00 g, 4.94 mmol) in 10 mL of THF. Anal. Calcd for $C_{20}H_{43}B_{20}NSi_2$ (**2**): C, 42.17; H, 7.60; N, 2.46. Found: C, 42.09; H, 7.64; N, 2.41. 1H NMR (THF- d_8 , ppm): δ 0.13 (s, 12H, 4 \times Si- CH_3); 1.20–3.61 (m, 20H, 2 \times $C_2B_{10}H_{10}$); 6.83–7.74 (m, 10H, 2 \times C_{cage} - C_6H_5). ^{13}C NMR (THF- d_8 , ppm): δ 1.05 (Si- CH_3); 60.30 and 66.90 (C_{cage}); 126.84, 128.15, 130.53, and 133.42 (C_{cage} - C_6H_5). ^{11}B NMR (THF- d_8 , ppm): δ -2.86 (1B, $^1J_{BH}$ = 144 Hz); -4.67 (1B, $^1J_{BH}$ = 151 Hz); -8.99 (3B, $^1J_{BH}$ = 160 Hz); -10.81 (3B, $^1J_{BH}$ = 147 Hz); -12.75 (2B, $^1J_{BH}$ = 152 Hz). ^{29}Si NMR (THF- d_8 , ppm): δ -113.75 (s). IR (KBr pellet, cm^{-1}): ν 3374 (br, vs), 3068 (s, s), 2962 (s, s), 2582 (ν_{BH} , s, m), 1957 (s, w), 1637 (s, s), 1497 (s, m), 1448 (s, m), 1403 (s, m), 1261 (s, s), 1218 (s, m), 1196 (s, m), 1162 (s, w), 1081 (s, s), 1021 (s, m), 957 (s, s), 857 (s, s), 803 (s, s), 755 (s, m), 730 (s, m), 691 (s, s), 562 (s, m), 455 (s, m).

2.4. Synthesis of [(*closo*-2-Me-2,3- $C_2B_{10}H_{10}$) Me_2Si_2N]Ta^V (3). In a glovebox, **1** (1.11 g, 2.49 mmol), 3.00 g (23.41 mmol) of dry naphthalene and 0.30 g (13.05 mmol) of fresh-cut sodium were suspended in 40 mL of dry THF, followed by addition of 1.60 mL of *n*-BuLi (1.6 M in hexane, 2.56 mmol). The reaction mixture was stirred at room temperature for 2 weeks. Tantalum(V) chloride ($TaCl_5$; 0.90 g, 2.51 mmol) was added, and the reaction was continued for 1 week. After filtering, solvent and naphthalene were removed under reduced pressure and a yellow-brown solid was obtained. The crude product was then purified by recrystallization from CH_2Cl_2 /pentane to give 0.33 g of pale yellow solid [(*closo*-2-Me-2,3- $C_2B_{10}H_{10}$) Me_2Si_2N]Ta^V (**3**) in 21.2% yield. Mp: 178–179 °C. Anal. Calcd for $C_{10}H_{38}B_{20}NSi_2Ta$ (**3**): C, 19.19; H, 6.12; N, 2.24. Found: C, 19.09; H, 6.20; N, 2.13. MS: m/z 626.76 ($[M + H]^+$). 1H NMR (THF- d_8 , ppm): δ 0.18 (s (br), 12H, 4 \times Si- CH_3); 1.14–3.29 (m, 20H, 2 \times $C_2B_{10}H_{10}$); 1.94 (s, 6H, 2 \times C_{cage} - CH_3).

Table 1. Results of Ethylene Polymerization by 3^a

run	temp (°C)	ethylene pressure (atm)	[Al]/[Ta]	activity ^b	wt % of fibrous PE ^c
1	25	5	100	13	2.54
2	25	10	200	37	7.06
3	25	10	1000	29	9.74
4	50	5	100	18	8.53
5	50	10	100	1500	13.22
6	50	10	200	2470	21.72
7	50	10	1000	2055	26.44

^a Polymerization time = 30 min. ^b Activity in units of kg of PE/(mol of Ta) h atm). ^c wt % = weight percent of fibrous polyethylene in products.

