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Note

Zirconocene compounds derived from boratastilbene, 4-boratastyrylstilbene, and 1,4-bis(boratastyryl)benzene and their reactivities to the ethylene polymerization

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Abstract

(η^6-Boratastilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**1**), (η^6-4-boratastyrylstilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**2**), [1,4-bis(boratastyryl)benzene]bis[(dichloro)(pentamethylcyclopentadienyl)zirconium] (**3**), and bis(η^6-boratastilbene)zirconium dichloride (**4**) were synthesized. The crystal structure of **1** was determined by X-ray crystallography. These zirconium complexes show activities in the presence of methylaluminoxane (MAO) for the polymerization of ethylene. The activities are in the following order: **1** > **2** > Cp_2ZrCl_2 > **3** > **4**. The activity of **1** is three times higher than that of Cp_2ZrCl_2 under similar conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium complexes; Polymerization; Boratabenzene ligands; Methylaluminoxane

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1. Introduction

The metallocene compounds of Group 4 have been developed as catalysts for polyolefin and are now reaching the early stages of commercialization [1]. Tremendous efforts have been made to search for new generation catalysts beyond metallocene compounds [2]. Boratabenzene ligands are isoelectronic with cyclopentadienyl ligand and have been used for zirconocene compounds [3–6,9]. The reactivity of the catalysts can be controlled by choice of the exocyclic substituent. Solution of $[C_5H_5B–N(^iPr)_2]_2ZrCl_2$ and MAO reacts with 1 atm of ethylene to give polyethylene [4], but under similar conditions $[C_5H_5B–Ph]_2ZrCl_2$ gives a mixture of 2-alkyl-1-alkenes (vinylidene olefins) [5]. For $[C_5H_5B–OEt]_2ZrCl_2$ and MAO, the addition of ethylene result in the formation of 1-alkenes [6].

Recently, boratastilbene [7], 4-boratastyrylstilbene and 1,4-bis(boratastyryl)benzene [8] were synthesized and their photophysics were studied compared with the isoelectronic stilbene and distyrylbenzene chromophores. In this paper, we report the synthesis, characterizations and the ethylene polymerization reactivities of zirconocene compounds derived from boratastilbene, 4-boratastyrylstilbene and 1,4-bis(boratastyryl)benzene ligands.

2. Result and discussion

The boratabenzene ligands are not soluble in diethyl ether but become soluble by addition of slight amount of THF. The solution was reacted with a slurry of Cp^*ZrCl_3 in diethyl ether to afford (η^6-boratastilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**1**), (η^6-4-boratastyrylstilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**2**) and [1,4-bis(boratastyryl)benzene]bis[(dichloro)(pentamethylcyclopentadienyl)zirconium] (**3**). The compounds, **1** and **2**, were purified by recrystallization from solution in toluene and pentane at −35 °C and **3** was

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recrystallized from a solution in methylene chloride at -35 °C. The direct reaction of $ZrCl_4(THF)_2$ with two equivalents of boratastilbene–Na in diethyl ether affords the bis(η^6-boratastilbene)zirconium dichloride (**4**) which was crystallized from a solution in toluene and pentane at -35 °C. The reaction of 4-boratastyrylstilbene-Na with $ZrCl_4(THF)_2$ under similar conditions gave orange solid but it could not be characterized due to its poor solubility.

The compounds, **1**–**4**, were characterized by ^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR spectroscopy and elemental analysis. The protons at C_4 in the boratabenzene rings were observed as a triplet triplet ($J = 6.8$, 1.6 Hz) at 5.67 ppm (C_6D_6), 6.22 ppm ($CDCl_3$) and 6.22 ppm ($CDCl_3$) for **1**, **2** and **3**, respectively. The protons at C_2 and C_6 in the boratabenzene rings were observed as a doublet doublet ($J = 11$, 1.6 Hz) at 6.6 ppm for **1**–**3**. In the case of **4**, the resonance of proton at C_4 appears at more down-field shifted region (6.80 ppm) than those of protons at C_2 and C_6 (6.72 ppm). The vinyl protons are easily distinguished by their characteristic feature of doublet with big coupling constant ($J = 18$ Hz). ^{11}B resonance was observed at 38–39 ppm.