¹³C NMR (THF-*d*₈, ppm): δ 0.15 (Si-CH₃); 24.24 (C_{cage}-CH₃); 66.08 and 69.18 (C_{cage}). ¹H NMR (THF-*d*₈, ppm): δ -1.25 (1B, ¹J_{BH} = 136 Hz); -4.92 (1B, ¹J_{BH} = 123 Hz); -9.19 (4B, ¹J_{BH} = 68 Hz); -10.44 (4B, ¹J_{BH} = 110 Hz). ²⁹Si NMR (THF-*d*₈, ppm): δ -110.92 (s). IR (KBr pellet, cm⁻¹): ν 3410 (br, vs), 2594 (ν_{BH}, s, m), 1634 (s, s), 1384 (s, w), 1261 (s, w), 1098 (br, w), 802 (s, m), 623 (br, s), 417 (s, w).

2.5. Synthesis of [(*closo*-2-Ph-2,3-C₂B₁₀H₁₀)Me₂Si₂N]Ta^V (4). A procedure similar to that used in the preparation of 3 was used to prepare [(*closo*-2-Ph-2,3-C₂B₁₀H₁₀)Me₂Si₂N]Ta^V (4). After purification, complex 4 (mp 154–156 °C) was obtained in 31.7% yield from the reaction of 2 (1.43 g, 2.50 mmol), 3.00 g (23.41 mmol) of naphthalene, 0.30 g (13.05 mmol) of sodium, 1.60 mL of *n*-BuLi (1.6 M in hexane), and 0.90 g (2.51 mmol) of TaCl₅ in 40 mL of THF. Anal. Calcd for C₂₀H₁₂B₂₀NSi₂Ta (4): C, 32.03; H, 5.65; N, 1.87. Found: C, 32.15; H, 5.64; N, 1.71. MS: *m/z* 749.90 ([M]⁺). ¹H NMR (THF-*d*₈, ppm): δ 0.16 (s, 12H, 4 × Si-CH₃); 1.27–3.70 (m, 20H, 2 × C₂B₁₀H₁₀); 6.72–7.64 (m, 10H, 2 × C_{cage}-C₆H₅). ¹³C NMR (THF-*d*₈, ppm): δ 0.18 (Si-CH₃); 66.89 and 69.94 (C_{cage}); 126.05, 126.88, 128.27, and 129.24 (C_{cage}-C₆H₅). ¹B NMR (THF-*d*₈, ppm): δ -2.88 (1B, ¹J_{BH} = 154 Hz); -4.76 (1B, ¹J_{BH} = 153 Hz); -9.09 (2B, ¹J_{BH} = 148 Hz); -10.99 (4B, ¹J_{BH} = 175 Hz); -12.92 (2B, ¹J_{BH} = 249 Hz). ²⁹Si NMR (THF-*d*₈, ppm): δ -108.20 (s). IR (KBr pellet, cm⁻¹): ν 3420 (br, s), 2950 (s, s), 2870 (s, s), 2521 (ν_{BH}, s, m), 1638 (s, s), 1489 (s, m), 1450 (s, m), 1375 (s, m), 1256 (s, s), 1097 (s, s), 1031 (s, m), 958 (s, m), 803 (s, m), 698 (s, m), 609 (s, w).

2.6. Evaluation of Catalytic Activity. The polymerization of ethylene, catalyzed by 3 (1.603 × 10⁻⁷ mol), was carried out for 30 min in 80 mL of toluene in the presence of the cocatalyst methylaluminoxane (MAO) in a Parr reactor. The argon pressure inside the predried reactor was reduced by high vacuum, followed by applied ethylene pressure. The reactor was adjusted to the optimized 50 °C and 10 atm. The ratio [Al]/[Ta] was selected as 200. As seen in Table 1, these conditions afforded the maximum catalytic activity. After 30 min, the reaction was quenched with 20 mL of a 10% HCl solution of MeOH. The toluene-insoluble polymers were collected by filtration and washed with copious amounts of MeOH and hexane, followed by drying under reduced pressure to produce 0.43 g of fibrous PE. The toluene filtrate was then precipitated by the addition of 200 mL of MeOH, collected by filtration, washed with MeOH (4 × 30 mL) and hexane (2 × 30 mL), and dried at 60 °C to a constant weight to give 1.55 g of powdery PE. A procedure similar to that described for 3 (above) was used to evaluate the ethylene polymerization using 4 as a catalyst. The results were essentially the same as found for 3, except that the weight percent of the fibrous PE was 11.35 instead of the value of 21.72 found for 3. Polymerization results are summarized in Table 2.

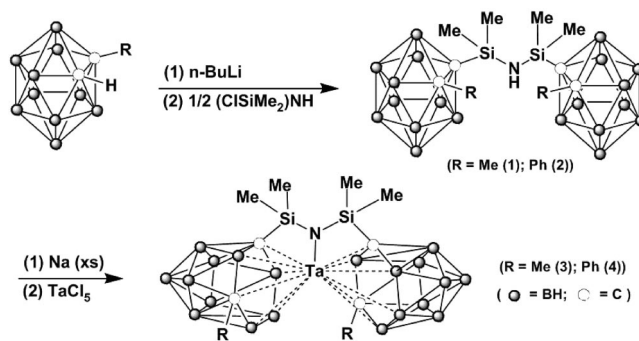
3. Results and Discussion

3.1. Synthesis and Characterization of Tetramethyldisilazane-Bridged *closo*-Carboranes and Derived Neutral Tantalum(V) Complexes. The reaction of 1,3-dichloro-1,1,3,3-tetramethyldisilazane with a twofold excess of the lithium salt

Table 2. Results of Ethylene Polymerization by 3–5

cat.	activity ^b	polymer ^a	
		<i>M</i> _w (10 ³ mol) ^d	<i>M</i> _w / <i>M</i> _n
3	2470 ^c	583.3	4.7
4	975	269	2.7
5	185 (47) ^e	47.9 (32.8) ^e	3.4 (1.8) ^e

^a Results for 3 were obtained under polymerization conditions of catalyst and cocatalyst: [Al]/[Ta] = 200, solvent toluene, *T* = 50 °C, *P*_{ethylene} = 10 atm, polymerization time 30 min. ^b Activity in units of kg of PE/(mol of Ta) h atm). ^c Calculated from all polymer, including fibrous and powdery polyethylene. ^d The molecular weight and molecular weight distribution of the polymers produced from the precipitate of toluene filtrate, powdery PE, were determined by means of gel-permeation chromatography (GPC: Polymer Laboratories, PC-GPC-220) at 160 °C using 1,2,4-trichlorobenzene stabilized with 0.0125% BHT as eluent. ^e Literature results for 5¹⁴ were obtained under polymerization conditions of catalyst and cocatalyst: [Al]/[Zr] = 2000, solvent toluene, *T* = 50 °C, *P*_{ethylene} = 1.5 bar, polymerization time 2 h.

Scheme 1. Synthesis of the Tetramethyldisilazane-Bridged *closo*-Carboranes and Tantalum(V) Complexes

of the carborane monoanions [*closo*-1-R-1,2-C₂B₁₀H₁₀]⁻ (R = Me, Ph) led to the formation of the tetramethyldisilazane-bridged dicarborane pentaanionic precursors [(*closo*-1-R-1,2-C₂B₁₀H₁₀)-Me₂Si₂NH] (R = Me (1), Ph (2)) in yields of 51.2% and 42.1% for 1 and 2, respectively (Scheme 1). The ¹H, ¹³C, and ¹B NMR spectra of 1 and 2 show normal group resonances that are consistent with substituted *closo*-C₂B₁₀H₁₀ cages, as described in Scheme 1.¹⁷ The IR spectra of 1 and 2 show the expected absorption band of ν_{BH} at 2521 and 2582 cm⁻¹, respectively. Compounds 1 and 2 were converted to their pentaanions by treatment with *n*-BuLi and Na in the presence of naphthalene as electron-transfer reagent in THF.