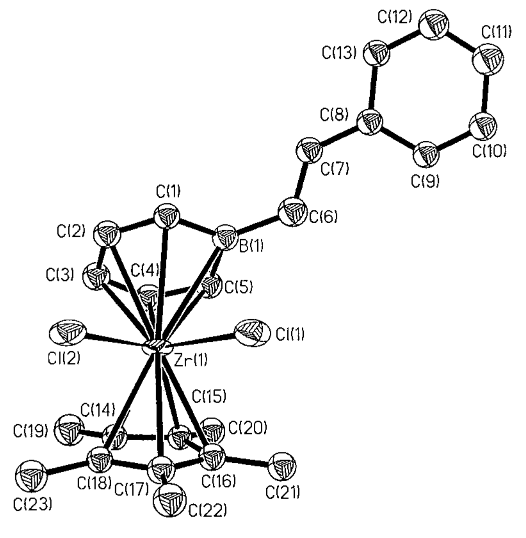
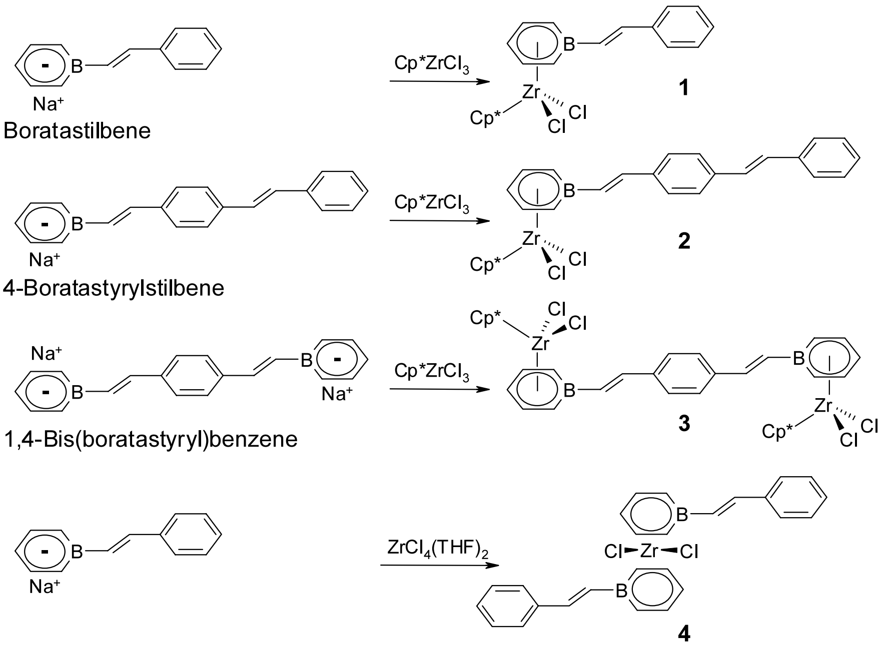


Fig. 1. ORTEP view of **1**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Zr(1)–Cl(1), 2.415(4); Zr(1)–Cl(2), 2.438(4); Zr(1)–B(1), 2.832(14); Zr(1)–C(1), 2.722(13); Zr(1)–C(2), 2.634(14); Zr(1)–C(3), 2.561(14); Zr(1)–C(4), 2.545(14); Zr(1)–C(5), 2.590(14); B(1)–C(6), 1.54(2); C(6)–C(7), 1.35(2); C(7)–C(8), 1.40(2).