The in situ synthesized “constrained geometry” pentaanionic ligands were metalated with tantalum(V) chloride to form the neutral carboranyl tantalum(V) complexes [(*closo*-2-R-2,3-C₂B₁₀H₁₀)Me₂Si₂N]Ta(V) (R = Me (3), Ph (4)) in 21.2% and 31.7% yields, respectively. The ¹H and ¹³C NMR spectra of 3 and 4 show normal group resonances, as described in the proposed structures. The near-IR spectra of 3 and 4 exhibit typical B–H absorptions at about 2594 and 2527 cm⁻¹. To verify the formation of the Ta–N bond, Cl₄TaN(SiMe₃)₂ was synthesized¹⁶ and its Raman spectrum was used for comparison (Figure 3). In the Raman spectrum of Cl₄TaN(SiMe₃)₂, no resonances in the region of 500–1200 cm⁻¹, where peaks for TaCl₅ should be seen, were observed. However, both Cl₄TaN(SiMe₃)₂ and 3 exhibited complicated absorption patterns in other regions. According to the literature,¹⁸ the strong

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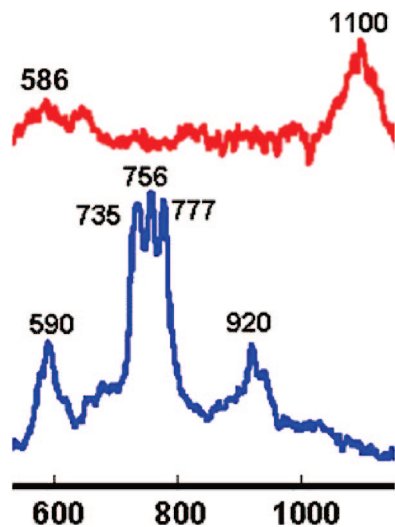


Figure 3. Raman spectra of $\text{TaCl}_4(\text{NSiMe}_3)$ (red) and **3** (blue).

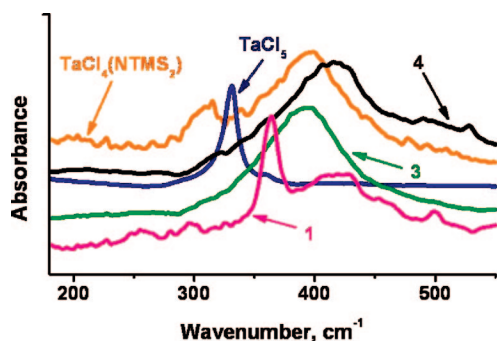


Figure 4. Far-IR spectra of TaCl_5 , $\text{TaCl}_4(\text{NSiMe}_3)$, **1**, **3**, and **4**.

absorptions at 1100 cm^{-1} ($\text{Cl}_4\text{TaN}(\text{SiMe}_3)_2$) and 920 cm^{-1} (**3**) may be assigned to $\nu_{\text{Si-N}}$ resonances. The peaks at 586 and 590 cm^{-1} found in **3** are tentatively attributed to the Ta–N resonances; there are no other reports regarding the location of the typical absorption of Ta–N bond in Raman analysis. The other absorptions of **3** at 735, 756, and 777 cm^{-1} may be caused by B–Ta, C–B, and Si–C_{cage} resonances.

In addition, the far-IR spectra of compounds **3** and **4** were compared to those of $\text{Cl}_4\text{TaN}(\text{SiMe}_3)_2$, TaCl_5 , and **1** (Figure 4). As can be seen from the figure, compounds **3**, **4**, and $\text{Cl}_4\text{TaN}(\text{SiMe}_3)_2$ show strong absorptions at 397, 416, and 400 cm^{-1} , respectively, which are consistent with reported $\nu_{\text{Ta-N}}$ absorptions.¹⁹ On the other hand, neither TaCl_5 nor **1** shows such absorptions (see Figure 4). These results clearly indicate the presence of a Ta–N bond in **3** and **4**.

3.2. Catalytic Evaluation of Carboranyl Pentaanionic Coordinated Tantalum(V) Complexes. In order to evaluate the catalytic activities of the novel neutral tantalum(V) complexes, compounds **3** and **4** have been investigated as precatalysts for ethylene polymerization in the presence of the cocatalyst MAO. Different conditions of reaction temperature, ethylene pressure, and the $[\text{Al}]/[\text{Ta}]$ ratio have been examined for compound **3**, and the results are given in Table 1. It was found that a temperature of $50\text{ }^\circ\text{C}$ with $[\text{Al}]/[\text{Ta}] = 200$ and $P_{\text{ethylene}} = 10\text{ atm}$ gave the highest catalytic activity ($2470\text{ kg of PE}/((\text{mol of Ta})\text{ h atm})$); these conditions were selected for the comparison of the catalytic activities of **3** and **4** (Table 2).

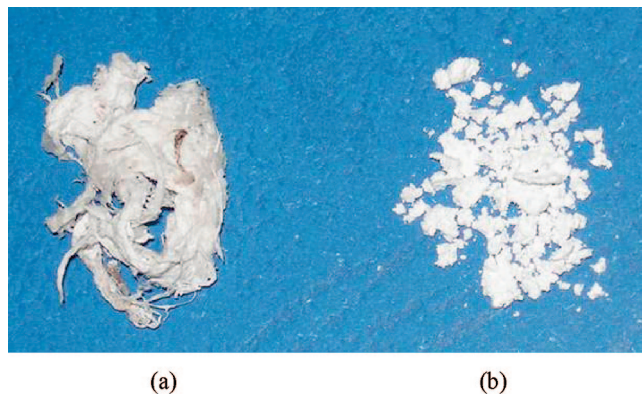


Figure 5. Polyethylene (PE) from catalyst **3** with cocatalyst MAO: (a) fibrous PE; (b) powdery PE.

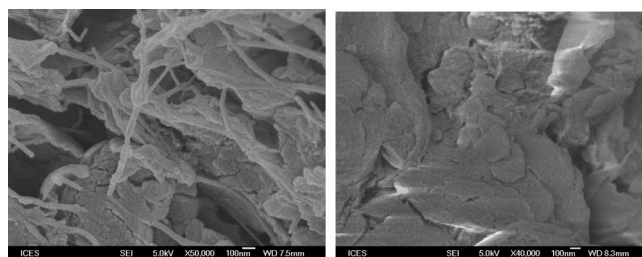


Figure 6. SEM images of PE from **3**: (a) fibrous PE; (b) powdery PE.