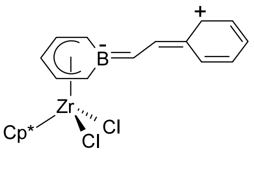


Single crystals of **1** suitable for X-ray crystal structure determination were grown by the addition of pentane vapor to a toluene solution at room temperature overnight. Fig. 1 gives an ORTEP view of the structure of **1** together with the atom labeling and the selected bond distances. The overall geometry resembles a Group 4 bent metallocene and does not deviate from the structure of the similar compound, $Cp^*[C_5H_5B{-}OEt]ZrCl_2$ [9]. The boratabenzene ring is rotated such that the styryl group is nearly above one chloride ligand. Zr–B distance (2.832(14) Å) is slightly shorter than that of $Cp^*[C_5H_5B{-}OEt]ZrCl_2$ (2.882(5) Å), implying more strong Zr–B orbital overlap for **1**. When the metrical parameters within the boratastilbene frame are compared with those of boratastilbene–$Na(Et_2O)$ [8], one observes that, by the coordination to zirconium atom, the distances of B–C(vinyl) and C(vinyl)–C(*ipso*) are contracted (1.54(2) and 1.40(2) Å for **1**, respectively and 1.575(2) and 1.476(2) Å for boratastilbene–$Na(Et_2O)$, respectively) while that of C(vinyl)–C(vinyl) is lengthened (1.35 (2) Å for **1** and 1.334(2) Å for

Table 1
Ethylene polymerization results

Catalyst	Yield (g)	Activity (kg PE–Zr h atm)	M_w	M_w/M_n	T_m
1	1.6	7000	248 000	2.72	137
2	0.91	4000	288 000	2.41	138
3	0.28	1200	475 000	2.92	137
4	0.17	740			
Cp_2ZrCl_2	0.58	2500	507 000	2.15	

boratastilbene–Na(Et_2O)). This metric change might result from some participation of the resonance structure shown below.



When ethylene was fed continuously under pressure of 40 psig to a toluene solution of **1**–**4** (0.10 μmol, 50 ml) activated with MAO (Al–Zr = 5000), polyethylene was obtained immediately. The activities and polymer properties are summarized in Table 1. Cp_2ZrCl_2 was used for the polymerization under the same condition for comparison. Metallocene compounds, **1** and **2**, bearing mixed ligands of pentamethylcyclopentadienyl and boratabenzene showed good activity. The activity of **1** reaches three times of that of Cp_2ZrCl_2. Compounds **3** and **4** show lower activity. Molecular weight (M_w) obtained with **1** and **2** are 248 000 and 288 000, respectively and these values are lower that those obtained with **3** and Cp_2ZrCl_2 ($M_w = 475\,000$ and $507\,000$, respectively). Molecular weight distributions of the polymer obtained with zirconocene compounds bearing boratabenzene ligand (**1**–**4**) are slightly broader (2.4–2.9) than that obtained with Cp_2ZrCl_2 ($M_w/M_n = 2.1$). m.p. of 137–138 °C indicate that the polymers are almost linear.

In conclusion, some zirconocene compounds bearing boratabenzene ligand were prepared and their ethylene polymerization reactivities were studied. Zirconocene compound bearing mixed ligands of pentamethylcyclopentadienyl and boratastilbene or 4-boratastyrylstilbene (**1** and **2**) showed good activities for the ethylene polymerization. The activity of **1** reaches three times that of Cp_2ZrCl_2.

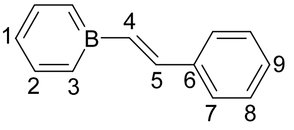
3. Experimental

3.1. General considerations

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl. Methylene chloride was purified by distillation over CaH_2. Anhydrous grade toluene was purchased from Aldrich and purified further with Na–K alloy for the solvent of polymerization reaction. Methylaluminoxane (MAO) was purchased from Akzo (9.2 w% of Al). Boratastilbene–Na(OEt_2), 1,4-bis(boratastyryl)benzene-Na_2, and 4-boratastyrylstilbene-Na was prepared according to the literature method [7,8]. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Unity 400 or 500 spectrometer. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters model 150-C+ GPC and the data were analyzed using polystyrene analyzing curve.

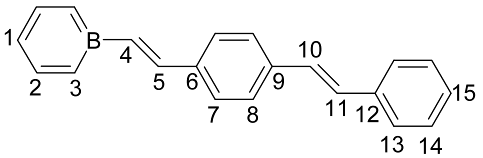
3.2. (η^6-Boratastilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**1**)