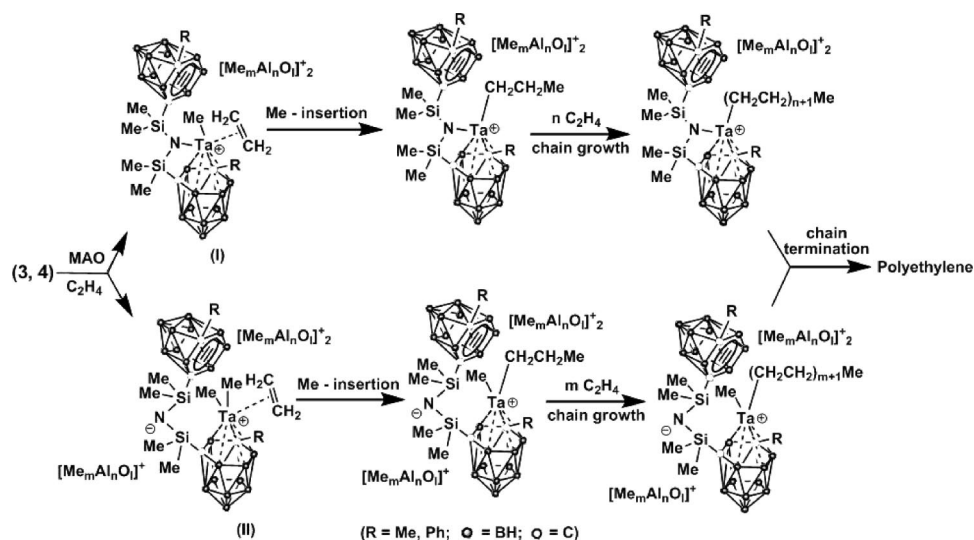
As can be seen from Table 2, under these conditions, compound **4** exhibited a much lower activity ($975\text{ kg of PE}/((\text{mol of Ta})\text{ h atm})$). However, both are substantially higher than the value of $185\text{ kg of PE}/((\text{mol of Zr})\text{ h atm})$ found for the carboranyl trianion, $[\text{nido-RR}'\text{C}_2\text{B}_9\text{H}_9]^{3-}$, coordinated zirconocarborane *closo*-1-Zr(Cl)-2-Ph-3-(2'- $\sigma(H)$ -*N*-cyclohexyl)-2,3- η^5 - $\text{C}_2\text{B}_9\text{H}_9$ (**5**, Figure 2),¹⁴ under the same conditions (see Table 2). Interestingly, morphologically different polyethylenes, one fibrous and the other powdery (Figure 5), have been produced from a one-pot polymerization reaction with **3** and the cocatalyst MAO. The fibrous polyethylene possesses a viscometric molecular weight of 5.7×10^6 , much higher than that of the powdery polyethylene (Table 1). The morphologically different PEs show different T_m values (based on DSC analysis) of 135 and $127\text{ }^\circ\text{C}$ for fibrous polyethylene and powdery polyethylene, respectively. Interestingly, they show dramatically different images in SEM analysis (Figure 6). Microscale rods comprising nanoscale particles are found for fibrous PE SEM images, which are not seen in the powdery PE. The catalytic activities of **3** and **4** compare favorably with those of other reported η^5 -coordinated *nido*-carboranyl metallocenes such as *closo*-1-Zr(Me)(η^5 - C_5Me_5)-2,3- η^5 - $\text{C}_2\text{B}_9\text{H}_{11}$ (activity $72\text{ kg of PE}/((\text{mol of Zr})\text{ h atm})$),²⁰ *closo*-1-TiCl₂-3-(π - η^2 -*N,N'*-dimethylaminomethyl)- η^5 - $\text{C}_2\text{B}_9\text{H}_{11}$ (activity $85\text{ kg of PE}/((\text{mol of Ti})\text{ h atm})$)²¹ and σ -bonded *closo*-carboranyl metallocenes such as $\{[\eta^5\text{:}\sigma\text{-Me}_2\text{C}(\text{C}_6\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{ZrCl}(\mu\text{-Cl})_{1.5}\}_2\{\text{Li}(\text{THF})_2\}$ (activity $2730\text{ kg of PE}/((\text{mol of Zr})\text{ h atm})$).²² The mechanism for the neutral carboranyltantalum(V)/MAO catalytic process is not known. However, the results suggest that two pathways might occur, one leading to the fibrous PE and the other to the powdery PE. A tentative polymerization scheme is shown in Scheme 2. In

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Scheme 2. Proposed Ethylene Polymerization by 3 and 4



keeping with other MAO-assisted schemes, the precursor **3** or **4** could react with MAO, leading to a metal–ligand bond rupture; either a N–Ta or a $(\eta^6\text{-C}_2\text{B}_4)\text{--Ta}$ bond could be broken to form catalytically active species (**I**, **II**) upon coordination with the ethylene monomer. For individual processes, the single-site polymerization mechanism of the conventional Ziegler–Natta catalysts may be operable.^{2–4} At this point it is impossible to predict which metal–ligand bond is broken or whether the two possible paths could lead to morphologically different forms of PE. More detailed mechanistic studies are currently underway in our laboratory, using FT-IR and NMR spectroscopy.

4. Conclusion

The novel carborane-based pentaanionic precursors [(*closo*-1-R-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $\text{Me}_2\text{Si}_2\text{NH}$] (R = Me, Ph) and their derived neutral tantalum(V) complexes have been synthesized and characterized. The complexes [(*closo*-2-R-2,3- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $\text{Me}_2\text{--}$

$\text{Si}_2\text{N}]\text{Ta(V)}$ (R = Me, Ph) were found to be active catalysts for the polymerization of ethylene in the presence of cocatalyst, MAO, to produce morphologically different polyethylenes in a single reaction.

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