Boratastilbene–Na(OEt_2) (50 mg, 0.18 mmol) was dissolved in Et_2O (1.0 g) by addition of slight amount of THF (ca. 0.1 g). The solution was added to a slurry of Cp^*ZrCl_3 (60 mg, 0.18 mmol) in Et_2O (2.0 g) at room temperature (r.t.). The mixture was filtered after stirring overnight. All volatiles were removed by vacuum to give oily residue, which was solidified by addition of pentane. Recrystallization from toluene and pentane (ca. 1:3) at −35 °C gave yellow crystals (48 mg, 56%). ^{1}H-NMR (400 MHz, C_6D_6): δ 7.61–7.58 (d, $J = 7$ Hz, 2H, H^1), 7.44 (d, $J = 18$ Hz, 1H, H^4 or H^5), 7.35 (d, $J = 18$ Hz, 1H, H^4 or H^5), 7.20–7.10 (m, 4 H, H^2 and H^8), 7.08 (tt, $J = 7.2$, 2.0 Hz, 1H, H^9), 6.61 (dd, $J = 11$, 1.6 Hz, 2H, H^3), 5.67 (tt, $J = 6.8$, 1.6 Hz, 1H, H^1), 1.72 (s, 15 H, CH_3) ppm. ^{13}C-NMR (100 MHz, C_6D_6): δ 143.49 (C^2), 143.22 (C^1), 139.99 (C^6), 129.18 (C^8), 128.32 (C^5), 127.69 (C^7), 126.52 (C^9), 108.28 (Cp), 12.91 (CH_3) ppm. ^{11}B-NMR (128 MHz, toluene): δ 38.8 ppm. Anal. Calc. for $C_{23}H_{27}B_1Cl_2Zr$: C, 58.0; H, 5.72. Found: C, 58.3; H, 7.42%.



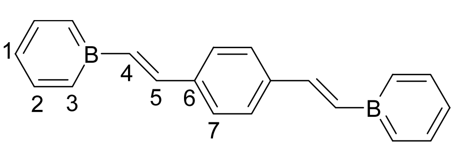
*3.3. (η^6-4-Boratastyrylstilbene)(η^5-pentamethylcyclopentadienyl)zirconium dichloride (**2**)*

The compound was prepared by the similar method and conditions of the preparation of **1**. It was purified by recrystallization from toluene and pentane (ca. 2:1) at −35 °C. The isolated yield was 49% (Yellow fluff). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58–7.47 (m, 8H, H^2, H^7, H^8 and H^{13}), 7.36 (t, $J = 7.6$ Hz, 2H, H^{14}), 7.26 (tt, $J = 7.6$, 1.2 Hz, 1H, H^{15}), 7.19 (d, $J = 18$ Hz, 1H, H^4 or H^5), 7.12 (s, 2 H, H^{10} and H^{11}), 7.03 (d, $J = 18$ Hz, 1H, H^4 or H^5), 6.63 (dd, $J = 11$, 1.6 Hz, 2H, H^3), 6.22 (tt, $J = 6.8$, 1.6 Hz, 1H, H^1), 2.05 (s, 15 H, CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.34 (C^2), 142.12 (C^1), 138.66, 137.64, 136.96 (C^6, C^9, C^{12}), 128.90 (C^{14}), 128.72, 128.58, 127.77 126.80 (C^5, C^{10}, C^{11}, C^{15}), 127.48, 126.86, 126.72 (C^7, C^8, C^{13}), 108.37 (Cp), 13.00 (CH_3) ppm. ^{11}B-NMR (128 MHz, toluene): δ 39.2 ppm. Anal. Calc. for $C_{31}H_{33}B_1Cl_2Zr$: C, 64.4; H, 5.76. Found: C, 64.6; H, 5.77%.



*3.4 [1,4-Bis(boratastyryl)benzene]bis[(dichloro)(pentamethylcyclopentadienyl)zirconium] (**3**)*

The compound was prepared by the similar method and conditions of the preparation of **1** with two equivalents of Cp*$ZrCl_3$. It was purified by recrystallization from methylene chloride CH_2Cl_2 (ca. 2:1) at −35 °C. The isolated yield was 51% Yellow fluff). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H, H^7), 7.54–7.48 (m, 2H, H^2), 7.19 (d, $J = 18$ Hz, 1H, H^4 or H^5), 7.01 (d, $J = 18$ Hz, 1H, H^4 or H^5), 6.63 (dd, $J = 11$, 1.6 Hz, 2H, H^3), 6.22 (tt, $J = 6.8$, 1.6 Hz, 1H, H^1), 2.06 (s, 15 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.30 (C^2), 142.40 (C^1), 138.70 (C^6), 127.3 (br, C^3), 127.26 (C^7), 126.79(C^5), 108.48 (Cp), 12.99 (CH_3). ^{11}B-NMR (128 MHz, toluene): δ 39.4 ppm. Anal. Calc. for $C_{40}H_{48}B_2Cl_4Zr_2$: C, 54.9; H, 5.54. Found: C, 55.3; H, 5.25%.



*3.5. Bis(η^6-boratastilbene)zirconium dichloride (**4**)*

Boratastilbene–Na(OEt_2) (50 mg, 0.18 mmol) and $ZrCl_4(THF)_2$ was weighed in a flask and cold Et_2O (1.0 g, −35 °C) was added. The slurry was stirred overnight at r.t. All volatiles were removed by vacuum and the product was extracted with toluene. Recrystallization from pentane and toluene (ca. 3:1) at −35 °C gave orange crystals (23 mg, 49%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78–7.71 (m, 2H, H^2), 7.66 (d, $J = 7.2$ Hz, 2H, H^7), 7.42 (t, $J = 7.2$ Hz, 2H, H^8), 7.42 (d, $J = 18$ Hz, 1H, H^4 or H^5), 7.33 (tt, $J = 7.6$, 2.0 Hz, 1H, H^9), 7.14 (d, $J = 18$ Hz, 1H, H^4 or H^5), 6.80 (tt, $J = 6.8$, 1.6 Hz, 1H, H^1), 6.72 (dd, $J = 11$, 1.6 Hz, 2H, H^3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.87 (C^2), 144.58 (C^1), 138.48 (C^6), 131.0 (br, C^4), 128.87 (C^8), 128.69 (C^5), 127.33 (C^7), 127.3 (br, C^3) 112.16 (C^9) ppm. ^{11}B-NMR (128 MHz, toluene): δ 38.1 ppm. Anal. Calc. for $C_{26}H_{24}B_2Cl_2Zr$: C, 60.0; H, 4.66. Found: C, 60.3; H, 4.53%.

3.6. Polymerization of ethylene

To a dried 500 ml glass reactor were added toluene (50 ml), metallocene compound (1.0 μmol) and MAO (0.5 mmol). Ethylene was fed continuously under pressure of 40 psig for 5 min at r.t. The reaction was quenched by venting ethylene and adding MeOH (10 ml) subsequently. The polymers were collected by filtration and dried under vacuum overnight. The activities and the polymer properties are summarized in Table 1.

3.7. Crystallographic studies

Crystals were mounted onto a thin glass fiber with paratone-8277 and immediately placed in a cold nitrogen stream at 150 K on a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo–K$_\alpha$ radiation). A full sphere of intensity data was collected in 2252 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). The number of reflections used for the least-squares refinement of unit cell parameters (at 150 K) was 1373. The empirical absorption corrections based on the equivalent reflections were performed using the program SADABS. The structures were solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL (version 5.0.3). Full-matrix refinements were against F^2. Hydrogen atoms were calculated at idealized positions and their atomic positions were refined as riding atoms of their parent carbon atoms.

*3.7.1. Crystal data for **1***

$C_{23}H_{27}BCl_2Zr$, $M = 476.38$, yellow crystals, size $0.24 \times 0.07 \times 0.07$ mm, monoclinic, space group $P2_1/n$, $a = 9.484(5)$, $b = 16.877(9)$, $c = 13.572(7)$ Å, $\alpha = 90$, $\beta = 96.930(11)$, $\gamma = 90°$, $V = 2157(2)$ Å^3, $Z = 4$, $D_{calc} = 1.467$ mg m^{-3}, $F(000) = 976$, wavelength (Mo–K$_\alpha$) = 0.71073 Å, 11 572 reflections collected in $h(12/12)$,

$k(-22/21)$, $l(-17/18)$, measured in the range $1.93 < \theta < 20.00°$, 2007 independent reflections, $R_{int} = 0.1928$, 129 parameters, 0 restraints, $R_1 = 0.0818$, $wR_2 = 0.1847$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.1226$, $wR_2 = 0.1963$, GOOF = 1.498, largest difference peak and hole: $1.400/-0.924$ e Å^{-3}.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (**1** CCDC no. 167137) Copies of this information may be obtained free of charge form The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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